PHOTOGRAPHIC CHEMISTRY

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PHOTOGRAPHIC CHEMISTRY

VOLUME ONE

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With a Foreword by
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FOUNTAIN PRESS · LONDON

Volume One
of the English language edition first published 1958

Translated into English in two volumes from the second French edition
(published 1957) with the authorization of the
Publications Photographiques et Cinematographiques Paul Montel, Paris

Printed in Great Britain by
J. W. Arrowsmith Ltd., Bristol

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FOREWORD
TO THE FIRST FRENCH EDITION

MR. P. GLAFKIDÈS, who was kind enough to ask me for a Foreword has certainly done useful work in writing this book on Photographic Chemistry. All the books on this subject, published in the French language, are at least thirty years old, and therefore very largely out of date; some, indeed, were already out-dated on publication!

The author, who has worked in a photographic research laboratory in the United States is highly qualified to undertake this important task, which embraces a very vast field, several aspects of which were, in France, covered only by fragmentary and widely dispersed writings. Precise directions are given for the preparation of several types of emulsion; the chapter devoted to colour sensitizers is treated as extensively as anyone could desire, and the theory of the latent image and development include the most recent information.

This book will not only be of great value to chemists in the photographic industries, but will also enable enterprising photographers—both professional and amateur—to acquaint themselves, at no great effort, with the rudiments of chemistry necessary for an intelligent practice of their profession or hobby. The great number of references will enable the reader to refer to original sources should he wish to give further study to a particular subject.

It is my very sincere wish that this useful book may enjoy all the success which it deserves.

L. P. CLERC

FOREWORD
TO THE SECOND FRENCH EDITION

IN THE FOREWORD to the first edition of this volume which I had pride in writing at M. Glafkidès request, I had the pleasure of affirming the excellence of this work. In the last few years considerable progress has been made in this field, and it is therefore pleasing that the author has prepared a new revised edition, always fully documented. If any fault can be found in this work it is that of being too complete, dealing with many matters alien to chemistry, but which are admirably treated. I hope that this second edition will be at least as successful as the first.

L. P. CLERC

PART ONE

The Formation and Development of the Photographic Image

CHAPTER I

NATURE OF LIGHT

1. The Wave-like Character of Light

1.—Light is propagated in a vibratory movement or *waves.*

This pronouncement, formulated by Huyghens in the seventeenth century, was revived by Young at the beginning of the nineteenth century, then developed successively by Fresnel and Maxwell. The latter, referring particularly to the idea of a transversal wave, considered it as an *electromagnetic disturbance.* It was thus possible to explain the effects of diffraction, interference and polarization.

According to the electromagnetic theory, a light-wave is represented at each point of its motion by a plane set at right angles to its direction of travel, and in this plane two vectors are present—one being electric and the other magnetic—which oscillate in mutually perpendicular directions. In other words, a radiation could be defined as a periodical variation in space of combined electric and magnetic fields.

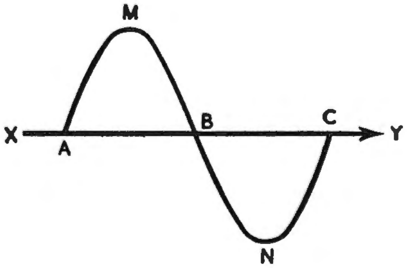

Fig. 1.

If we represent (Fig. 1) the resultant elementary wave by an oscillation AMBNC proceeding in the direction XY, the length λ of this wave will be shown by the distance AC.

The speed of travel c, or distance covered in one second, is constant: 300,000 km per second.

During one second, a light ray performs a number of complete oscillations (AMBNC) equal to $\nu = c/\lambda$

ν is the *frequency* of the wave. It is higher as the λ is smaller. Since ν oscillations take one second, a single oscillation will take a time or *period* equal to $T = 1/\nu$ seconds.

The wave-length λ is characterized by the colour (also its frequency ν to which it is related). Wavelengths are measured by taking as units the micron μ (or thousandth of a millimetre), the millimicron mμ (or millionth of a millimetre) and the Ångstrom unit Å (or ten-millionth of a millimetre). One mμ is therefore equal to 10 Å.

2. The *range of electromagnetic waves* is continuous from the radio waves measured in thousands of metres, to the γ rays of radium, which are lower than one-thousandth of an Å as follows:

Radio waves	from several tens of kilometres to 1 millimetre
Infra-red (or heat radiations)	from 1,000μ to ·74μ
Visible spectrum	from 740 mμ to 400 mμ
Ultra-violet	from 400 mμ to 10 mμ
Undefined rays	from 100 Å to 20 Å
Soft X-rays	about 12 Å
Hard X-rays	about 0·05 Å
γ rays of radium	about 0·001 Å

The visible spectrum occupies no more than a very limited band in the range of radiations. It is situated in the centre of the spectrum produced by the optical systems, between the ultra-violet and the infra-red, and is subdivided into a certain number of colours, or rather groups of monochromatic light, as follows:

Violet	395 to 435 mμ	Yellow	570 to 595 mμ
Blue	435 to 500 mμ	Orange	595 to 625 mμ
Green	500 to 570 mμ	Red	625 to 740 mμ

All radiations carry energy. This energy can be discerned by the human eye within narrow limits; over a greater range by means of a photographic plate, a photoelectric cell, a thermopile, a bolometer (resistance variation of a metallic strip) or a Crooke's radiometer. It is thus possible to observe a flux of energy of 10^{-9} to 10^{-15} watt.

2. Structure of Light

1. According to the theory of the wave system, a sine wave emitted by a light source should lose itself in space through progressive dispersal. But this does not occur, since—even after having travelled for a considerable distance—a ray of light is capable of producing photochemical and photoelectrical effects which necessitate a certain amount of energy.

Light is made up of units which cannot be sub-divided. We already know the discontinuity of matter, which is made up of complete and independent fragments such as molecules, atoms and electrons. That light should display an equally discontinuous nature should cause no surprise, and this hypothesis, formerly propounded by Newton, was later revived with success by Einstein.

Yet a ray can travel around an obstacle, as proved by the effects of diffraction and interferences—a property which is absent in a projectile, which would be completely deviated from its course.

The undulatory character of light being an unquestionable, though unexplained, fact, it became necessary to devise a logical explanation. This was accomplished by the ingenious association of the two theories—corpuscular and undulatory—a point which had in fact, been considered by Newton himself.

2. The *wave mechanism*, developed by L. de Broglie and Schrödinger, is based upon Planck's *quantum theory*, perfected by Bohr.

This theory suggests that corpuscular movements occur according to an *unbroken* sequence of entire values, or *quanta*. In other words, all action proceeds in abrupt and independent steps.

Since light is of a vibratory nature, it is not divisible infinitely. Each complete oscillation (Fig. 1) corresponds to a fixed amount of energy h, equal to $6{\cdot}55 \times 10^{-27}$ erg/second.⁽¹⁾ *h is Planck's constant.*

If ν is the frequency of the radiation under consideration (number of cycles per second) *the smallest quantity of isolated energy which it is possible to bring into play is $h\nu$. $h\nu$ is a quantum of energy or photon.*

It will consequently be seen that the higher the frequency—i.e., the shorter the wave-length—the higher will be the amount of energy conveyed by the radiation. Thus X-rays are stronger than ultra-violet rays, which in turn are stronger than the blue and green radiations, and these latter are in turn more energetic than the red or infra-red radiations.

By considering each single vibration h, or quantum, as a corpuscle, the conclusion is reached that *light is formed of units of energy, or photons, associated in a wave movement.*

3. The Photon

The *photon* is an electically neutral particle, with an extremely small mass. It can only acquire energy by reason of its very high speed.

The quantum theory, applied to the electromagnetic fields, had suggested zero mass for the photon, in order to comply with Maxwell's equations. But the calculations of undulatory action, on the other hand, demand that there should be some mass, however small. If the mass of the electron is $m = 0{\cdot}9 \times 10^{-25}$ grammes, that of the photon μ_0 would be in the region of 10^{-45} to 10^{-65}. It follows, therefore, that *the velocity of light is a maximum velocity which the photon never reaches*, and that the relativity phenomena do not depend on light.

When studying the electron, it will be observed that it displays a *spin*, or rotary movement on its own axis, accompanied by a magnetic effect.

Spin is measured in units $h/2\pi$. The spin of an electron is rated at $1/2(h/2\pi)$; in other words, the electron has a spin of 1/2.

Photons are also subject to spin, but in this case the figure is 1. Now since spin is the result of three straight line components, a photon may thus pass through different states according to the value of these components. One of these may be positive, negative or neutral, i.e., equal to $+h/2\pi$, 0, or $-h/2\pi$. If the component is positive, then perpendicular electric and magnetic fields are formed, which accompany the photon. The area formed by the directions of these two fields is animated by a rotary movement towards the left, around the third axis, viz., that of propagation. The angular speed of rotation is $2\pi\nu$. This pattern corresponds with that of Maxwell's representation given in paragraph 1. It is similar when the component of the spin, according to the axis of propagation, is negative, except that the plane of the electromagnetic fields revolves to the right. The wave is described as having a left or right circular polarization. The combination of a right circular wave with a left circular wave produces a straight or elliptical polarized wave, according to the equivalence of the two elementary waves, or to the predominance of one of them.

In the case of a neutral-spin component, the photon is accompanied solely by an electrical wave, travelling in the same direction.

A photon with a spin of 1 therefore conforms very well with the result of Maxwell's equations on electromagnetic waves. However, there are other types of equation, bringing in a *photon with a spin of* 0, which is still unknown.

It may even be considered that photons with a spin of 1 or 0 are the result of the fusion of two corpuscles with a spin of 1/2, whose respective spins add up or cancel out. Those two hypothetical corpuscles, the ergon and the anti-ergon, have been the object of many suppositions, and it has been felt that they should be associated in the same manner as electrons and positrons. Indeed, a photon with an energy exceeding a million electron-volts is capable of materializing in the form of a positron and an electron when it passes through an atom. Conversely, it is possible to de-materialize a positron-electron combination in the shape of two photons of half a million electron-volts each. This is the reversible conversion of light to matter.

The associations of photons follow the *Bose-Einstein statistical law*, by which the same state may apply to any number of corpuscles. Electrons, on the other hand, follow the *Fermi-Dirac statistical law*, in which a single corpuscle is present in one particular state, to the exclusion of all other corpuscles. This latter principle, formulated by Pauli, states that two electrons cannot follow exactly the same orbit.

In short, *light consists of corpuscles of energy, or photons, which carry an anisotropic electromagnetic wave.*

4. The electromagnetic wave

Actually, the wave itself, which characterizes the vibratory condition of the photon, does not carry any energy. *The wave has no physical existence.* It is a function of *probability*, of fixed frequency, which defines the position of the corpuscle in time. In other words, the photon is guided by a *wave of probability.*

The *wave-function* $\psi(x, y, z, t)$ of the photon, called the *field*, is based upon a function of Lagrange, with sixteen components,⁽²⁾ but in this case a linear operative term H (called 'Hamiltonian and Hermitian') is brought in. The evolution of the wave-function ψ, in time, is then written as follows:

$$\frac{h}{2\pi i}\,\frac{d\psi}{dt} = \mathrm{H}\psi$$

Since there are sixteen components, sixteen simultaneous partial differential equations are obtained. ψ is thus a complex quantity formed by ψ_1, ψ_2, ψ_3, etc. By substituting other quantities of a particular character, for the sixteen original components, it is possible to represent the potentials and the fields of the orthodox electromagnetic theory.

Let us now consider a number *n* of photons in all the possible states of energy. Their evolution in space accords with a *distribution function* R which presumes that at the instant t there are n corpuscles in state 1, n_2 corpuscles in state 2, etc.; i.e., as shown by $[R(n, n_2 \ldots t)]^2$. This function of distribution progresses according to the same type of equation as that given for ψ, but in this case the operative factors H influence the variable n. The quantum theory, when applied to electromagnetic fields, gives the electromagnetic quantities (which depend on space x, y, z and time t) to these operative factors H which act upon n.

5. Theory of the annihilation of photons

L. de Broglie developed a theory whereby the photons can 'exist' in a particular state of annihilation (represented by a wave-function $\psi(_0)$) which renders them unobservable. In order to disappear in this manner, the photons must give up their energy and their movement quantity to such material elements as electrons, and this is what happens in the case of any photon absorbed by matter. Conversely, under the influence of electric charges, the electromagnetic field which was cancelled reappears and the photon becomes observable again.

Space, known as vacuum, would thus be the repository of an immense and constant number of annihilated photons, whose field, of course, is nil.

But photons may be unobservable without being annihilated, e.g., photons exchanged by two neighbouring electrons.

The theory of annihilation provides an explanation for the existence of an electrostatic field between two electrons, as well as the creation by the latter of an electromagnetic field and the emission of radiations by matter.

In order to introduce the function of the annihilated state $\psi(_0)$ in undulatory action, it is necessary to agree that propagation occurs, not in a four-dimensional space (x, y, z, t), but in a five-dimensional space (x_0, x, y, z, t) in which x_0 is beyond our perception. The components of the function ψ of the normal state of the photon depend on x_0 by the factor $e^{ik_0x_0}$ which, when introduced into the equation, produces the following for the non-disintegrated states:

$$\psi_{\sigma\tau} = f_{\sigma\tau}(x, y, z, t)e^{ik_0x_0}$$

where σ, τ = 1, 2, 3, 4.

6. Emission of radiation by matter

Let us consider an atom in a state of repose (or stationary). Each electron travels around the smallest orbit it can adopt, provided that the length of its trajectory is an exact number of times the length of the associated wave. In this stable condition of *minimum energy* the atom does not emit any radiation.

If, for any reason, an electron 'jumps' from the minimum orbit to an orbit of higher degree, with an absorption of a 'finite quantity' of energy, the atom is then in an *activated state*, similar to that of a tightened spring ready to be released. The potential energy of the atom is increased.

It may happen that the spring will be released, i.e., that the activated electron will revert either to its original orbit, or to an intermediary orbit, with a decrease of its activation. The surplus energy which the electron has acquired is then naturally released *in the form of radiation.*

Since the smallest particle of theoretical energy is h (1 oscillation), and that the energy of a photon is $h\nu$, the frequency is equal to the quotient of lost energy E by h: $\nu = E/h$, since one must have $h\nu = E$.

When the energy released is sufficiently low, the luminous emission occurs near the visible spectrum. *This emission is the result of the activation of the surrounding levels only*, which are more readily affected. This is what happens with the *average incandescent substances.*

One particular method of activation of atoms consists in bombarding them in high vacuum by cathode rays (which are themselves formed by streams of electrons of various speeds). When it has been de-activated, an activated element (or anticathode) emits a very high-frequency radiation, viz., X-rays. It is observed that the spectrum of these X-rays varies with, and characterizes, each element. This spectrum is formed of groups of lines corresponding with the various levels of energy of the electrons, which may thus be located and studied. It is then possible, by means of X-rays, to determine the electronic structure of the elements.

The energy lost by an electron $E_n - E_m$ is approximately related to the characteristics of the latter by the formula

$$\frac{E_n}{h} = \frac{2\pi^2 me^4}{n^2 h^3}$$

in which m is the mass of the electron, e its charge, h is Planck's constant and n is an integral positive number. E_n/h is called the *spectral term.* The division in two of the hydrogen emission lines led Sommerfeld to a more complete formula, which was then generalized by Rydberg, viz.:

$$\frac{E_{n,k}}{h} = \frac{R}{(n+\Delta)^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right]$$

in which α is the 'fine structure constant', n and k integral numbers, and Δ a characteristic quantity for each element.

In fact, a line of light emitted by a body consists of more than two lines in close proximity. By taking as a basis the properties of spin, Dirac made the spectral term depend from three quantum numbers, n, l, and j. In order that an emission should occur at a certain frequency, it is necessary that the probability of transition of the electron from one state to another should not be nil.

In the case of radioactive bodies the γ-radiation (or very high-frequency photons) is due to the effect on the nucleus caused by the departure of helions (nuclei of helium). The corpuscles constituting the heavy nucleus of the radioactive body are distributed over the energy levels, as are the planetary electrons. Any departure of a helion produces a redistribution of energy levels with a rearrangement accompanied by an emission of photons.

7. The action of radiation on atoms

A photon which meets an atom may, by electromagnetic action, disturb the movement and the state of an electron. If the energy of this photon does not correspond with any state of excitation in the atom, it is emitted again in another direction, i.e., *scattering* takes place. The scattering is the more pronounced as the frequency is higher.

If the energy of the photon corresponds with an excitation level in the atom, the photon disappears after having given out its energy. This is called *absorption.* The frequency of the absorbed photon corresponds with that of the photons which can be emitted.

A disturbed electron may transfer to a more distant orbit if the energy of the photon agrees with that of the level considered (*resonance*). The greater the difference of energies, the lesser will be the probability of detachment.

The excited electrons can, however, resume their original orbit, or successive intermediary orbits, until the original orbit is reached, while emitting each time a weaker radiation, i.e., a radiation of longer wavelength.

In the action of X-rays upon atoms, the wavelength of the absorbed photons is constant and characteristic for each level of electrons (X-rays spectra).

8. Photoelectric effect

When the photons bring about the complete extraction of an extra-orbital electron, the latter escapes from the atom, thus creating an electric current. This is the photoelectric effect. The photons disappear in giving out their energy.

$h\nu =$ exciting energy + kinetic energy taken away by the electron.

The energy required for the extraction corresponds with the ionizing energy of the atom, which amounts, for instance, to 4·3 electron-volts for potassium.

In this manner, a luminous ray will produce from a thin film of alkaline metal (potassium or caesium) placed at the bottom of a bulb filled with an inert gas under low pressure, a number of electrons proportionate to the number of photons received, i.e., proportionate to the intensity of the light. The weak electric current obtained is amplified before use.

It may happen that the energy of the photons does not agree with the states of excitation of the electrons in the atom. If the frequency of the incident radiation is high (X- and γ-rays) it is possible to have a scattering of photons as well as an ejection of electrons. This is the *Compton effect.*

9. Absorption of light by molecules

Any light which penetrates through a substance emerges minus a certain number of photons of given wavelengths. A *selective absorption* occurs. This absorption is constant and characteristic of the substance considered. If the absorbed radiations are situated outside the visible spectrum, the substance appears colourless to the human eye. If certain radiations are absorbed, it appears coloured by transmitted or reflected rays. Finally, if most of the visible radiations are absorbed, the substance looks black or dark in appearance.

The absorption which occurs in the areas between the ultra-violet and infra-red depends on the molecular constitution, and molecules are the source of three kinds of movement (i.e., of variations of energy), viz.:

(*a*) *Rotary movement* of the molecules themselves around an axis perpendicular to the main coordinating axis of the atoms.
(*b*) *Vibratory movement* of the nuclei.
(*c*) Movement of the electrons, especially the outer orbital electrons.

Each one of these movements causes an absorption of photons. The very long wavelengths of infra-red (10 to 100 μ) usually correspond with the molecular rotations, and those from 1 to 10 μ to the vibratory movements. However, certain vibrations may cause thin lines of absorption in the ultra-violet (see para. 11). But the radiations near the visible part of the spectrum (infra-red to ultra-violet) correspond with an electronic state of the molecule, which is shown by a system of absorption bands.

This electronic condition depends not only on the nature and number of atoms present in the molecule, but also on the relative distances of their nuclei and their position. It depends therefore on the orbits described by the outer orbital electrons of the associated system, and on their various states of energy. In order that absorption may occur, *resonance* must be present between the vibratory condition of the incident photons and that of the electronic system of the molecule.

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1. The term 'erg' is used to describe the work accomplished by a force of 1 dyne acting through 1 centimetre in the same direction as the force. A dyne is the unit of force which, applied to a mass of 1 gramme, imparts to it a velocity of 1 centimetre per second. $F = m\gamma$. 1 kilogramme-metre = approximately 10^8 ergs, and 1 watt = 10^7 erg/seconds.
2. de Broglie L., *Mécanique Odulatoire du Photon et Théorie Quantitique des Champs.* (Gauthier Villars, Paris, 1949.)

Chapter II

PHOTOCHEMISTRY

Photochemistry is the study of chemical reactions brought about by light.

The photochemical action consists of two main phases, viz.:

(*a*) The reception of luminous energy; and
(*b*) The actual chemical process.

Depending on whether a single substance is involved, or of a system comprising several substances together, it is possible to obtain either a *decomposition* of the compound into its elements (*photolysis*), or a *combination* of several substances into a single one (*photosynthesis*).

10. Basic laws

1. *Grotthus-Draper's absorption law.* A radiation cannot bring about a chemical action unless it is *absorbed* by a body (or a system of bodies). Otherwise it is impossible for any transmission of luminous energy to take place.

It may be appropriate to note that the radiations which constitute the colour of a body are precisely those which are not absorbed, and they consequently have no effect upon it. On the other hand, the complementary radiations of this colour are absorbed and are capable of action. For instance, a green substance will reflect green, but absorb the blue and red, and can be decomposed only by these two colours.

However, absorbed radiation *does not necessarily act* upon the substance which receives it. It must, in addition, satisfy several other conditions.

2. *Energizing law.* In order to act efficiently, a luminous radiation must possess an amount of energy at least equal to that required by the chemical process.

It is known that the radiations are more energetic as their wavelengths are shorter (or that their frequency ν is the higher), the energy carried by a photon being expressed by the formula

$$\mathrm{E} = h\nu = \frac{hc}{\lambda} \; (c = \text{velocity of light})$$

in which h is Planck's constant equal to $6{\cdot}55 \times 10^{-27}$ erg.

One *gram-photon* (containing N photons, i.e., 603×10^{-21} photons, of which the total energy is $\mathrm{U} = \mathrm{N}hc/\lambda$ ergs.) corresponds to one gram-molecule containing N molecules (para. 838). By converting to equivalent calories, the calorific energy of a gram-photon is obtained by the formula

$$U = \frac{28{,}420{,}000}{\lambda_{m\mu}} \text{ calories}$$

The following table gives an idea of the energy of the various radiations:

	Radiations		Calories
Ultra-violet	200 mμ	=	142,500
,,	250 mμ	=	114,000
,,	284 mμ	=	100,000
,,	300 mμ	=	95,000
Violet	400 mμ	=	71,250
Blue-green	500 mμ	=	57,000
Green	568 mμ	=	50,000
Orange	600 mμ	=	47,500
Red	700 mμ	=	40,700
Infra-red	800 mμ	=	35,600

3. *Law of photochemical equivalence* (or Einstein's Law). For each absorbed photon there is a corresponding decomposed or synthesized molecule.

It is understood that the active photon complies with the foregoing law of energy.

Yet it is found in practice that the number of active photons absorbed in a chemical process seldom agrees with the number of molecules formed or decomposed. If one calls the ratio of the number of molecules decomposed to the number of photons absorbed, *quantum ratio* ρ.

$$\rho = \frac{\text{no. decomposed molecules}}{\text{no. absorbed photons}}$$

then a quantum yield is obtained which varies considerably within extensive limits (between ·1 and 1000 and over). A few reactions only have a theoretical yield of unity.

However, this contradiction does not bring any doubt to the validity of Einstein's Law, and the reason for the experimental variations is simple:

(*a*) When the chemical action demands an addition of external energy (endothermic reaction)—and this is the case with the silver halides—then ρ is equal to 1 at the most. Usually it is less, as in the photochemical decomposition of hydrochloric gas (1) since this process is reversible

$$2HCl \rightleftharpoons H^2 + Cl^2$$

In order to decompose ammonia NH^3 into nitrogen and hydrogen by means of ultra-violet rays, 4 photons are required for each molecule ($\rho = \cdot 25$).

Depending on the wavelength, it is possible to cause a variation in the photochemical balance, either in one direction or in the other. The following is a typical reversible reaction:

$$\text{Maleic acid} \rightleftharpoons \text{fumaric acid}^{(2)}$$

in which, with the ultra-violet $\lambda = 313$ mμ, there is 44% of maleic acid and 56% of fumaric acid, while with a shorter wave-length ($\lambda = 200$ mμ) the maleic acid re-forms with 75% of maleic acid and 25% of fumaric acid. In the first instance, the quantum yield amounts to ·03 (30 photons) while it rises to ·1 (10 photons) for the reverse process (re-formation of maleic acid).

A similar process can be observed in the formation of sulphuryl chloride SO_2Cl_2 from sulphur dioxide and chlorine, viz.:

$$\underset{\text{Sulphuryl Chloride}}{SO_2Cl_2} \rightleftharpoons \underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Chlorine}}{Cl_2}$$

(*b*) When the absorbed radiations first result in an activation of the molecule, the activated molecule will then react upon a second neutral molecule, to give products of decomposition, according to the following pattern:⁽³⁾

$$AB + h\nu = [AB]$$
$$[AB] + AB = 2A + 2B$$

The quantum yield is then in the neighbourhood of 2. An example of this is the decomposition of nitrogen peroxide NO_2 into nitric oxide NO and oxygen by the action of ultra-violet light (260 to 360 mμ), as follows:

$$2NO_2 + h\nu \rightarrow 2NO + O_2$$

When $\lambda = 400$ mμ the yield ρ drops to ·75, and decreases to nil in the visible spectrum.

(*c*) When the reaction is purely exothermic (with production of heat) the quantum yield becomes very high. In this case it is only necessary for the light to initiate the reaction for the latter to continue of its own accord by means of its own self-produced heat, in a chain of reactions.

A classical example is the combination of chlorine with hydrogen (in the presence of a trace of water vapour) under the influence of light. ρ may reach up to 100,000 (it varies with the pressure in, and size of, the vessel), and a whole range of similar combinations may be noted:

$$\underset{\text{Carbon monoxide}}{CO} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Phosgene}}{COCl_2} \text{ with } \rho = 1000$$

$$\underset{\text{Methane}}{2CH_4} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Methyl Chloride}}{2CH_3Cl} + \underset{\text{Hydrogen}}{H_2} \text{ with } \rho = 10{,}000$$

as well as the combinations of chlorine with a number of organic substances, such as alcohol, ether, acetic acid, benzene, toluene, etc. With the latter, $\rho = 30$.

In order to take place, a photochemical reaction sometimes demands the presence of a sensitizer, e.g., the action of hydrogen on benzene⁽⁴⁾ and the photochemical reactions of propane⁽⁵⁾ are catalyzed by *mercury*. The photodecomposition of oxalic acid is sentitized by *uranyl ions*. Here, a transfer of electrons occurs, from the excited uranyl ions to the oxalate ions. Other reactions are sensitized by zinc oxide.

The *intensity* of the light is sometimes an important factor to consider. Thus a 10-kW electric discharge lasting from ·1 to 3 minutes will produce different substances from those obtained with radiations of moderate intensity.⁽⁶⁾

11. Photochemical dissociation

The photochemical decomposition of a molecule is shown by its *absorption spectrum*.

A spectrum will thus consist of two adjacent parts, viz., a *broken spectrum* formed of fine absorption lines which correspond with a vibration of the nuclei of the atoms within the molecule; and a *continuous spectrum* whose absorption varies continuously.

The vibratory movements are such that the atoms oscillate around their point of balance and escape as soon as the vibratory energy exceeds a certain value. The molecule then dissociates.

Thus the spectrum of a substance displays, on the one side, some narrow bands of absorption which, although clearly separated at first, finally unite in one continuous spectrum. The region in which these two forms of spectrum separate is called the *limit of convergence*. Now, *the power to decompose substances is present only in radiations which form part of a continuous spectrum*; and if the temperature is increased, the bands nearest to the continuous spectrum will merge with the latter, and the radiations belonging to these bands, formerly inert, become active.

This effect, discovered by Victor Henri, is called '*predissociation*'. Many examples exist, e.g., photolysis of acetaldehyde (effective $\lambda < 315$ mμ); of benzaldehyde (effective $\lambda < 250$ mμ); of carbon disulphide CS_2 (two limits of convergence in ultraviolet); of sulphur dioxide SO_2 (also two limits corresponding with two regions of absorption); of nitrogen peroxide NO_2 ($\lambda < 400$ mμ and $\lambda < 245$), etc., etc.

The narrow bands of absorption correspond with a vibration of atoms or groups of atoms which cancel out at the limit of convergence, in the case of active radiations. The molecules are then in a state of predissociation or *electronic excitation*, without any true dissociation, due to the absorption of photons.

12. Organic photochemical reactions

All known types of organic reaction may be subject to the influence of light, and some of these are noted below:

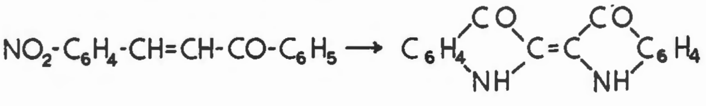
Decomposition: Acetone,⁽⁷⁾ acetamide,⁽⁸⁾ methyl formate,⁽⁹⁾ mercaptans.⁽¹⁰⁾ At 253·7 mμ a quantum will decompose 1·7 molecules of mercaptan. Rotenone⁽¹¹⁾ is also susceptible to photochemical decomposition.

Hydrolysis: Carbon tetrachloride into hydrochloric acid and carbon dioxide;⁽¹²⁾ mono- and dichloracetic acids into glycolic and glyoxylic acids;⁽¹³⁾ cyclohexanone into caproic acid.⁽¹⁴⁾

Oxidation: When under the influence of light, and in the presence of oxygen, alcohols, phenols, ketones, aldehydes and acids will oxidize. Some of the di- and triarylmethanes will convert to peroxides, and this effect is particularly marked in the case of 9-phenylxanthane.⁽¹⁵⁾ Many catalyzed photo-oxidations have been used in the preparation of organic compounds.⁽¹⁶⁾

Addition reactions occur with halides, ammonia, aniline, etc., and in the latter case anilides are obtained.

Isomerizations and polymerizations: o-nitrobenzaldehyde, when dissolved in benzene or ether, will be converted to o-nitrosobenzoic acid. o-nitrobenzylideneacetophenone forms indigo:(17)



There may be changes of form, such as with dibenzoylethylene and dibenzostyrol. Carvone is converted to carvocamphor.

Acetylene polymerizes into benzene(18) (the same applies to its derivates). Stilbene dimerizes into distilbene. Anthracene, phenylacetaldehyde, cinnamylidenemalonic acid, α-naphtoquinone, etc. also produce dimers.

Methyl acrylate and methacrylate will polymerize in the presence of benzoin or diacetyl, acting as catalysts. In this way it is possible to obtain reliefs for printing purposes.(19)

Under the influence of ultra-violet rays, on the other hand, many polymers undergo a marked degree of *depolymerization*. It is thus possible to observe a decrease in the viscosity of solutions of cellulose nitrate and acetate,(20) or of methyl-cellulose.(20) Any radiation of a λ lower than 340 mμ will degrade most fibres, while between 340 and 400 mμ the action must often be activated by atmospheric humidity and oxygen, or by traces of metals.

13. Inorganic photochemical reactions

The allotropic modification of certain elements by the action of light are commonplace operations in inorganic chemistry. White phosphorus will change to red phosphorus, yellow arsenic to grey arsenic, yellow antimony to black antimony, and red selenium to black selenium. The final product is always the more stable. The hydrogen and sulphur derivates of all these substances are also light sensitive. The photolysis of hydrazoic acid and of the alkaline nitrides has also been studied.(22) This is a chain reaction, the intermediate substance being activated nitrogen.

Most of the *metallic salts* are photo-sensitive. Sulphides in suspension in water may undergo a slow oxidation, while a blue colouring has been obtained with ammonium molybdate or sodium tungstate+HCl.

The point which distinguishes the behaviour of the salt substances from that of the above-mentioned compounds is essentially their *ionic character*. Whereas, in gaseous systems, molecules alone would come into play, here we have only to consider the movement of the valency electrons, since the metallic salts—crystallized or in aqueous solution—dissociate into ions.

Among the photochemical decompositions, the most noticeable are those of the following elements—iron, chromium, manganese, cobalt, uranium, copper, mercury, and especially *silver*. The reaction is often reversible.

Examples:

$$\underset{\text{Ferric Chloride}}{2FeCl_3} \rightleftharpoons \underset{\text{Ferrous Chloride}}{2FeCl_2} + \underset{\text{Chlorine}}{Cl_2}$$

$$\underset{\text{Silver Chloride}}{2AgCl} \rightleftharpoons \underset{\text{Silver}}{2Ag} + \underset{\text{Chlorine}}{Cl_2}$$

If the chlorine is absorbed as and when it is formed, only the photolytic reaction occurs (decomposition).

The sensitivity to light of *iron* salts has given rise to several applications which we shall examine later, and the same applies to *chromium* salts.

In common with the ferric salts, the *manganic* (Mn^{+++}) and *cobaltic* (Co^{+++}) salts revert, under the action of light, to the state of manganous (Mn^{++}) and cobaltous (Co^{++}) salts, by each acquiring one valency electron.

Cuprous chloride CuCl assumes a violet-brown colouring, while *cupric* chloride $CuCl_2$, dissolved in alcohol, is reduced to cuprous chloride. Similarly, salts of *uranium*, *lead* and *thallium* are sensitive to the action of light.

Among the salts of *mercury*, mercurous nitrate $HgNO_3$, basic mercurous tartrate, basic mercurous oxalate and especially *mercury-ammonium oxalate*, display interesting reactions.

Eder's reaction. A mixture of mercuric chloride $HgCl_2$ and ammonium oxalate in an unsaturated solution will decompose rapidly into insoluble mercurous chloride HgCl (calomel) which precipitates. This very sensitive reaction may serve as a photometer. The action would be as follows:(23)

$$C_2O_4^{-} + Hg^{++} \rightarrow 2CO_2 + Hg^{+}$$
$$Hg^{+} + C_2O_4^{--} \rightarrow Hg + C_2O_4^{-}$$
$$Hg + Hg^{++} \rightarrow Hg_2^{++}$$

Eder's reaction is sensitized by plane-molecule cyanines and erythrosine This sensitizing appears to operate by means of a transfer of energy.(24)

14. Phototropy

Certain organic substances, when subjected to the influence of light, will change colour and, when placed in darkness again, will revert to their original colour. This is a *reversible change of colour* which is called *phototropy*.

Phototropic compounds are relatively numerous. An exposure of 1 minute to a 50-watt lamp at a distance of 2 inches is generally sufficient for a change of colour to take place, the phototropic substance being dissolved in water, alcohol or acetone, or also in the crystalline state. Sometimes the new colour remains for several days, in the dark, before disappearing, but in most cases the reversion to the original state is rapid. We append a list below of a few of the many phototropic compounds:

Benzaldehyde-phenylhydrazone(25)—colourless, becomes scarlet—as well as many other *phenylhydrazones*.(31)

Quinoquinoline hydrochloride(26)—yellow crystals become green.

α-Naphthylamino-camphor(27)—colourless (chloroform solution), becomes green.

Tetrabenzoylethylene(28)—colourless, becomes yellow.

Triphenylfulgide—yellow, becomes brown, and other *fulgides* are affected.(29)

Diacetylamino-p-2-*stilbene*-o-2-sulphonic acid, a light yellow powder, becomes red.(30)

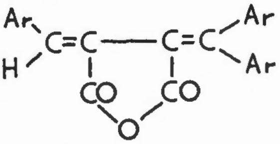
Derivates of *salicydene-amine*: salicydene-o-anisidine, β-naphthylamine-salicydene, salicydene-aniline, m-phenylenediamine-disalicydene.

Naphthylosazones: anisyl-α-naphthyl-osazone, piperyl-α-naphthylosazone.

Acetanilide-p-disulphoxide.

Certain dyes.(32)

The phototropic *fulgides*, for instance, have a general constitution represented by the following formula:



The *carbazones*, such as cinnamaldehyde-phenylsemicarbazone, when subjected for several hours to diffused light, produce an invisible *latent change* which, after a return to darkness followed by a second exposure to light, will give a visible yellow colour. This is the effect called *inverse phototropy*.(33)

Phototropy is attributed to the reversible displacement of electrons, corresponding with several mesomeric forms of a same substance. The coloured state is an intermediate state resulting from the superimposition of several extreme structures. One of the mesomeric forms may predominate, as in substances which are already coloured (β-tetrachloro-α-cetonaphthalene, fulgides, Schiff's bases). This is an electrotropic effect.(34)

A particular case of phototropy on plates has been observed by J. Sivadjian(35) in the following manner:

Photographic plates, after being fogged, developed, fixed, washed, bleached in a 1% solution of mercuric chloride, then rinsed, are sensitized in ·5% potassium iodide. Yellow layers of mercury iodide are obtained. After rinsing and drying, the plates are exposed to light and the coating assumes a purplish-black tone, but becomes colourless again in darkness. This process is accelerated by washing. It can provide images suitable for copying.

Cupric bromide and cupric chloride, when damped with water, become dark green. They decolourise in darkness—in a few hours at an ordinary temperature, and instantly at 75°C.(35a) This change is accelerated by the Br^- and Cl^- ions.

Phototropy of 4-(*p-dimethylamine-benzene-azo*)-*phenylmercuric acetate*: see *Jl. Am. Chem. Soc.*, 1955, 77, p. 5011.

15. Fluorescence and phosphorescence

A *fluorescent* substance, when subjected to the action of radiation of a certain wavelength (ultra-violet, for instance) will convert these incident rays into other *emitted* and visible radiations of a greater wavelength.

This is because the molecule M, having absorbed a quantum $h\nu$, passes through an unstable activated state M′, then deactivates when reverting to its stable condition, while emitting a quantum $h\nu'$ of a lower frequency. This lowering of the frequency is explained by the fact that activated molecules are in continuous rotation. Deactivation stops the movement of the molecule, then causes the expulsion of a photon with less energy than that of the absorbed photon.

The length of time between activation and deactivation varies from one hundred-millionth to a thousandth of a second (*uranyl salts*) according to the nature of the substance. The yield varies also: the ratio between emitted and absorbed photons comes near to unity for diluted *fluorescein.* The light emitted by a fluorescent body may be compared, according to J. Perrin, with a 'discontinuous sum of minute identical sparks'.

2. In the effect of *phosphorescence,* the irradiated substance retains its luminosity for a comparatively long time (often for several hours). This property is due to the presence of what are known as phosphorogenic substances, particularly *sulphides.* The presence of *impurities* such as copper, manganese, calcium, rare earths, etc. is essential to maintain the instability of the crystalline structures thus deformed.

A molecule, activated by an absorbed photon, will produce an unstable molecule when deactivated at a slightly lower level. This molecule, by reason of thermal agitation, will receive a little energy, which will enable it to revert to the activated state by returning to its original level of activation. The same cycle is repeated until the gap between the level of activation and that to which it drops becomes too wide to be closed.

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Chapter III

THEORY OF THE LATENT IMAGE

In order to obtain a photographic image, it is necessary to expose a *sensitive emulsion*(1) to light. Inside this 'emulsion' a change occurs, invisible yet factual, which bears the name of *latent image.* It is given this name because a visible image is obtained from it when a substance known as a *developer* is caused to act upon the latent image, in the operation of *development.* The sensitive medium on a photographic plate is a heterogeneous mixture formed of a dispersion of very fine crystals of *silver bromide* AgBr in *gelatin.* It may contain a certain proportion of silver iodide.

16. The silver bromide crystal

Silver bromide cyrstallizes in a *cubic pattern,* like the halides of alkaline metals (NaCl, KBr, etc.).(2)

The cubic system, which is the simplest form of the seven systems of crystallization, is characterized by three axes of symmetry which are all perpendicular to one another. The arrangement of the atoms, called the pattern or *crystal lattice,* takes place on the upper surfaces of the cubes. The outer appearance of the crystal may vary, according to the nature of the substance and the way in which it was obtained, by a truncation of the angles (dihedral angles) or of the summits (trihedral angles). Thus the silver bromide appears in the form of hexagonal or triangular tablets (Fig. 2) and cubes or short needles with rounded ends. The former are obtained by precipitation in a neutral medium, and the latter in an ammoniacal medium.

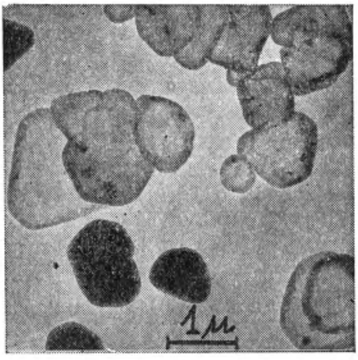

FIG. 2. Silver bromide crystals (neutral emulsion).

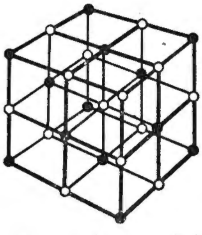

FIG. 3. Crystal lattice of silver halides. The silver ions (●) and halides (o) alternate on the top of the cubes. The effect is shown here in diagram, whereas in reality the ion spheres are closer.

The *crystal lattice* constitutes the true structure of the cr tal. It is formed by an assembly of *ions* situated at equal distances in the three directions, following a regular pattern. The entire assembly resembles a pile of cannon-balls.

The Ag^+ and Br^- (or Cl^-) ions are situated alternately at the intersection of the lines of a cubic lattice according to the diagram in Fig. 3. The lattice is 'face-centred', since each silver ion is connected with six halide ions, and *vice versa*. The distance between the centres of two identical atoms, or *mesh*, is 5·774 Å for AgBr, and 5·55 Å for AgCl. The halide ions are larger than the silver ions.(2a)

The crystals of photographic emulsions correspond mostly with cross-sections made along the octahedral sides, i.e., at right angles to the diagonals of the cube.

As for *silver iodide*, in the cold state it has a hexagonal shape, of the ZnO type. However, Oshino and Miyaka noted that silver iodide may have crystals of two shapes according to temperature,(3) especially a cubic α shape, of the blende ZnS type, which is stable up to 137°C, and hexagonal β shape, of the wurtzite type, stable from 137° to 146°C. Using a pressure of 3,500 Kg, Jacobson obtained inward faced cubes.

The study of crystals. When studying the photochemical effects which take place inside the silver halides, it is possible to use either large crystals or strips cut out of fused halide. In the latter case, the strips (obtained by sawing) must be heated above melting-point for forty-eight hours, then allowed to cool slowly for twelve hours.(4) The best procedure is to work in an atmosphere of pure nitrogen.(5) It is also possible to prepare strips of 10^{-4} or 10^{-3} centimetres thickness by crushing fused salt between two strips of quartz.(6) Another method consists in sublimating some silver on a sheet of glass and to expose it afterwards to bromine or chlorine vapour. Considering, however, that the igneous fusion produces crystalline structures which differ from those produced at an ordinary temperature, Tamura and Tukihosi obtain polycrystalline layers by precipitation on a sintered glass partition separating the two reagent solutions of 0·5N silver nitrate and potassium bromide.(7)

Mixed crystals. The various silver halides will crystallize readily together. Mixed crystals are produced by fusion as well as by precipitation, and the size of the mesh is, of course, related to their composition. The variations in structure may be revealed by X-ray diffraction, by examining the reflection spectra and by measuring the birefringence and the specific gravity.(7a) Silver bromide and chloride produce mixed crystals in all proportions, but an introduction of silver iodide causes a disturbance of the crystalline structure. With any quantity up to 4% of AgI, in relation to AgBr, and 11·5% in relation to AgCl, it is possible to obtain inward-faced cubic crystals. (This is the most usual case in practice.) With a very high content of silver iodide, mixed crystals belong to the hexagonal group, while with medium contents there is a mixture of both types of crystal. Silver iodide produces local deformations (since the ions I^- are larger), and moves the absorption spectrum towards the longer wavelengths. This displacement relates to the presence of cubic, and not hexagonal, AgI. (The limit of absorption of the latter is, on the contrary, of a λ lower than that of silver bromide.)

17. Adsorptions on the surface of crystals

The crystals of silver bromide or chloride emulsions are prepared by precipitation in the presence of a protective colloid—i.e., gelatin—and an excess of alakli halide. The latter is solvent of silver salts and forms several complex negative ions such as $(Br_2Ag)^-$, $(Br_3Ag)^{--}$, etc., adsorbed on the surface of the crystals, particularly on the surface defects.

Enlarging upon Helmoltz's conceptions of the double layers of parallel ions and of opposite symbols, and also on Gouy's, which considered the outer layer as a diffused ionic atmosphere, Stern showed⁽⁸⁾ that there are indeed two successive layers, but that the inside layer is attached rigidly to the crystal, while the outer is diffused. The crystal of silver bromide has thus two inter-faces,⁽⁹⁾ i.e., crystal to adhesive layer, and adhesive layer to diffused layer.

According to Bourne and Loening,⁽¹⁰⁾ the *OH ions* are also adsorbed by the silver salt precipitate. This adsorption increases with the pH, and at pH 9·5 there would be an OH group for five ion sites on the surface.

Finally, *gelatin* should not be forgotten. Its ions are charged negatively, and it is readily adsorbed. The gelatin covering which encloses the crystal may be seen under an electron microscope,⁽¹¹⁾ and photolysis under the action of electrons shows a transparent covering containing the liberated silver and possibly formed by a silver-gelatin complex.

Strictly speaking, apart from unproved and hazardous suppositions, we do not know the exact, yet extremely important, mechanism by means of which gelatin contributes to the formation of the latent image.

18. Absorption spectra and photoconductivity

The spectral regions of photographic sensitivity belonging to the silver halide crystals correspond with their *absorption bands*. Now, the absorption spectrum of a crystal depends on the nature of its constituent parts and consequently on the *deformations of the electronic orbits* occasioned by the mutual reactions of the adjacent elements. The deformations are the more pronounced as the atoms are the larger; thus the halides of alkaline metals—which are lighter—have two absorption bands in the ultra-violet, while the silver halides have their bands in the near ultra-violet, violet and blue. The limits of these bands, moreover, are the less abrupt as their wavelengths are the higher. One of De Boer's formulae⁽¹²⁾ enables the frequency of these main absorption bands to be calculated.

The movement of the electrons within the halide crystals is evidenced by means of *photoconductivity*, and the latter is specific for a given spectral absorption band.

In any photo-sensitive crystal a potential difference occurs when it is subjected to unilateral lighting. The process has been studied on cuprous oxide by Dember,(13) then on silver halides, particularly by Kotlyarewski.(14) An electrode (formed by the sublimation of silver on the crystal), which is illuminated by a light of given λ, will assume a positive charge (normal effect) or negative charge (reverse effect). On silver chloride the effect is normal at room temperature with its maximum at 340 mμ. The reverse occurs on silver bromide with its maximum at 320 mμ. At −18°, the effect is seven times more pronounced. On strips of 1 to 10 μ thickness, Barschevski(15) obtained the following maximum effects:

AgBr—313 mμ
AgCl—365 mμ
AgI—365 and 420 mμ

On AgBr which has already been exposed to light the maximum reaches 575 mμ.

The photoconductivity of silver bromide is considerably accentuated by the addition of cadmium or lead bromide.

Photoconductivity in emulsions. West and Carroll(16) have measured photoconductivity, not, in this case, within isolated crystals, but directly within the photographic emulsion. A piece of film was placed between two electrodes subjected to a difference of potential. Under the influence of light, the resistance of the system decreases and the current in the circuit increases. The incident luminous energy is measured by means of a thermopile. Miller and Hamm(17) made a similar study by using an electrometer and an oscilloscope. They observed that the current continues to increase after exposure to light has ceased, the maximum being reached two seconds later. This effect may be due to an electrolytic current resulting from a re-arrangement of the ions in the double layer enclosing every crystal, in the vicinity of the specks of the latent image.

19. Alkali halides

The alkali halides (sodium chloride, potassium bromide, etc.) are sensitive to light. This can be explained by the fact that *the photo-sensitive element is not a metal ion but a halide ion.*

The crystals of alkaline halides become coloured when exposed to ultra-violet, X- and γ-rays; likewise when exposed to electrons, and when heated in metal vapour. When exposed to light, these crystals show several absorption bands (in addition to the main ones) which result from defects in the crystal lattice, particularly the following:(18)

(*a*) *F band*, resulting from defects in the lattice, with an excess of metal ions.
(*b*) *M band*, resulting from a surplus of electrons.
(*c*) *V band*, resulting from positive holes (absence of halogen).
(*d*) Various bands resulting from impurities.

The F and M bands will form readily by exposure to X-rays (about 10^8 röntgen per sq. cm.). After a further exposure—to light, in this case—additional bands, called R bands, are formed, as well as infra-red N bands situated beyond the M band.(19)

An excess of metal ions in an unusual position will form *F centres*, and the radiations absorbed in this band will discolour the crystal, although only partially. Some of the F centres will return to an F′ state, of which the corresponding absorption band is weaker and of longer wavelength.(20)

The alkali halides may be sensitized by the corresponding hydride. When coloured by X-rays, the alkali halides emit an ultra-violet and visible fluorescence, and the effect is intensified when the temperature of the crystal is increased from that of liquid air to that of ordinary air.(21) A blue fluorescence may be obtained by exposing mineral salt to X-rays, in liquid nitrogen; and by a slow heating process an ultra-violet phosphorescence will be produced.(22)

Potassium chloride, crushed with 2·28% of silver chloride, becomes phosphorescent (12 seconds).(23) If it contains metallic thallium it is photoelectric, with a maximum at 550 mμ.(23b)

20. Defects of the crystal lattice

The photochemical sensitivity of a crystal of silver bromide (and generally of any photosensitive crystal) depends on the imperfection of the crystal lattice. Löhle, Stasiw and Teltow, and Pohl have shown that light has no effect upon a perfect crystal.

But before looking for local imperfections, it must be pointed out that the crystal lattice shows a certain *structural deformation*. In the ionic crystals it is, as we have seen, the ions and not the atoms which are the constituent units. Thus silver appears with one electron less, i.e., in the state of an ion Ag^+, and bromine in the state of an ion Br^-, having appropriated the ion lost by the silver atom. The nuclei of the atoms are surrounded by their clouds of electrons, which revolve in their respective orbits.

It so happens that a closer grouping of the nuclei will produce, by reciprocal action, a *deformation of the electron orbits*. This deformation depends on the nature, hence on the size, of the elements present. It is more pronounced in the silver halides than in the alkaline halides, whose ionic feature is more perfect. The deformed ions produce crystalline structures of weak coordination. Since it is the halide ion which is attacked by the photon, it will become more sensitive as its electronic orbits are more deformed, and for this reason, silver—which produces a greater degree of deformation than alkali metals—will produce salts which are more photo-sensitive than those produced by alkali halides.

Let us now examine the *local defects*. A crystal may be considered as an imperfect grouping of more perfect polyhedric blocks. The joins form areas of dislocation which are sometimes in a spiral, with cracked meshes, holes, and badly fitting ions. This dislocation is assisted by the *gelatin*, which exerts a considerable amount of physical tension (as revealed by examination under a polarizing microscope). Also, an addition of iodide to the bromide will increase the mesh in an irregular manner, with a confusion of the ions. The same result could be obtained by adding thallium salts. The resulting internal tension assists the movement of the electrons and ions, as in such phenomena as phosphorescence, in which impurities play a similar part.

The diffraction patterns of silver chloride, in fused crystalline blocks, show diffused patches and streaks attributed to a displacement of the rows of atoms parallel to the axis of the elementary mesh. The process of irradiation will cause photolytic silver to collect at the defective points of the lattice.(24)

The *degree of perfection* of a crystal is measured by a comparison between its true density and its theoretical density, calculated from the mass and volume of matter (Straumanis, *Phys. Rev.*, 1953, t.92, p. 1155). Its mesh is measured by X-ray diffraction. Corrections are carried out by Nelson and Riley's extrapolation technique, and Wilson's for X-ray refraction.(26)

Two kinds of defects are usually present *together* in crystals of silver bromide and chloride, i.e., Frenkel and Schottky defects.

Frenkel defects. These are formed by interstitial Ag^+ ions and an equal number of locations devoid of cations ($Ag_{\overline{\square}}$). The anion network remains intact. The study of the effects of conductivity reveals that an abrupt increase in the specific heat of the crystal of AgBr conduces to the formation of these defects.(25) The number of interstitial Ag^+ ions increases with the temperature.

Schottky defects. Schottky's defects consist of shallow vacant sites of Br^- and Ag^+ ions, in equal quantity. The equality of the vacant sites is confirmed by studies with radioactive ions carried out by Kolthoff and O'Brien,(26) followed by Langer.(27) The existence of Schottky's defects has been verified by taking measurements of the expansion of crystals (H. Kanzaki).(25)

The defects in the network of a crystal of AgBr are called *traps.* Berg even accepts the existence of shallow secondary traps which act as an intermediate image, the electrons captured by these traps being reduced by thermal agitation and the silver ions dispersed. In addition, Seitz calculated that the number of defective atoms in relation to the number of normal atoms is $r = e^{-\epsilon kT}$, in which $\epsilon = 0{\cdot}36$ electron-volt.

21. Sensitivity specks

The physical defects in the crystal lattice form during the first phase in the preparation of a photographic emulsion (precipitation and physical ripening). But in the second phase, digestion or chemical ripening—they can bring about the production of *sensitivity specks.* These specks are on the surface, and they occur especially along the lines of dislocation.

The existence of sensitivity specks was suspected in 1897 by Abbeg, but it was not until 1921 that their presence was demonstrated by Svedberg and Anderson.(28) Their size is, of course, too small to initiate development. Each grain has its own distribution of centres, and it is on this assumption that Webb based his calculations on the probabilities of distribution of the centres within an emulsion. This is in opposition to Silberstein and Trivelli, who assumed in their calculations that same-sized grains have the same sensitivity.(30)

The question now arises as to the *composition of the sensitivity specks.* They may be formed either by *silver*(31) derived from a reduction process, or by *silver sulphide* originating from the sulphur introduced by the gelatin. Mitchell and Meĭklyar, on the other hand, have accepted the fact that chemical ripening produces stable aggregates of a few shallow *F centres.* F centres, whose existence has been proved by Anastasevitch and Frenkel,(32) are formed by the appropriation of electrons by sites devoid of halides, while thermal diffusion will produce large aggregates of from 3 to 10 F centres, which form sensitivity specks.

At all events, it is extremely difficult to study crystals free from any impurity, for one always finds traces of Ag_2O, Zn, Cu, Al, Fe, Si, etc.

But let us return to the ***sulphide sensitivity specks.*** To them is rightly attributed the largest part in the sensitivity of a photographic emulsion. How do they operate? The X-ray diffraction patterns of silver bromide crystals containing Ag_2S produce wider lines than with pure silver bromide, which indicates a deformation of the crystallites.⁽³³⁾ The bivalent ion S^{--}, confronted by the vacant bromide ion site $Br^{+}_{\square}$ changes to a monovalent sulphur ion by losing an electron and forming an F centre (as the electron occupies the positive hole):

$$S^{--}+Br^{+}_{\square} \rightarrow S^{-}{}_{G}+F$$

It has been possible, thanks to the researches of Stasiw and Teltow⁽³⁴⁾ on the formation of absorption bands in fused crystals of combined AgBr and Ag_2S, to identify some complexes, the main type of which is

$$[S^{-}{}_{G}\ Br^{+}_{\square}]$$

formed by the coupling of a monovalent interstitial ion of sulphide S^{-} with a vacant bromide site.

The chemical sensitivity specks will act only at low intensities. Berg has estimated that it is possible to have up to 10 molecules of silver sulphide for every centre.⁽³⁵⁾

22. Process of latent image formation according to the Gurney-Mott theory

The relation between the movement of electrons released by light, and the formation of the latent image, has been prompted by the effects of photoconductivity in crystals of silver halides—effects which were made known by Arrhenius (1887). This induced Dauvillier (in 1920), then Fajans and von Beckeroth, and also Sheppard and Trivelli, to present the first hypotheses on the process of the formation of the latent image.⁽³⁶⁾ But it was not until 1938 that Gurney and Mott⁽³⁷⁾ were able to produce a consistent theory, which has since become standard.

According to Gurney and Mott, the latent image forms in three phases:

(*a*) *Primary photochemical effect.* A quantum of luminous energy $h\nu$ (or photon), penetrating into a silver bromide crystal, reacts—at the outer energizing level—upon a *bromide ion* Br^{-}, simultaneously yielding its energy to the latter. This energy enables the bromide ion to expel its supplementary electron in order to revert to the state of free bromine Br (with seven surrounding electrons, instead of eight for the Br^{-} ion). The reaction may be written thus (e signifying one electron):

$$Br^{-}+h\nu = Br+e$$

Since the decomposition of silver bromide is a reversible effect, it is necessary—in order to prevent the bromine from re-combining—to fix the latter.

This fixing of a halide is effected by water and, with better effect, by the gelatin which acts as a binder for the crystals. Gelatin is a bromine acceptor.

(*b*) *Electronic current.* The electron expelled by the bromide ion is, at the outset, at a higher energy level than that of the surrounding orbit of the (missing) valency electron of the corresponding silver ion Ag^+ (since the valency electron of silver is at O level, while that of bromine is at N level, of lower degree and therefore of higher energy).

The electron, then, will jump to O level. But in the assembly of Ag^+ ions formed by the crystal, the many O levels of these ions, being empty, form a wide band in which the electron can travel freely before dropping to a slightly lower level.(38) This *conductivity band* O corresponds with the F absorption band.

In fact, the second phase in the formation of a latent image resolves itself in the *migration of electrons* through a crystal lattice. This migration is facilitated when the ions adjacent to this lattice do not display any reciprocally abrupt potential differences, since the atoms are very close together; this in opposition to the effect produced in purely ionic crystalline structures, such as those of potassium bromide or sodium chloride, in which the potentials are more marked.

What becomes of the electrons in motion? They eventually meet, encounter a *lower energy level*, than that which they are in, and are trapped by it.

Now, this lower energy level is a *sensitivity speck* ($Ag+Ag_2S$). The electrons will accumulate in this centre and, naturally, form *negative electric fields*.

(*c*) *Ionic current Ag^+*. This is the third and last phase of the latent image speck formation.

The electric field—increasing in size through the arrival of new electrons—attracts the (positive) silver ions Ag^+, and this *migration of Ag^+ ions* constitutes an ionic current, which, in fact, can be studied, as done by Tubandt, by external application of artificial electric fields.

But the ions do not travel as fast as the electrons, and do not always succeed in discharging the negative field soon enough, in which case the latter may oppose the arrival of new electrons. The formation of the image is thus retarded.

The ions Ag^+, in turn, capture the electrons assembled around the sensitivity centres, by giving out atoms of *metallic* silver fixed on the same centres, i.e., $Ag^+ + e = Ag$. They then constitute—when in sufficient number—the *latent image centres.* These specks are separated from one another and are each formed by a certain number of silver atoms.

The Ag^+ ions, attracted by the field created by the assembled electrons, are detached under the influence of *thermal agitation*, more readily as they are less firmly attached. Those which depart first are the ones which are situated on the *irregularities of the lattice* (distorted parts or breaks). This is why we have previously insisted upon the necessity for having crystals of AgBr as imperfect as possible, especially if the photographic emulsion is to be fast.

23. Positive holes

Atoms of bromine are formed from the loss of photoelectrons by the Br^- ions. These bromine atoms have no action upon the latent image at low intensities. But an electron may attach itself to a bromine atom, to produce a Br^- ion, which enables another bromine atom to undergo the same reaction, and so forth, in the manner of a cascade. Everything occurs as if the Br moved irregularly through the lattice, as far as the interface, where it combines slowly with the gelatin. It is possible, in conformity with de Boer's hypothesis, to liken the bromine atoms to a mobile 'positive hole'. The same process is to be found again in other crystalline systems studied by Wagner, such as NiO and Cu_2O. The mobility of the Br^- ions is very low, a fact which Zimens observed after having exchanged Br for the radioactive bromine 82 and comparing its speed with that of radioactive silver 106, whose mobility is high.

When a halogen acceptor is added to the emulsion, the photoconductivity is doubled. To do this West used β-naphthyl semicarbazide hydrochloride or the β-naphthothiazole semicarbazone.(39)

24. Mitchell's theory

As stated above, the crystal lattice contains some Frenkel defects (interstitial Ag^+ ions) as well as some *Schottky defects* (vacant sites of bromine and silver ions). The vacant sites of anions form positive holes $Br^+_\square$, which should not be mistaken for bromine atoms.

The electrons which are produced in the course of the primary photochemical phase are, according to Mitchell's original theory(40) captured by these mobile vacant sites of bromine ions $Br^+_\square$, and produce *F centres*. Anastasevitch and Frenkel(41) had already stressed the function of these centres formed by an electron in a positive hole. F centres exist also in the alkali halides, where they result in coloured centres characterized by the corresponding absorption band.

An F centre may also be considered as an electron surrounded by six potential silver atoms. Several F centres will unite in *aggregates*, which are comparatively stable when formed in the neighbourhood of a sensitivity speck such as an ion $S^-{}_G$. But when these F aggregates reach a critical size they produce—with their surrounding silver ions—metallic silver, which is a constituent of the latent image.

It will thus be seen that, in this theory, there is no migration of ions Ag^+, but a *redistribution of the metallic silver*, after exposure, by reason of the movement of the F centres. In addition, a photon, instead of acting upon a Br^- ion can act upon an existing F centre. The latter will release its electron, which is captured by other F centres, and the association $F+e$ can in turn attract interstitial ions. No release of bromine is required, as in the orthodox theory.

Mitchell's second theory. Mitchell later(41a) revized his conception of the formation of the latent image, which may be summarized as follows:

(*a*) Liberation of electrons with a simultaneous formation of an equal number of positive holes by the photons. Or action of the excitation waves upon the Br^- ions occupying the indentures and other imperfections of the crystal; since these superficial Br^- ions surrounded by only a small number of Ag^+ ions, are at a lower potential, which always requires less energy to eject the electrons.

(*b*) If there are positive holes, these are appropriated first by the ions Br^- occupying the indentures, with a formation of rapidly-absorbed bromine atoms. In addition to the binder, *the chemical sensitizer acts as an acceptor of halide.*

(*c*) The electrons set free are raised to the energy level of the conduction band (or to levels lower than the locations of sensitivity specks with a lower potential). The electrons are appropriated by sensitivity specks together with the surface Ag^+ ions situated at the defective parts of the crystal, or emanating from the surroundings of the missing bromine ions, and give rise to *isolated and mobile silver atoms.*

(*d*) Formation of *latent sub-image* consisting of dispersed pairs of silver atoms, less mobile than the isolated atoms, by a concentration of the latter at the sensitivity specks.

(*e*) Formation of a *stable latent image* consisting of the specks of at least four silver atoms, by a grouping of the pairs of the neutral silver atoms of the sub-image, in positively charged aggregates—a charge which is balanced by the superficial Br^- ions. The stable specks are more active for the catalysis of development than the unstable specks.

The latent image is produced in the regions of tension where the sensitizers are located, mostly in the *centre of the crystal,* in the case of hexagonal tablets prepared in a neutral medium; also at the *junctions of the elementary crystals* which constitute the structure of the cubes, when the precipitation of the silver bromide is effected in an ammoniacal medium.

25. Stasiw and Teltow's theory

We saw in para. 21 that a sulphide ion $S^-{}_G$ joins with a vacant $Br^+_\square$ site to form a complex $[S^-{}_G\, Br^+_\square]$. The sign G indicates here an interstitial position, and the sign $\square$ a vacancy.

Now, the above complex is a trap. It is capable of capturing a photoelectron to give a negative-charged unstable complex,

$$[S^-{}_G\, Br_\square]$$

which, in turn, can attract an interstitial silver $Ag_0{}^+$ ion and become(42):

$$\text{neutral } Ag_0{}^+[S^-{}_G\, Br_\square]$$

possessing an absorption band at 560 mμ. This complex is very mobile. It may assemble in *aggregates* which, in turn, may disperse to produce *free colloidal silver* (several thousand atoms).

In the process proposed by Stasiw, the specks of atomic silver are thus formed in the immediate vicinity of a sensitivity speck, itself resulting from a sulphide ion and the neighbouring vacant site of a bromide ion. At low temperatures, it is even possible to observe the following primary effect:

$$[\mathrm{Ag_0}^{+}\ \mathrm{S^{-}}_{\mathrm{G}}]+h\nu \rightarrow [\mathrm{Ag^{+}}\ \mathrm{S_G}]+e^{-}$$
$$[\mathrm{Ag_0}^{+}\ \mathrm{S_G}] \rightarrow \mathrm{Ag^{+}}+\mathrm{S_G}$$

the subsequent reaction occurring as described above.

A more recent study by Seifert and Stasiw(42a) showed that the complex $[\mathrm{S^{-}}_{\mathrm{G}}\ \mathrm{Ag_0}^{+}]$ absorbs at 436 mμ. On the other hand, the centres formed by the electrons appropriated by the vacant bromine ions sites absorb radiations of 480 to 490 mμ, but the complex $[\mathrm{S^{-}}_{\mathrm{G}}\ \mathrm{Br}^{\pm}_{\square}]$ shows an absorption band at 630 mμ. By an appropriation of electrons, it forms a line at 720 mμ, corresponding with the larger aggregates. In silver chloride, the mobility of the interstitial silver ions is greater than in silver bromide, but the low concentration of these ions will only allow a lower degree of conductivity.

26. Constitution of the latent image

It was formerly believed that, under the influence of light, bromide would convert to a silver sub-bromide $\mathrm{Ag_2Br}$ or $\mathrm{Ag_3Br}$, alone reducible by the developer. Some authors even claimed to have succeeded in chemically preparing these sub-bromides and sub-chlorides in an isolated state. Nowadays, the existence of these compounds is refuted, since they are merely a mixture of a normal silver salt and colloidal silver.

What, then, constitutes the latent image? Solely *metallic silver*. This can be proved by a study of the patterns produced by an electron beam acting upon a coating of silver bromide. The pattern of the latter will soon be converted to the pattern of free silver.(43)

The appropriation of $\mathrm{Ag^{+}}$ ions takes place in the [110] orientation of the irregular features of the lattice.(43a)

The average proportion of metallic silver forming the latent image is about 1 atom for 10 million silver bromide molecules.

The formation of a latent image in a crystal produces a *modification of the absorption spectrum* of the latter. Whereas the normal absorption band, covering ultra-violet, stops at about 400 mμ, a second band appears in the visible portion and the infra-red, with its maximum at 690 mμ. Hilsch and Pohl,(44) who carried out these experiments, used the letter F for this characteristic band. It corresponds with the upper energizing level of the silver ions in the crystal lattice.

The latent image has a discontinuous structure, being formed of points scattered in the emulsion coating. As a result, *the density of the image is governed by the number of specks* distributed on the grains which can be developed *completely*. The number of these grains will therefore increase with the amount of light.

By computing the number of latent image specks produced by a given number of quanta (or photons), then taking a microscopic count of the actual number of these specks which has been produced, it is found that the quantum yield (or ratio of the number of released silver atoms to that of the quanta absorbed) approaches 1. With gelatino-bromide it is 0·92 to 0·96.

The quantum yield of photolysis in vacuum is shown by the formula $\phi = Q(1 - e^{-ka})$ in which Q is the superficial efficiency, k the coefficient of absorption, and a a parameter equal to 0·5 μ for AgBr and 0·24 μ for AgCl, at an average t (see Luckey, G. W., *Jl. Chem. Physics*, May 1955, pp. 882–890).

The grain becomes developable when a critical condition is achieved. Little information is available on the nature of this critical condition:(45) it may depend on the size of the silver grain, its structure, or the properties of its interface with the halide.

Sub-specks. According to Burton,(46) the latent image utilizes the specks which can be developed, but there also exists some incomplete specks(47) which form a sub-latent image. These grains, whose specks have not yet reached an optimum size, may respond to development in the course of a second and very low intensity exposure. The larger of the incomplete specks tend to increase in size, while the smaller ones shrink.

When a latent image is kept in darkness, the sub-specks increase in size, the electrons necessary for this growth being supplied by thermal agitation. This is the basis for the intensification of a latent image by time.

In Webb's opinion(48) the sub-image centres are formed of two silver atoms, while the normal centres contain eight. They do not occur in any great numbers except at high luminous intensities, since they form in a shorter time than that required for exposure. On the other hand, development is slower when the exposure is at high intensity (*Cabannes-Hoftmann effect*).

Huggins's hypothesis. Huggins(49) propounded a hypothesis according to which the latent image is constituted, not by silver, but by silver bromide which has changed from its normal B1 structure (of the sodium chloride type) to B3 (of the zinc sulphide type) (*Jl. Chem. Phys.*, 1943, 412). The B3 structure, stabilized by photoelectrons and possibly also by Ag^+ ions, is the structure of silver iodide. It would contain positive and negative potential holes, and the former would be possible positions for photoelectrons.

Junghanns and Staude, who tested this hypothesis by determining the specific masses of the crystals before and after irradiation, did not observe any expansion.(50)

27. Internal latent image

The suggestion of an internal latent image, touched upon by Kogelmann in 1894, was not considered seriously until 1931 by Luppo-Cramer. Belliot, in admitting its existence, made a distinction between the surface latent image—which can be eliminated with a solution of *chromic acid*—and the internal latent image, inside the crystal, which is not attacked by oxidizing agents. Various authors have even separated a 'sub-surface' image, thicker than the surface layer, and soluble in a more concentrated solution of chromic acid. Thus, starting from the outside, the following will appear:

surface specks;
intermediate specks (at ten reticular distances);
deep specks (clearly separated).

The internal image which, according to Hautot and Falla, is sensitive to yellow and red, is formed at *high intensities* when electrons are produced in great numbers. As the latent image grows, so the electron levels become deeper. In order to produce deep specks it is necessary for the exposure to be 1,000 to 100,000 times longer (according to the emulsions) than the time required to obtain surface specks. The internal latent image forms *after* the external image. The opposite occurs in the case of X-rays,(51) and the process is examined by using the radioactive tracer method.(52)

The internal latent image is of the same constitution as the external image. When over-exposure occurs, that part of the image which constitutes the over-exposure will move to the surface in colloidal form. The internal image is the cause of the second solarization maximum. The reciprocity failure at high intensities is smaller, and *vice versa.*

In Hautot's view(53) the formatory mechanism of the internal latent image is identical with that of Gurney and Mott, while the formatory mechanism of the external latent image follows the pattern outlined by Mitchell. The aptitude of an emulsion to produce an internal image depends on the degree of physical ripening.

Methods of treatment. The intermediate (sub-surface) specks will resist a 0·2% solution of chromic acid for about 2½ minutes, while the deep specks are resistant to 5% chromic acid for 3 mins. It is thus possible to dissolve the surface specks without touching the others. It is also possible to eliminate the external latent image by means of ammonium persulphate.

In order to develop the surface image alone, use a ferrous oxalate or glycin developer without sulphite.(54) After an oxidizing treatment, the internal image can be developed (para. 70).

To develop the internal image(55) use a metol-hydroquinone developer containing a solvent, in this case 0·6 to 1·8% of hypo. Another developer frequently used contains paraphenylene-diamine+6% of sulphite+0·11% of caustic soda; development time, 2 minutes. It is also possible to develop by means of a physical developer.

To dissolve a surface layer of the grains, use a solution containing 1·6% of hypo and 0·1% of sulphite. Time: from 30 seconds to 4 minutes.

28. Printing out

The decomposition of an insoluble silver salt is limited by the reverse action, when the vapour pressure of the gas (chlorine or bromine) reaches a certain value for a given temperature.

In the case of a latent image, the bromine set free in the primary photographic reaction is in very minute quantity, since there is only one molecule affected in ten million. The gelatin is capable of absorbing this bromine, and the photochemical process may proceed in the same direction.

But the decomposition of silver chloride by light is a more vigorous process than with bromide. The number of molecules affected is very great, and as a result a relatively dense deposit of metallic silver is formed, as well as a fair amount of *chlorine* which the gelatin can no longer hold. Indeed, the system is self-sensitized by the liberated silver.(56)

It is therefore necessary to add a *chlorine acceptor* to the gelatino-chloride. The most common are silver nitrate, sodium nitrite and acetone-semicarbazone.

The visible image is formed by violet-coloured *colloidal silver*, distributed within the remaining gelatino-chloride.

29. Effects of low temperatures

Above —20°C (—4°F) the radiation absorbed is completely used for photolysis (quantum yield is about 1). Between —20°C and —150°C (—228°F), only a fraction of the luminous energy is absorbed. The free electrons can move, while the interstitial ions are immobilized. Below —150°C a large proportion of the energy is liberated as a green fluorescence, by a recombination of the electrons with the bromine atoms.(57)

The loss of speed (about ten to forty times) is most apparent in the surface image.(58) It is more pronounced in fine-grain emulsions and in those ripened with sulphur sensitizers, thus proving that a loss of energy occurs in the chemical sensitivity specks.

30. Effect of high pressure

High pressure (1,000 to 2,000 kg/cm^2) bearing upon photographic emulsions will produce two simultaneous variations of sensitivity, i.e., *a decrease in the external sensitivity, and an increase in the internal sensitivity.*(59) In this desensitization, two processes are present, i.e., ***reversible desensitizing*** and ***irreversible desensitizing***,(60) which represents only 10 to 15% of the total loss of sensitivity.

Desensitizing appears to be due to a retarding of the ionic conductivity of the crystals, and the effect is at its maximum at high intensities with short exposures. The larger grains are those most affected by pressure, and a smaller amount of gelatin will increase the effect. Amongst the manufactured emulsions, the make which, up to now, has been the most sensitive to pressure is 'Radio Crystallix' film.(61)

The speed of compression, and pressure after exposure have no effect. The wavelength, however, has a considerable influence, i.e., the desensitizing is more pronounced in the violet than in the green.

As far as internal sensitizing is concerned, this is probably due to dislocations of the crystals, with formation of internal traps.(62)

Finally, we would note that Eggert and Zund(63) have obtained pressures ranging up to 10,000 kg/cm^2, using a steel-ball system.

Friction. Friction on the surface of a sensitized coating produces fog due to heat, accompanied by desensitizing due to pressure. The fog is usually sufficient to render the coating useless for practical purposes; hence the value of anti-abrasion supercoatings.

Furthermore, it is often observed that films show accidental foldings, called 'creases', in the shape of small crescents. When unexposed film is developed, they appear as black marks on a transparent ground, while after exposure they are light against a grey ground. As well as an emission of heat, the gelatin is probably removed from some crystals, which, thus become spontaneously developable.

31. Intensification of the latent image

There are several methods (64) for intensifying an underexposed latent image—methods which consist in converting the sub-specks into developable specks. This intensification—commonly called *latensification*—is an auxiliary operation which takes place *after exposure* and before development. It should not be confused with hypersensitizing (which is an operation performed before exposure), nor with normal intensification which takes place on the developed image. The various processes of latent image intensification are usually critical operations to perform in practice, since the results obtained will vary, not only with the type of emulsion, but also between two identical operations on the same emulsion.

(*a*) *Second-exposure method.* After exposure, the sensitive surface is subjected to a uniform additional exposure of low intensity and long duration. If this exposure is at high intensity, it will merely increase the number of sub-specks. The intensification is more effective if the emulsion is previously subjected to the Herschel effect. (65) It is nil with X-rays.

The second exposure method is used in the processing of cinematograph films, and in this case an exposure of some 15 minutes must be given at a sufficient intensity to develop a density of 0·05. The sensitivity at the toe of the curve is multiplied by 3. (66) Sometimes it is necessary to go up to a fog density of 0·2. When making a record of oscilloscope images, an exposure of 20 minutes is given at a distance of 2·4 metres from a 10-watt lamp in a safelight fitted with a No. 3 Wratten filter, and lined with a sheet of white paper. (67) It is possible for the developed image to be intensified further chemically. Second-exposure has also been used for colour films, such as Ektrachrome.

(*b*) *Mercury-vapour method.* This is carried out in a closed vessel, at an absolutely constant temperature and humidity. The latent image continues to intensify after leaving for a time, and the cycle may be repeated several times. The latensification can be explained by the condensation of the mercury on the smallest specks, coupled with some adsorption on the silver sulphide.

The intensification of the latent image by mercury vapour is, however, less effective than hypersensitizing (before exposure) by the same medium. (68) Furthermore, it is very irregular, and the operation is tedious. Operating conditions: t = 20°C (68°F); humidity = 50% R.H. duration of process = 6 to 24 hours.

(*c*) *Organic acid method.* The acids used are, for instance, formic, acetic and propionic acid (vapours, or solutions in carbon tetrachloride or benzene). (69) After the evaporation of the acid absorbed by the emulsion the effect remains for one or two weeks. When latensifying, traces of moisture must be present, but immersion in an aqueous solution of acid will desensitize. However, it is possible to use an aqueous solution of oxalic acid. (70) The gain in speed is from 100% to 300%. Sheppard, Vanselow and Quirk explain this method of latensification by the hypothesis that the Ag^+ ions situated on the surface of the grains are moved, due to the neutralization, by the acid, of the amine or imide groups of the gelatin.

(*d*) *Sulphur dioxide method.* The intensification of the latent image by an atmosphere of sulphur dioxide, at 50% humidity, was shown in 1943 by Simmons.(71) The duration of the process is from 2 to 24 hours, for a three- to five-times increase in sensitivity and a fog density increase of 0·2 to 0·4. The contrast decreases, which the experimenters compensate by developing twice as long—then praising latensification for the increased speed thus obtained.

A container of liquid sulphur dioxide may be used or a solution of bisulphite or metabisulphite may be acidified. Example:

Sodium bisulphite liq.	40 cc
Water	50 cc
Acetic acid	10 cc

It is possible, however, to latensify by immersion in a *solution of sulphur dioxide* (at 1 or 1½%). The speed is doubled.

With *bisulphite*, the procedure is the same. For example, immerse the exposed negative for 5 minutes in the following solution:

Potassium metabisulphite	3 g
Sodium sulphite, anhydrous	1 g
Water	100 cc

Rinse for one minute before developing.

The latent image may also be intensified by *sulphite* and *hypo* in 2% solution. A few minutes' treatment is sufficient, but if prolonged too far, would produce a reversal of the image.(72)

(*e*) *Oxidation method.* This method calls for the use of such media as hydrogen peroxide, ozone and sodium perborate, which activate the Ag^+ ions in the neighbourhood of the specks.

Hydrogen peroxide was used by Lüppo-Cramer in 1915 (for a complete exposition, see Wightman, Trivelli and Sheppard).(73) Immersion: 5 minutes in a one-volume solution, before development.

With an atmosphere of oxygen containing 4% of *ozone*(74) a 90-minute treatment is necessary, followed by a further one of 24 hours in a normal atmosphere. The increase of speed with a rapid emulsion is only 30%, whereas it is 90% with an X-ray emulsion. It has, however, been possible to obtain an increase of 100% in a rapid emulsion by using air with only 1 millionth part of ozone.

The simplest method is to immerse the exposed negative for 60 seconds in a 0·2% solution of *sodium perborate*, and develop without washing; the speed is doubled. The increase is greater if a 1% solution is used, with antifoggant added (0·15% of bromide or 0·003% of benzotriazole). The treatment time must then be reduced to 5 seconds.(75) The efficiency of the latensification decreases when development is prolonged.

(*f*) *Ammonia and amines method.* In this case the Ag^+ ions are liberated as complex $(NH^3)Ag^+$ ions and lose their ammonia (or other basic radical) after precipitation on the specks. This method is seldom used. With ammonia gas it is possible to double the sensitivity of a negative emulsion.

(*g*) *Gold method.* The exposed material is immersed for 5 minutes at 20°C in the following solution(76):

Heat until boiling just starts:

0·1% solution of potassium chloroaurate	40 cc
Potassium thiocyanate	0·5 g

then *add*

Potassium bromide	0·6 g
Water to make	1000 cc

Wash for 20 minutes before developing. The sensitivity is increased two or three times.

It would appear that the sensitivity specks containing silver react with the aurous thiocyanate and that metallic gold forms a deposit there. The latter no doubt enables the development to be initiated more easily.

1. This is actually a *suspension*, viz., a dispersal of a solid, and not of a liquid.
2. Solids will usually crystallize in one of three forms: *atomic*, *ionic* or *molecular*. Sulphur and diamond produce atomic crystals, in which the atoms are retained by powerful covalent forces. Salts produce ionic crystals, in which the atoms (in the state of ions) are kept together by electrovalent bonds. Organic substances will form molecular crystals, and in this case, the atoms are retained in less rigid groups by weak cohesive forces, known as Van der Waals' forces.

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Chapter IV

REDOX POTENTIAL

Development consists in converting the latent image into a *visible image*, but before explaining its mechanism it is essential to give a few brief notes on the meaning of *pH* and *redox potential*, which affect it closely.

32. The pH

We know (para. 845) that *water* H(OH) is formed by two *ions* H^+ and $(OH)^-$.

On the other hand, a *base* results from the union of a positive ion, such as Na^+, with the negative ion $(OH)^-$, while an *acid*, on the contrary, is formed by a negative radical Cl^-, for example, with the positive ion H^+ (para. 844). All these expositions call for a knowledge of the nature of *ions*, which it is advisable to master before pursuing the matter further (para. 841).

By reacting an acid AH with a base B(OH), a salt AB and water H(OH) or (H_2O) will be produced according to the following equation:

$$\underset{\text{Acid}}{AH} + \underset{\text{Base}}{B(OH)} = \underset{\text{Salt}}{AB} + \underset{\text{Water}}{H(OH)}$$

But acids, bases and salts in solution will dissociate into ions.

$$AH \rightleftharpoons A^- + H^+ \qquad B(OH) \rightleftharpoons B^+ + (OH)^- \qquad AB \rightleftharpoons A^- + B^+$$

The former reaction may then be written:

$$\underset{\text{Acid}}{A^- + H^+} + \underset{\text{Base}}{B^+ + (OH)^-} \rightleftharpoons \underset{\text{Salt}}{A^- + B^+} + \underset{\text{Water}}{H(OH)}$$

If we now eliminate the similar terms, there remains:

$$H^+ + (OH)^- = H(OH)$$

This means that the neutralizing of an acid by a base is no more than a reaction between the ions H^+ and $(OH)^-$ with a forming of water and a neutralizing of the electric charges. It seems obvious that the number of H^+ and $(OH)^-$ ions which combine depends on the degree of dissociation of the complete molecules AH and B(OH) into their ions, i.e., the *degree of ionization.*

As the acid and the base are the stronger, so they ionize the more fully. Sulphuric acid will ionize almost completely in dilute aqueous solution: This is a strong acid. Acetic acid, on the contrary, ionizes but slightly, and is a weak acid.

Since the operation is carried out in an aqueous solution, it is necessary to take into account the *ionization of the water* itself:

$$H(OH) \rightleftharpoons H^+ + (OH)^-$$

If we call $[H^+] + [(OH)^-]$ the number of ions H^+ and $(OH)^-$, and if we call $[H_2O]$ the total number of molecules of water, then the following equation ensues:

$$\frac{[H^+] \times [(OH)^-]}{[H_2O]} = K_{H_2O}$$

The number of dissociated molecules of water being small, the total quantity of water shows no practical variation, so that the following formula will result:

$$[H^+] \times [(OH)^-] = K_{H_2O} \times [H_2O] = K_O$$

K_0 is a characteristic constant of the ionic dissociation of water, equal to 10^{-14} at 25°C and $0{\cdot}6 \times 10^{-14}$ at 18°C.

The concentrations of H^+ and $(OH)^-$ being naturally equal, it suffices here to know one of them, viz., that of ions H^+, which is the square root of K_O, i.e.:

$$[H^+] = \sqrt{K_O} = 10^{-7} \text{ as an average.}$$

A concentration in hydrogen ions equal to 10^{-7} is characteristic of a *neutral solution* (pure water). *If the concentration in ions H^+ is higher than* 10^{-7}, *then an acid is present, but if it is lower than* 10^{-7}, *a base is present.* (In this case (OH) ions predominate.)

For greater convenience, the *logarithm of the reciprocal of the* $[H^+]$ *concentration* is used, and the value thus obtained is called the pH, thus:

$$pH = \log_{10} \frac{1}{[H^+]}$$

For a *neutral medium* in which $[H^+] = 10^{-7}$, the pH is 7. For an increasingly *acid* medium, the pH drops from 7 to 0. For a *basic* (or alkaline) medium, the pH rises from 7 to over 14.

In short, *the pH is a measure of acidity or alkalinity of a medium.*⁽¹⁾ It is very important to know this, since the properties of compounds vary considerably in this connection—solubility, speed of reaction, stability, redox potential, all depend on the pH. In every chemical process, it has to be specified in the same manner as temperature.

Buffer solutions. Buffer solutions contain either a mixture of a weak acid with a salt of a strong base and this acid (e.g., acetic acid plus sodium acetate), or a mixture of a weak base with a salt of a strong acid and this base (e.g., ammonia and ammonium chloride).

The pH of a buffer solution depends on the relative proportion of its active constituents.

The pH of a buffer solution is independent of the concentration.

Buffer solutions which are used as standards for comparison are as follows:

$KCl+HCl$ for pHs varying from 1 to 2·2.
Potassium acid phthalate $+HCl$ for pHs varying from 2·2 to 3·8.
Potassium acid phthalate $+NaOH$ for pHs varying from 4 to 6·2.
KH_2PO_4+NaOH for pHs varying from 5·8 to 8.
$H_3BO_3+KCl+NaOH$ for pHs varying from 7·8 to 10.

33. Measuring the pH

1. *Electrometric method.* In order to determine the concentration of hydrogen ions accurately, the 'electrometric method' is commonly used, and consists in measuring the potential of a *hydrogen electrode* immersed in the liquid under examination. A comparison is made with a known reference electrode, which is connected with the former by a solution of potassium chloride serving as an electrolyte. The hydrogen electrode consists of a platinum plate surrounded with hydrogen which is continuously bubbled past it. The reference electrode is a standard calomel electrode of known e.m.f.

If E is the e.m.f. of the cell formed by the hydrogen electrode—calomel electrode (measured by means of a potentiometer)—then the pH is expressed by the formula $pH = E-a/b$, in which a and b are two constants depending on the temperature and the connecting electrolyte. If the latter is potassium chloride at a concentration of 1 molecule per litre (74·5 g pl) at 20°C, then $a = 0{\cdot}2835$, and $b = 0{\cdot}0581$.

The hydrogen electrode requires complicated equipment and precise handling. In everyday practice, a *glass electrode* is used.

The glass electrode is based upon the following principle:

Two solutions, each with a different pH, will—when separated by a thin glass partition—produce a potential difference in relation to a standard (calomel) electrode.

Electrode | Sol. A | Glass | Sol. B | Standard electrode. The potential E is given by $E = A(pH_A-pH_B)+E_0$, in which A and E_0 are constants of the electrode depending on the nature of the glass; A varies also with the temperature.

The glass electrode is a very thin blown glass bulb and must possess a comparatively low electric resistance, so that a galvanometer with a sensitivity of 10^{-7}A will be adequate for measuring. The orthodox type contains a liquid of known potential, but some people prefer a glass electrode metallized on the inside.

A glass electrode has the disadvantage of being prone to attack by very alkaline solutions (e.g. caustic developers).

The normal pH-meters fall into two categories: (*a*) the direct-reading type, consisting of an amplifier and millivoltmeter, which is simple to use, and (*b*) the null reading type, in which the e.m.f. is measured without the system supplying any current. Accuracy up to 0·01 pH unit. Finally, the supply of current can be taken from the mains or from a battery.

2. *Colorimetric method.* The colorimetric method for determining the pH does not call for any expensive equipment, but it is much less accurate than the electrometric method. It is based upon the use of *colour indicators*.

In order to ascertain the pH of the solution under examination, a diluted solution is added, of an indicator whose *colour changes with the pH* (the concentration of this solution must be a known quantity, e.g., from 0·02 to 1%). The colour obtained is compared with that of a solution of known pH (*standards* which are obtainable commercially in the form of ready-to-use liquids).

The full list of coloured indicators is very long, but a few only are sufficient to test over the whole pH range.

Indicator	*pH Range*
Methyl violet I	0·2 to 1·8
Thymol blue	1·2 to 2·8
m-Dinitrophenol	2·2 to 3·8
Bromophenol blue	3·0 to 4·6
Bromoscresol green	4·0 to 5·6
Chlorophenol red	5·2 to 6·8
Bromothymol blue	6·0 to 7·6
Phenol red	6·8 to 8·4
Cresol red	7·2 to 8·8
Thymol blue	8·0 to 9·6
Phenolphtalein	8·6 to 10·2
Alizarine yellow GG	10·2 to 11·8
Tropeoline O	11·2 to 12·8

There exist some mixed indicators, known as 'universal', which give a large number of colours over a very extensive pH range. They are also to be found in the form of very convenient *indicator papers* for rapid, though approximate, measurements.

33a. Oxidation and reduction

The process of oxidation and reduction consists of a *transfer of valency electrons*. It has nothing to do with oxygen itself.

When a positive ion *loses* a surrounding electron, it increases in valency; it is said to oxidize. For instance, a ferrous ion Fe^{++} is bivalent; it is derived from an atom of iron Fe, with the loss of two electrons. If it loses a third electron, it becomes still more positive by changing to a trivalent ferric ion Fe^{+++}. The ferrous ion has been *oxidized* into a ferric ion according to the reaction:

$$Fe^{++} - e \rightarrow Fe^{+++}$$

Conversely, a ferric ion may be *reduced* to a ferrous one by appropriating an external electron. The valency decreases from 3 to 2 by increasing the number of the surrounding electrons, i.e., $Fe^{+++} + e \rightarrow Fe^{++}$.

In the same manner, cuprous salts Cu^{+} will be 'oxidized' to cupric salts Cu^{++}, stannous salts Sn^{++} to stannic salts Sn^{+++}, mercurous salts Hg^{+} to mercuric salts Hg^{++}; or conversely, the cupric, stannic and mercuric salts will be reduced to cuprous, stannous and mercurous salts.

If, instead of starting from an ion, one starts from an electrically neutral metallic atom, the latter may be 'oxidized' by losing an electron. It passes to the state of a positive ion: thus metallic silver will be oxidized to an Ag^{+} ion.

$$Ag - e \rightarrow Ag^{+}$$

and the ion Ag^{+}, on the other hand, may be reduced to metallic silver Ag by appropriating an electron: $Ag^{+} + e \rightarrow Ag$.

Any substance capable of appropriating electrons is an oxidizing agent and any substance capable of supplying electrons is a reducing agent.

The oxidizing agent itself will be reduced while it oxidizes another substance, and the reducing agent itself will be oxidized while it reduces the other substance. This is why oxidation and reduction are two closely connected processes, since when there is oxidation on the one hand, there is certainly reduction on the other and *vice versa*. For example, potassium permanganate $KMnO_4$ is mixed with ferrous chloride, according to the procedure described in para. 848. We shall now write this in a different manner, viz.:

The permanganate contains the permanganic anion $(MnO_4)^-$, in which Mn is heptavalent (secondary valency): Mn^{7+}. But the latter lacks five electrons to produce the ion Mn^{++} (main valency), according to the formula $Mn^{7+} + 5e \rightarrow Mn^{++}$.

The permanganate, therefore—capable as it is of absorbing 5 electrons—is a strong oxidizing agent. These 5 electrons are supplied by a reducing agent, i.e. the ferrous chloride $FeCl_2$, of which the ion Fe^{++} will oxidize to a ferric ion F^{+++}, thus:

$$Mn^{7+} + 5Fe^{++} \rightarrow Mn^{++} + 5Fe^{+++}$$

The permanganate (oxidizing agent) is reduced to manganese chloride, and the ferrous chloride (reducer) is oxidized to ferric chloride.

34. Electrode potential

Let us immerse a strip of *metal*, such as a silver electrode, for instance, into an aqueous solution of one of its salts.

The metal may give off *ions* to the solution, while itself assuming a negative charge. *A difference of potential is established between this solution and the metal.* This potential is due to the electrons released by the positive ions which have passed into the liquid and those remaining in the metal.

The pressure P of the metallic electrode ions, to become a solution, is the *solution potential of the metal.*

If p denotes the pressure on the electrode (osmotic pressure) of the ions already contained in the saline solution—in this case, silver ions Ag^+—three situations may arise, viz.:

(*a*) $P = p$. There is an even balance and nothing occurs.

(*b*) $P > p$. The electrode gives off Ag^+ ions and is brought to a negative potential in relation to the solution.

(*c*) $P < p$. The ions Ag^+ of the solution pass to the electrode, which is brought to a positive potential.

The electric field, which is formed immediately, balances the difference of pressure, and the movement of the ions stops. But if the metallic electrode is connected with a second and non-attackable electrode immersed in the same liquid, then the current of ions will continue.

The *potential of a metallic electrode* immersed in one of its salts is given by the formula:

$$E = \frac{RT}{nF} \log \frac{P}{p}$$

in which T is the absolute temperature (273+t°), R the gas constant $(83{\cdot}155 \times 10^4)$, n the valency of the ions, F a Faraday equal to 96·490 coulombs, and log-natural logarithms.

The *osmotic pressure* p of the ions is proportionate to their concentration c.

For Ag^+ ions, this is represented by $[Ag^+]$. Since $p = K[Ag^+]$ and since $n = 1$ for silver, the above formula becomes:

$$E = \frac{RT}{F} \log \frac{P}{K[Ag^+]}$$

which may be written:

$$E = \frac{RT}{F} \log \frac{P}{K} + \frac{RT}{F} \log [Ag^+]$$

The expression RT/F log P/K is constant and is designated by E_0.

The *silver electrode potential* thus becomes:

$$E = E_0 + \frac{RT}{F} \log [Ag^+]$$

in which E_0 is the potential of a silver electrode immersed in a solution containing one gram-ion of silver per 1000 cc, i.e., $[Ag^+] = 1$.

E_0 is the *normal potential* of the metal. For silver, it is +0·86 V the normal potential of hydrogen being 0.

All calculations made, the formula resolves itself as follows:

$$E_{Ag} = 0{\cdot}86 + 0{\cdot}06 \log_{10} [Ag^+] \text{ volt}$$

and generally speaking:

$$E = E_0 + \frac{0{\cdot}06}{n} \log [X] \text{ volt}$$

As a standard electrode for comparison, a *standard hydrogen electrode* is used (strip of platinum covered with platinum black surrounded with hydrogen gas), or alternatively a *calomel electrode* formed by the following chain:

mercury | calomel HgCl | normal solution of potassium chloride.

The mercury is connected with the conductor by a platinum wire, and a syphon enables contact to be established with the silver solution. Since the potential of this electrode is 0·283 in relation to that of hydrogen, the true value of the potential of the measured silver electrode is $E = E_0 + 0{\cdot}283$ V at 25°.

35. Redox potential

1. Let us revert to the example of permanganate,⁽²⁾ which oxidizes the solution of a ferrous salt. We have seen (para. 33a) that:

$$Mn^{7+} + 5Fe^{++} \rightarrow Mn^{++} + 5Fe^{+++}$$

Instead of making up the solutions in the usual manner, let us place them in two concentric containers M and F (Fig. 4). M contains the permanganate solution, and F—made of *porous material*—contains the solution of ferrous salt. A platinum electrode is immersed in each of these solutions, and if the two electrodes M and F are connected, a current will be observed flowing from M to F. At the same time, the bivalent iron Fe^{++} is oxidized into trivalent iron Fe^{+++} by a loss of electrons, while the permanganate is reduced to the state of manganous salt Mn^{++} by the appropriation of electrons. These migrating electrons start from the ferrous solution, travel along the conducting wire from F towards M (in the reverse direction from the conventional current) and disperse in the manganic solution.

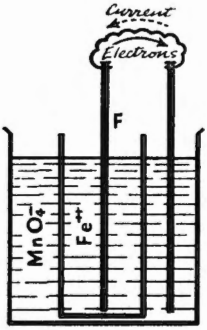


FIG. 4.

The migration of these electrons can readily be explained if one notes that in F and M we have two electrodes necessarily possessing their own potentials in relation to their respective solutions, according to our remarks in the previous paragraph. In order to produce a current from M towards F, it is necessary for electrode M to possess a greater potential than that of electrode F, so that $E_M - E_F > 0$.

Since these potentials depend on the power of emission or absorption of electrons in the reducing and oxidizing solutions, in which the electrodes are immersed, the potentials E_M and E_F must represent respectively the redox potentials of permanganate and ferrous salt.

If the concentrations of permanganate, ferrous salt and resulting ferric salt are indicated by the expressions $[MnO^{4-}]$, $[Fe^{++}]$ and $[Fe^{+++}]$, the following will be produced by applying the general formula previously established:

$$E = E_0 + \frac{0{\cdot}06}{n} \log [X]$$

For permanganate $E_{MnO_4} = 1{\cdot}45 + 0{\cdot}06/5 \log [MnO_4^-]$
For the ferrous-ferric mixture:

$$E_{Fe} = 0{\cdot}7 + 0{\cdot}06 \log \frac{[Fe^{+++}]}{[Fe^{++}]} \text{ volt}$$

In short, the *oxidizing and reducing powers of a substance are measured by its redox potential.* Knowing the concentration in gram-molecules of this substance per 1000 cc, and the *normal potential* or the proportionate potential to a normal solution (1 valency gram/l) it is possible to calculate the redox potential by means of the above formula.

The normal potential is measured once and for all in relation to a standard electrode, i.e., a hydrogen electrode.

It should be remembered, however, that the *redox potential depends on the pH*. For every value of the latter there is a corresponding and different value of the redox potential⁽³⁾:

For instance, with pH = 0, the following potentials occur⁽⁴⁾:

$(MnO_4)^-$: 1·45 V	permanganates
Fe^{+++}/Fe^{++} : 0·70 V	ferric salts
Ferricyanides/Ferrocyanides	0·70 V
I/I^- : 0·65 V	iodine
Cl/Cl^- : 1·30 V	chlorine
S_2O_8 : 2 V	persulphates
Cr^{6+}/Cr^{3+} : 1 V	dichromates
V^{5+}/V^{4+} : 1 V	vanadates
V^{4+}/V^{3+} : 0·4 V	vanadium
Ce^{4+}/Ce^{3+} : 1·45 V	cerium
H_2SO_3(at pH = 1) : 0·50 V	sulphurous acid

It will thus be seen that permanganates, chlorine, persulphates and cerium salts Ce^{4+} are very strong oxidizing agents.

At pH = 0 potassium permanganate has a potential of 1·45 V while at pH : 4·5 it drops to 1·10 V and at pH : 10 it is only 0·72 V. With vanadates, the difference is still more striking, for at pH : 0, E = 1 V; while at pH : 8, E is nil. Iodine, on the contrary, does not alter with acidity.

2. *Ag^+ ions* have a comparatively high normal redox potential, viz., 0·8 V. Ag^+ is reduced to metallic Ag by appropriating an electron according to the pattern $Ag^+ + e \rightleftharpoons Ag$, in which *$Ag^+$ is an oxidizing agent.*

As we saw in para. 34, the relative potential to a given $[Ag^+]$ concentration is calculated by the formula $E_{Ag} = 0{\cdot}80\ V + 0{\cdot}06 \log [Ag^+]$, which means that the solution oxidizes more strongly as more Ag^+ ions are present. It is much less when the silver salt is insoluble, because then $\log[Ag^+]$ becomes negative. Example:

Silver chloride, insoluble in hydrochloric acid medium, produces only 10^{-10} ions; $\log 10^{-10}$ is $\overline{10}$; the expression $0{\cdot}06\ V \log[Ag^+]$ becomes equal to $0{\cdot}06\ V \times (-10) = -0{\cdot}60\ V$ to subtract from 0·80 V leaving only 0·20 V.

3. *The redox potential is measured* by means of a *platinum wire* immersed in the liquid under examination, in an atmosphere of nitrogen. The cell is connected with a *calomel electrode* by means of a right-angle tube filled with gelose saturated with potassium chloride. A potentiometer shows the potential of the platinum electrode at a given temperature and pH.

The *colorimetric method* is quicker, though often subject to error. In this case, indicator dyes are used (safranines, sulphonated indigoes, methylene blue, indo-phenols, etc.) which change colour in a certain range of the redox potential. (They lose their colour in a reducing medium.) Some indicator systems show two ranges of change, e.g., a mixture of starch paste, iodine and colourless potassium iodide (at an acid or neutral pH) becomes blue at 0·65 V and loses colour again at 0·9 V. As a general rule, it is advisable to check the accuracy in the colour change of an indicator, for a given substance and under given conditions, by the potentiometric method.

1. *Note.*—The pH of pure water, fixed at 7, is theoretical. Distilled water is acid (pH = 5·5). Double-distilled water is less so, with a pH of 6·2.
2. Charlot G.: *Annales de Chimie Analytique*. Importance of theoretical knowledge in analytical chemistry.
3. The redox potential is linked to the pH by the expression $E_H = -0{\cdot}06\ pH - 0{\cdot}03 \log P$, in which P is the *hydrogen pressure* in equilibrium with the solution. $-\log P$ is designated by the symbol *rH*. In practice, the following occurs in measurements:

$$E_H = a - \frac{b}{2} rH + b.pH$$

in which a and b are constants. *Oxidizing systems have an rH higher than* 27.

Chapter V

THEORY OF DEVELOPMENT

36. Development centres and redox potential

1. As we have already seen, the latent image is formed of microscopic aggregates of *metallic silver* dispersed on the surface of the silver bromide crystal.

Development consists in reducing the grains of silver bromide to metallic silver which forms the visible image. But only the grains affected by light, that is, the grains having *centres* are reduced. This means firstly that the visible image obtained is discontinuous, for it is formed of individual points, separate or in groups depending on whether the light was weak or strong; therefore a grain begins to be blackened *around the centres* in successive concentric spheres until the grain is completely reduced (Fig. 5). The gelatino-bromide layer is then at its normal limit of blackening and its *maximum contrast* or 'γ-infinity'; it is then composed of completely reduced grains, and grains which are unaffected, with no intermediate state. The initial amount of silver in the development centres is increased about ten billion times.

FIG. 5.

Development is carried out by immersing the exposed sensitive layer in a bath (developer) containing a *reducing agent* for a certain time. Study of redox potentials teaches that a reducing substance is one which has a much lower potential than the compound to be reduced. The reducer *parts with electrons* which are received by the oxidizing agent; in these conditions, the reducer becomes oxidized and the oxidizing agent is reduced. The oxidizing agent is in this case the Ag⁺ ion which is converted to metallic silver, by acquiring an electron according to the scheme:

$$\text{Reducer} + \text{Ag}^+ = \underbrace{\text{Ag}^+ + e}_{\text{Ag}} + \text{ oxidized reducer}$$

2. It was explained in para. 35 that for a reaction to take place between an oxidizing agent and a reducer, the potential of the oxidizing agent must be greater than that of the reducer. In this case the oxidizing agent is the Ag^+ ion and the reducer is the developing agent: there must therefore be a positive potential difference between E_{Ag} and E_{red}

$$\Delta E = E_{Ag} - E_{red}$$

But the redox potential of silver is a function of the concentration of Ag^+ following the formula

$$E_{Ag} = E_0 + \frac{RT}{F} \log Ag^+$$

As the silver ion concentration is reduced by the presence of bromide ions, whose usual concentration is 0·01 gram-ion, E_{Ag} is, at the most, 0·202 V at 18°C.

Reinders⁽¹⁾ has shown that for development to take place it is insufficient for the developer to have a lower potential than the silver; there must be a substantial minimum which varies with the exposure. This potential difference must be about 0·07 V for the high exposures and 0·1 V for the low ones. If an average value of 0·08 V is chosen, then the *maximum potential of a reducing agent, for development to take place must be 0·12 V*, for $0{\cdot}08\ V = 0{\cdot}202\ V - E_{red}$

$$\text{Therefore } E_{red} < 0{\cdot}12\ V.$$

The potential (or activity) *of development* therefore diminishes as the oxidation potential increases.⁽²⁾

In other words, *any substance* with a redox potential below 0·120 V can develop a photographic image. Abribat⁽³⁾ has successfully tried a wide range of products: sugars, leuco bases, haemoglobin, anaerobic bacteria cultures, old Burgundy wines made alkaline, etc.

3. The developing power of a developer towards a silver halide is not only dependent on its reducing power, but also on the potential of the halide, and consequently on the composition of the latter: *silver chloride is more easily reduced than silver bromide*⁽³ᵇ⁾ whilst *the iodide is very difficult to reduce.* Similarly, of the bromides which contain a proportion of iodide, those with the highest content need a more powerful developer.

The size and structure of the grain also have an effect. In general, fine-grain emulsions can be developed at a higher redox potential (that is, a weaker developer) than fast coarse-grain emulsions.

As a general rule, it can be considered that the silver halides can be reduced even without exposure; but the rate of reduction is slow. The centres formed on exposure accelerate the phenomenon considerably.

37. Adsorption of developer and development theory

1. In practice, reduction only takes place around the development centres, for the silver bromide crystal is surrounded by a *potential barrier* which can

only be breached in the neighbourhood of the centres.⁽⁴⁾ Each surface silver ion is surrounded by only 5 Br ions instead of 6; to saturate its affinity it adsorbs a Br^- from the potassium bromide. The layer of Br^- protecting the Ag^+ is itself surrounded by a layer of K^+ ions.

Sheppard and Meyer⁽⁵⁾ in 1920 put forward the hypothesis that the developing agent is first *adsorbed* by the silver bromide. James and Vanselow⁽⁶⁾ have recently confirmed this chromatographically, and have shown that the developing agent is found in the ionized state.

Luppo-Cramer, however, stated in 1924 that the induction period of a hydroquinone developer is shortened by the presence of its *oxidation products*. Frotzsher, then Luther⁽⁷⁾ considered that these products were essential to the triggering-off of development. Staude⁽⁸⁾ stated more precisely that they behave as intermediates for the adsorption of the reducing agent. Further experiments of Staude and Brauer⁽⁹⁾ have just confirmed this: *without the presence of quinone, the hydroquinone is not adsorbed, and will not develop, and furthermore the quinone itself, oxidation product, is only adsorbed by exposed silver*; *the quantity increasing with the exposure received.*

Rabinovitch⁽¹⁰⁾ has shown also that the reduction of the adsorbed developer takes place at the silver-bromide boundary, and that the metal resulting from the reaction in turn adsorbs further developer. According to the same worker, all metals in a finely divided state, whose crystal lattice is cubic (silver, gold, platinum, copper) bring about catalytic oxidation of the developer.

It might be, however, an *interface catalysis* at the crystal-centre-developer point of contact.

Sheppard, applying James' hypothesis⁽¹¹⁾ has disputed Rabinovitch's theory according to which the adsorption takes place on the centres only. He thought that this takes place more on the silver ions surrounding the silver metal of the latent image. Holes form around the centres: migration of silver atoms on one hand (uncovering fresh silver bromide surfaces to the developer) and passage of bromide ions on the other. Harker and Sheppard have put forward the hypothesis that the migration of freshly formed silver atoms on the surface of the metal, before they are incorporated in the lattice results in the formation of filaments.

For a developer to develop, it is not sufficient that it should have a suitable redox potential; it is also essential that both the developer and its oxidation product should be adsorbed by the development centres of the latent image.⁽¹²⁾

2. *Electrolytic theory*. According to the Gurney-Mott theory, extended to development by Webb and Evans, there is a potential difference between the interior and exterior of the silver bromide grain. Normally, the electrons cannot cross the barrier formed of Br^- (themselves surrounded by K^+ ions). However, the silver specks of the latent image break it down, like an *electrode* buried in the grain. The reducer (developer) then gives electrons to the Ag metal and the potential of the speck rises.

The interstitial silver ions of the lattice are displaced by thermal agitation, and are attracted towards the speck to form new layers at the interface, $Ag^+ + e = Ag$. Having no room, the silver metal is pushed out (into the gelatin) as spongy filaments. The crystal becomes more deformed as development proceeds, which further accelerates the production of silver ions capable of being neutralized by the electrons.

Berg does not bring in the interstitial silver ions: the growing specks leave empty places where positive holes collect. The Br^- ions can then reach the surface to pass into solution.

Jaenicke, Kruger and Hauffe(13) combine the role of electrode played by the specks with the theory of Wagner and Traud (1936) following which the oxidation of the developer and the reduction of the silver ions are two phenomena which take place at different places.

38. Structure of the developed grain

1. The electron microscope shows that during development, *filaments* of metallic silver are pushed out of the crystal, the grain being finally made up of a mass of irregular metallic threads, similar to masses of seaweed (Fig. 5a). The length of each filament is greater than the diameter of the crystal. On the other hand, the distance of projection depends on the rigidity of the gelatin. The developed grain therefore appears as a spongy, filamentary mass. When the grains are very small, as in Lippmann emulsions (0·04 μ diameter) a single filament, longer but thinner than the grain is formed.

Hydroquinone produces thick filaments; metol and amidol give fine filaments. Physical development, contrary to chemical development, results in compact grains, or crystalline plates. When physical development takes place before fixing, however, ribbons are formed, 0·1 μ wide and several μ long.

FIG. 5a.

If the reducing power of a chemical developer decreases, there is a transition of the grain structure from filamentary to plate;(14) for example, by developing for twenty-eight hours in a solution containing ferrous sulphate, ferric nitrate and sodium citrate. According to Levenson and Tabor, in the beginning the silver tends to form a thin plate structure; this is during the induction period. Then, as the rate of growth increases, the silver tends to reform into filaments. The silver of the plates must therefore be quite mobile to be re-used for the production of these filaments.

2. In the previous paragraph it was shown that these are several *processes* by which the 'tangled seaweed' structure of the developed grain can be

explained. Thus for James and Kornfeld(15) the filaments are due to the migration of the silver from the point of its production at the Ag- AgBr-developer interface along the surface of the already reduced metal. Levenson and Tabor considered that it takes place along the fissures and other crystal defects, and insist that it is from the labile mass of silver and not from the AgBr itself, which is caused by the great mobility of the Ag^+ ions along the filament. On the other hand we have seen that following the Gurney-Mott electrolytic theory the developer provides the specks with electrons which produce a negative electric field, to which the interstitial ions are rapidly attracted, producing a pressure which pushes the silver out of the grain. For Keith and Mitchell(16) the electric negative charges are concentrated at the extremities of the specks where they are neutralized by the Ag^+ ions.

We would note that the formation of fine filaments of silver was studied in 1932 by Kohlschütter.(17) Then, at the conclusion of the electrolysis studies of Samartsev and Vagramyan,(18) Gorbunova and Dankov stated that the growth of the crystal takes place on one face.(19) The laws of the crystallization of fine filaments was then studied by Gorbunova and Zhukova,(20) Boisson(21) and Vuille(21b) who noted that the silver polygonal figures in AgBr crystals, caused by the arrival of Ag^+ ions, grow up along the intersection of the crystal surface and the [111] or [100] orientations.

3. *Electron microscope studies* of the structure of silver bromide grains have been made successively by the following workers who have reported their operating technique: Von Ardenne,(22) Hall and Schoen,(23) Kuster,(24) Selme,(25) Hamm and Comer.(26) The emulsion, dissolved in warm water, is generally deposited on an extremely thin colloidon film forming the carrier. This film can be obtained by placing a drop of 1-2% nitro-cellulose solution (in amyl acetate) on a sheet of water; it is removed on a thin disc of perforated platinum or on a fine metal gauze. After putting it in position the apparatus is exhausted. The images are photographed on electron-sensitive plates or on normal plates if an intermediate fluorescent screen is used. The actual enlargement of the apparatus, assisted by an enlargement of the negative gives a final magnification of 25,000 to 10,000 diameters. Only very thin crystals can be examined due to the low penetrating power of the electrons: 10–50 mμ layer thickness for a resolution of 5 mμ.

To separate the gelatin from the crystals in order to study the latter under the microscope, the emulsion can be hydrolysed with an enzyme. The suspension is then centrifuged and washed before being placed on the carrier.(26)

The structure of unexposed grains cannot be recorded directly as they are sensitive to electrons. They must be strongly overexposed to bring about complete photolysis: dark aggregates can be seen formed on the surface of the grain, at certain well-defined spots, probably the sensitivity centres or the fissures, whilst the droplets of silver form a halo around the grain. The double moulding technique used by Hamm and Comer(26) enables the action of the electrons on the crystal to be avoided. A better method is to protect the crystals by a carbon deposit which can be obtained either by sublimation(26b) or action of effluvia in benzene vapours.(26c)

39. Influence of pH on the development potential

As the redox potential of a solution is a function of its pH, it is obvious that the *development potential (or activity) of a developer increases with the pH, that is with the alkalinity*. The development potential becomes higher as the redox potential drops, and also, this diminishes with the pH following the equation

$$E_{red} = E_0 + \frac{RT}{nF} \log_e \frac{[Ox]}{[Red]} + \frac{RT}{nF} \log_e [H^+]$$

in which [Ox] represents the concentration of the oxidized form of the developer, [Red] that of the normal form, $[H^+]$ the concentration of hydrogen ions. All calculations made with the preceding formula become

$$E_{red} = E_0 + \frac{0{\cdot}058}{n} \log_{10} \frac{[Ox]}{[Red]} - 0{\cdot}058\ pH$$

If the curve of the change in redox potential is plotted against pH, it is seen that the development of an image is only possible, with the reservation of adsorption, above a certain pH value (which varies with the developing agent) from which the redox potential has a value less than 0·120 V.

Some substances, which are oxidizing agents in acid solution become reducers (and hence developers) in strongly alkaline or even neutral solution; this is the case with hydrogen peroxide, a powerful oxidizing agent at pH 0 with E equal to 0·88 V falling to 0·1 V at a pH of 11 (very alkaline). We have already shown similar cases of change of potential as a function of the acidity: the vanadates for example give E = 0·5 V at pH 4 and 0·1 V at pH 7 (neutral).

When the developing agent is neither acid nor basic the pH has only a slight influence on the development potential; this is the case with ferrous oxalate which shows no appreciable variation between pH 4 and 9.

It is therefore evident that for consistent development the ***pH must be kept constant.***

Now the decomposition of silver bromide by the reducing agent produces both metallic silver making up the image and hydrobromic acid resulting from the liberation of the bromide ions, which tends to reduce the pH of the solution. It is therefore necessary to neutralize the acid as it is produced by a buffering agent: this is why a *large excess of alkali* which maintains the pH constant is added to a developer.

The chemical constitution of the alkali is of relatively slight importance in itself as long as it can fulfil its two roles:

1. Produce the required pH of the solution;
2. Neutralize the resulting hydrobromic acid and maintain the pH constant by its buffering action.

40. Influence of the sulphite

Consider the redox potential formula of a developer at fixed pH

$$E_{red} = E_0 + \frac{0{\cdot}058}{n} \log_{10} \frac{[Ox]}{[Red]}$$

where $\frac{0{\cdot}058}{n} \log_{10} \frac{[Ox]}{[Red]}$ is a negative term.

The ratio [Ox]/[Red] must be very small in the case where E_0 is greater than 0·12 V; thus log [Ox]/[Red], sufficiently great, subtracted from E_0 brings E_{Red} to less than 0·12 V, anyway.

By eliminating the *oxidized form of the developer* as it is formed, the ratio of the concentrations [OX]/[Red] can be kept sufficiently low for E_{Red} to remain substantially constant below 0·12 V, even with substances apparently possessing a high redox potential. Pouradier and Abribat(27) have shown that the reduction of silver bromide by a ferrous salt produces ferric ions (oxidized form) which are eliminated by converting them to a ferri-hydrofluoric complex, $(FeF_6)^{---}$, by adding sodium fluoride. Otherwise, the normal potential of the system Fe^{++}/Fe^{+++} being 0·75 V, the ferrous solution would not develop.

The *sodium sulphite* which is added to a developer in order to preserve it, by preventing atmospheric oxidation also brings about, during development, the elimination of the oxidized form of the reducing agent by converting it to the *sulphonate*.

If, for example, the developing agent is *hydroquinone* with the empirical formula $C_6H_4(OH)_2$ the sequence of reactions is as follows:(28)

The hydroquinone is first ionized to *quinone ion* $(C_6H_4O_2)^{--}$ and hydrogen ions H^+

$$\underset{\text{hydroquinone}}{C_6H_4(OH)_2} \rightarrow \underset{\text{quinone ion}}{(C_6H_4O_2)^{--}} + \underset{\substack{\text{hydrogen}\\ \text{ions}}}{2H^+}$$

and the quinone ion gives 2 electrons to 2 silver ions which become 2 atoms of silver metal, and is itself converted to quinone

$$\underset{\substack{\text{quinone}\\ \text{ion}}}{(C_6H_4O_2)^{--}} + \underset{\substack{\text{silver}\\ \text{ions}}}{2Ag^+} \rightarrow \underset{\substack{\text{silver}\\ \text{metal}}}{2Ag} + \underset{\text{quinone}}{C_6H_4O_2}$$

The hydrogen ions combine with the bromide ions to produce hydrobromic acid.

$$2H^+ + 2Br^- = 2HBr.$$

The *quinone* combines with *sodium sulphite* to form the *mono* and *disulphonates* of quinone.

Thus the oxidized form of the developer disappears and the ratio [Ox]/[Red] drops. The redox potential is consequently lowered, having the result of increasing the development potential.

In the presence of aerial oxygen, colourless hydroquinone monosulphonate and sodium sulphate are formed by the action of sulphite on hydroquinone:

$$\underset{\text{hydroquinone}}{C_6H_4(OH)_2} + \underset{\substack{\text{sodium}\\ \text{sulphite}}}{2Na_2SO_3} + \underset{\text{oxygen}}{O_2} = \underset{\substack{\text{sodium hydroquinone}\\ \text{monosulphonate}}}{C_6H_3(OH)_2 . SO_3Na} + \underset{\substack{\text{sodium}\\ \text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{NaOH}$$

In the absence of sulphite, strongly coloured brown oxidation products are formed.(29)

The sulphite also prevents *autoxidation* of the developing agent. There are, however, other inhibiting substances which are more effective such as cysteine, thioglycolic acid and especially ascorbic acid.(30)

Action of sulphite on emulsion speed. The sulphite increases the speed of emulsions more effectively if they are incompletely developed. The effect is marked with double-charged developers such as hydroquinone, especially if the oxidation products are accelerators. It is less with single-charge developers (metol).

This action of sulphite appears to be due to the solution of the surface layer of the grains, exposing the development centres and probably forming *argentisulphites*. Thiosulphate produces a similar effect at a much lower concentration.

Sulphite is therefore a solvent. A 50-g.p.L. solution dissolves 0·9 g of silver bromide and 2·1 g of chloride.

To sum up, the addition of sodium sulphite to a developing solution has the purposes:

(1) To *preserve* the developer by inhibiting autoxidation and slowing down aerial oxidation.
(2) To *stabilize* the reduction of the silver salt by removing the oxidation product as it is formed, as the sulphonate.
(3) To act as a *solvent* (see para. 43/5).

Solvents of silver halides, like sulphites, bromides, thiocyanates, thiosulphates or ammonia, when added to developers, produce silver complexes which, in turn, result in *physical development* (see para. 71), which is slower than chemical development.(30b)

41. Modification of the potential barrier

We have already seen that the silver bromide crystal is surrounded by a *double barrier of Br^- ions and K^+ ions*. The height of this *potential barrier* can be increased or reduced with retarders or accelerators.

1. *Soluble bromide.* A small quantity of potassium bromide is normally added to a new developer to avoid chemical fog produced by a violent reduction of silver bromide even without exposure. Development is also slowed down by the addition or formation of soluble bromide resulting from the reduction of silver bromide. A used developer necessarily contains a large amount of bromide and cannot therefore develop normally even though it still contains a high proportion of developing agent. The emulsion speed is therefore greatly reduced.

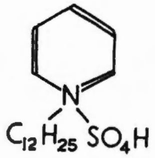
The action of soluble bromide in development is due to the raising of the potential barrier following the mass action of Br^- ions. This barrier protects the unexposed parts of the crystal but at the same time lengthens the induction period.

Soluble bromide has no influence on developers with a zero charge.

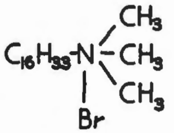
2. *Development accelerators.* The opposite effect to the addition of potassium bromide—the reduction, cancellation or reversal of the potential

barrier—can be achieved by adding certain strongly electroactive compounds, especially cationic *surface active agents* of the ammonium quaternary type, in the concentration of 0·05%. In this way development is greatly accelerated—the period of induction being considerably reduced.

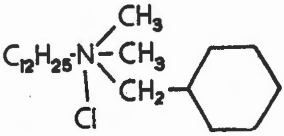
The most interesting among the cationic surface active agents are *laurylpyridinium chloride* (or sulphate) used by Lottermoser and Steudel in 1938,⁽31⁾ *laurylpyridinium p-toluene-sulphonate*, *β-phenylethyl-α-picolinium bromide.*



Lauryl pyridinium sulphate
(Repellat T 59) (33)



Cetyl trimethylammonium bromide
(Cetavlon) (34)



Dimethyl-benzyl-lauryl ammonium chloride
(Zepyrol) (35)

Tests have been made with ammonium derivatives having the structure:⁽32⁾

$$[CH_3-(CH_2)_n-N \equiv RR'R'']^+X^-.$$

It is probable that the developer *oxidation products*, which, for the smooth progress of development, must, as we have seen, have been adsorbed on to the development centres, act by reducing the potential barrier. It is the same with the *weakly-charged developers*, which, associated with other developers, facilitate development and reduce the induction period: this is the phenomenon of superadditivity (which will be examined in the following chapter).

Finally it should be noted that certain dyes (safranines, pinacyanols, etc.) act as development accelerators. They are used in some ultra rapid developer formulas. (See following chapter.)

42. Induction period

The intitial phase of development, the period which precedes the start of development, is called the *induction*. It is logically the result of the existence of the *negative potential barrier* which surround each silver bromide crystal. The charges which accumulate there are not neutralized and the barrier is broken down, in a greater or less time, denoting the induction period.

James⁽36⁾ has shown that the induction period increases with the charge of the developer: a developer with a charge of 2 has more difficulty in overcoming the potential barrier than a developer with a charge of 1. Development as a whole takes much longer as the developer has a stronger electric charge, or alternatively a high valency.

Charge (or valency) 0: diaminodurene, substituted p-phenylene-diamines, etc.

Charge (or valency) 1: metol, p-aminophenol, dimethyl-p-aminophenol, p-aminocarvacrol, pyrocatechin.

Charge (or valency) 2: hydroquinone, glycine, ascorbic acid, ferrous oxalate, etc.

Charge (or valency) 3: sodium hydroquinone-monosulphonate.

The added bromine ions which raise the barrier have less effect when the developer has a low charge.

Burton stated that the apparent induction period is longer for the deep silver bromide crystals than for the surface crystals, the difference can be 30 secs. In addition it is possible that the small centres are less effective for an equal surface than the large silver specks making up the latent image.

The induction period increases with the dilution. However, it is nil with the zero charge reducers even when very dilute. It decreases with the exposure and the bromide concentration as well as with fast colour sensitive emulsions; the dyes reduce the potential barrier.

The addition of quinone to hydroquinone in the absence of sulphite accelerates development (acceleration due to the decomposition products of quinone in alkaline solution). With less rapid emulsions and medium contrast it has been stated that lower curved part of the development curve disappears with increase of contrast at the beginning of reduction.

The sulphite, which destroys the oxidation products of the developing agent, prevents the preceding phenomenon from taking place, and consequently lengthens the toe of the characteristic curve.

The addition of bromide to an unbromided developer, during development, changes the rate but not the maximum density except where the addition is excessive. In the latter case, a variation in the number of developed grains occurs, due to the increase in the induction period of the grains which have not, at that moment, been affected.

James has also given evidence of the influence of the charge of the developer on the speed: the densities corresponding to the low exposures are higher with the reducing ions which have a single charge, and still greater with the zero charge ions. Thus at $\gamma = 0{\cdot}65$ the following H and D speeds are obtained: zero charge 65, single charge 32, double charge 2.

On the other hand, a *reduction of the potential barrier* with the benefit of an increase in speed by adding a *safranine* or *pinacyanol* dye, or even with *thallous* ions, is only effective with the double-charge developers (hydroquinone). Some action is produced by preliminary immersion in a 0·01 M solution of *lead* acetate. However, better results are obtained with a 0·001 M solution of a *dodecylpyridinium* salt.(37)

The effect of the developer charge is mainly apparent for the low exposures. It becomes negligible with large exposures.

For a mathematical study of the kinetics of development, see Bagdassarian's work.(38)

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Chapter VI

THE DEVELOPING SOLUTIONS

43. Composition of the developing solution

The developing solution, as we have seen, is a solution of adsorbable developing agents having a redox potential less than 120 mV. This potential can in fact be negative, between zero and —200 mV for example: as the potential becomes lower, so the activity of the developer increases.

In practice the developing solution generally contains:

1. An *organic reducing agent* which is the essential constituent of the bath. Its function is to convert the silver ions Ag^+ of the silver bromide crystals into silver metal, by supplying the necessary electrons.

The number of reducing, or developing agents, is extremely great, and their chemical constitution will be studied in a following chapter. The most widely used are hydroquinone and metol, but p-aminophenol, diaminophenol, glycin, pyrogallol, p-phenylenediamine are also useful.

The concentration of developing agent is of the order of 5 g per litre.

2. An *alkali*, whose purpose is to maintain the reduction potential at a sufficiently low value by working at a *high pH* (that is, alkaline) for we know that the redox potential is decreased as the pH is increased. In addition, the pH must be kept constant, and by using excess alkali, the hydrobromic acid liberated during the development reaction is neutralized.

Generally, *sodium carbonate* and *borax* are used; less frequently, caustic soda.

The pH depends on the nature of the alkali.

3. *A preservative*: *sulphite* which also has the function of controlling development. The sulphite is an essential constituent of the bath. The amount used can vary from 25 to 100 g per litre. If the quantity is reduced to 2 g per litre the oxidation products of the developing agent are not completely neutralized and tan the gelatin in proportion to the image density. In the third part formulas for these tanning developers will be given.

4. *An anti-fogging retarder*: *potassium bromide.* Quantity: 0·3–2 g per litre. During development the concentration is however increased, the bromide being provided by reduction of the silver salt to such an extent that the quantity added to the new bath becomes negligible compared with the considerable quantity resulting from prolonged use of the solution: the slowing down of development becomes greater and greater. At the same time, a reduction in sensitivity of the emulsion occurs and the contrast is increased.

Organic anti-foggants used in stabilizing emulsions can be used to replace potassium bromide. Those currently used are 6-*nitrobenziminazole nitrate* and *benzotriazol.* Concentration 0·25–0·5 g per litre. They are necessary for development at high temperatures.

5. *A silver bromide solvent.* The one most frequently used is the sulphite itself which has this action. It can be used up to 100 g per litre. But it is also possible to add in low concentration *potassium thiocyanate* KCNS; *sodium thiosulphate* or even *ammonia.* A high solvent action encourages the formation of fine grains of silver.

p-phenylenediamine is at the same time a developer and a solvent (less than ammonia). This property is attributable to its oxidation products.

6. *A calcium sequestering agent.* This is optional, most frequently it is omitted.

7. *A wetting agent*, also optional.

44. Water used for developers

Tap water or drinking-water is not chemically pure: it contains among other things *calcium* bicarbonate and sulphate, chlorides, *iron* oxide, silica, carbon dioxide, and dissolved *oxygen.* Also traces of hypochlorite are added to sterilize it. The degree of acidity varies according to the source.

The *calcium* in the water is *precipitated* in a newly prepared developer and makes it turbid. Calcium carbonate and sulphite which are deposited on standing as whitish mud, are not very inconvenient: the solution can be decanted and filtered. But the smears of calcium and other products which may appear after drying from drops adhering to the washed films, are composed of these materials.

Silica can be formed in acid-fixing baths as fine *colloidal particles* which stick to the gelatin and spoil the surface after glazing.

Dissolved oxygen is the most awkward constituent present as it leads to premature oxidation of the developer.

Unusual impurities: these are *hydrogen sulphide, rust* from defective pipes, and copper from water stills. These are very objectionable.

Ordinary drinking water must not contain more than 60 mg of *chloride* per litre. It contains 5–30 mg of *sulphuric acid* as sulphates. Its content of organic matter must be less than 2 mg (expressed as oxygen) or less than 40 mg of actual material; with a higher concentration, the water under consideration is suspect.

The presence of *ammonia* (and of nitrite) is an unfavourable indication. The water has probably been fouled by animal materials.

Water are classed by *degrees of hardness* (1 degree being 10 p.p.m. calcium carbonate). This depends on the behaviour of a sample towards a standard soap solution and the persistence of the lather. Ordinary drinking-water has a hardness of less than 30°. Water of 60° hardness or above is not suitable for any purpose.

For developers it is preferable to use *boiled water*. Boiling expels the dissolved gases and precipitates part of the calcium as carbonate. Distilled water is not necessary. In the absence of boiled water, ordinary tap water can be used without harmful effects.

45. Hard Waters

Hard water produces deposits of calcium carbonate in developers and sensitive layers. With borax developers, calcium sulphite is formed (lower pH). Henn and Crabtree have pointed out that 0·3 g per litre $CaCl_2$ in a normal developer produce this effect, 0·07 g per litre in a borax developer and 1·7 g per litre in a caustic bath.

The calcium salts can be eliminated by precipitation (this does not remove the calcium from the gelatin) or they can be sequestered by forming innocuous complex ions with citric or tartaric acid (5–10%).

This effect is dependent upon the pH. It is better to use sodium *hexametaphosphate* $(NaPO_3)_6$, *pyrophosphate* or *tetraphosphate* $Na_6P_4O_{13}$. These compounds are hydrolyzed in warm water to the orthophosphates and lose their sequestering power. Of the three compounds, only the tetraphosphate has no effect on the pH of the bath, and is therefore preferable to the other two; in addition to which, it is stable in the solid state. For carbonate and borax developers, about 2 g per litre is used, and about 0·5 g for acid developers. Under tropical conditions, hydrolysis is prevented by the addition of 2–4 times the weight of sodium citrate (*Jl. Soc. Mot. Pict. Eng.*, 1944, 426).

Sodium hexametaphosphate in a 1% solution has a pH of 7·2; it is known under the name of Calgon.

The crystalline *pyrophosphate* has the formula $Na_4P_2O_7 . 10\,H_2O$. Its pH in 1% solution is 9·8.

Tripolyphosphate (Giltex O) has the formula $Na_5P_3O_{10}$. pH = 9·8.

A simple method for obtaining calcium-free water is to soften it by passing through one or more ion *exchangers* in special apparatus filled with permutit or, better, with certain synthetic resins. With permutit the calcium is replaced by sodium, and the exchanger is regenerated with a solution of sodium chloride. With the synthetic resins the metal and acid radicals are substituted by H and OH, that is with water. Regeneration is then carried out with soda and hydrochloric acid.

46. Developer alkalis

We have said that the energy of a developer increases with its alkalinity. In order of increasing alkalinity we have: borax, sodium metaborate, sodium carbonate, caustic soda.

Borax is sodium tetraborate $Na_2B_4O_7 . 10\,H_2O$. Slightly soluble cold, it should be powdered before dissolving.

Metaborate (Kodalk) is obtained by fusing borax with caustic soda. Its pH is greater than that of borax. It is very soluble in water.

Borax or metaborate are frequently used together with boric acid H_3BO_3 to give a buffer, which however is not very effective.

	Concentration			
	2%	4%	6%	8%
Borax	pH 9·4	pH 9·6	—	—
Metaborate	ph 10·4	pH 10·6	pH 10·7	pH 10·8
Boric acid	pH 4·5	pH 3·9	—	—

Sodium carbonate. Sodium carbonate Na_2CO_3 is generally used in the anhydrous form or as the monohydrate $Na_2CO_3\,H_2O$. The ordinary crystalline form $Na_2CO_3\,10\,H_2O$ effloresces rapidly in air, and its use is not advised.

100 g of anhydrous sodium carbonate is equivalent of 117 g of the monohydrate and 275 g of the decahydrate.

Caustic soda NaOH is a very strong alkali which is used in high contrast developers. It is dangerous to handle as it attacks the skin and gelatin. It is preferably used in granular form. Caustic soda is deliquescent, and in air is quickly converted to carbonate; it must therefore be kept in well-stoppered bottles:

$$2NaOH+CO_2 = Na_2CO_3+H_2O$$

Trisodium phosphate $Na_3PO_4\ 12\ H_2O$. This compound, not frequently used, owes its alkalinity to its ready decomposition, in solution, into disodium phosphate and caustic soda.

Potassium salts. The potassium alkalis, although having similar chemical properties to the sodium compounds, alter the developing properties of the solution.(1) The K^+ ions are photographically more active than the Na^+ ions, particularly towards the internal latent image of the silver bromide grains. The emulsion sensitivity is increased. The simultaneous presence of K^+ and Na^+ ions increases the efficiency of anti-fogging compounds.

Potassium carbonate K_2CO_3 is available as a deliquescent anhydrous powder. Its molecular weight is 148 compared with 106 for sodium carbonate and therefore chemically 130 grams of potassium carbonate must be used in place of 100 grams of sodium salt. However, as it is photographically more active, 80 grams of potassium carbonate are sufficient to replace 100 grams of anhydrous sodium carbonate.

Caustic potash KOH has the same uses as caustic soda. It also has the same physical properties. 100 g of anhydrous sodium carbonate corresponds photographically to 10·4 g of caustic soda and 14·5 g of caustic potash.

47. Sulphite

Anhydrous sodium sulphite with the formula Na_2SO_3 is stable when dry. It has a higher purity than the crystalline sulphite $Na_2SO_37H_2O$ which is efflorescent and readily oxidized to sulphate.

100 g of anhydrous sulphite is equivalent to 200 g of crystals.

Sulphite solutions of less than 20% concentration are rapidly oxidized. The oxidation is retarded in the presence of another reducing agent by a reciprocal anti-oxidation action.

Instead of sulphite, *potassium metabisulphite* $K_2S_2O_5$ can be used by first adding a caustic alkali which converts it into neutral sulphite. *Bisulphite* $NaHSO_3$ as the commercial 32% lye can also be used. 100 cc of bisulphite exert the same action as 47·5 g of potassium metabisulphite. Do not use sodium metabisulphite which is not so pure, and less stable than the potassium salt.

100 g anhydrous *sodium sulphite* are equivalent to: 200 cc sodium bisulphite lye+32 g caustic soda or 95 g potassium metabisulphite+32 g caustic soda (or 79 cc 30% lye).

Conversely 100 cc of bisulphite can be replaced by 50 g of sulphite and 10·5 cc (19·3 g) sulphuric acid dissolved in 65 cc of water.

Solubility of anhydrous sodium sulphite in a litre of water: 210 g at 10°C, 280 g at 20°C, 380 g at 30°C.

We would finally note that *acetone* added to a sulphite solution of hydroquinone with no alkali present forms the compound $[2(NaHSO_3)2(CH_3—CO—CH_3)]$ and the sodium salt of hydroquinone $C_6H_4(ONa)_2$: the latter behaves as a developer in alkaline solution.

48. Developers preparation

Developers are prepared in units of 1, 2, 5 litres or more.

Dissolving. Use a flask three-quarters full of tepid *boiled water* (50°C). Add successively the following products in the order given: metol, sulphite, hydroquinone, carbonate, bromide.

Make sure that each item is *completely dissolved* before adding the next one. After each addition shake the flask.

Add each item gently, sprinkling it with the aid of a sheet of clean paper.

To finish preparation: Make up to the required volume using cold water. Stir and leave for several hours. Check that the volume is correct and if necessary filter through paper which should be pleated and placed in a funnel the same size as the paper. 500 cc or 1,000 cc bottles should be completely filled with the solution and carefully stoppered.

If the developer is poured directly into a tank, cover with a floating lid.

Aerial oxidation fog: even when not used a developer when exposed to the air becomes oxidized by the oxygen in the air. It is particularly the hydroquinone which is affected. At the same time sodium sulphate is formed together with caustic soda and *tanning organic compounds*. Each reduction of sulphite in a developer, whether accidental or not, encourages the oxidation of the developing agent by loss of protective power. A bottle of partly used developer becomes more and more brown as it is oxidized and gives off an unpleasant smell.

Packed developers: ready prepared photographic products are commercially available for the preparation of developing and fixing baths. Even when these products are already weighted and mixed, great care is necessary when using them. In general they are packed in temporary paper or card containers and unless they are to be used at once it is advisable to transfer the contents to bottles.

Packed developers for 250 cc quantities are often marketed in glass tubes; these glass tubes have a separating division; one side is filled with metol and hydroquinone, the other with carbonate, sulphite and bromide. The metol hydroquinone mixture is first dissolved in water, then the remainder of the packet.

49. Energy of a developer

An energetic reducer develops all parts of the image rapidly, both shadows and highlights: the resulting *contrast* is necessary *low* and the image appears greyish. *Diaminophenol* and *metol* have this action.

A less energetic reducer first develops the parts of the image which have had the greatest exposure; the *contrast* then becomes great. This happens with *hydroquinone.*

Dilution of the developer slows down development, promotes the development of the less exposed areas, and reduces the contrast.

The *addition of bromide* slows down development, but on the contrary, prevents the development of underexposed areas (reduction of sensitivity) and increases the contrast.

Instead of measuring the redox potential, developing agents are often classified by their ability to withstand the retarding influence of a given quantity of potassium bromide. The greater the reducing power, the less the loss of density caused by the addition of bromide, and conversely. The following table reproduces the Nietz-Tschibissoff series⁽²⁾ in which the reducing power of hydroquinone is taken as 1. The higher the number, the higher the reducing power.

Ferrous oxalate	0·3
p-phenylenediamine HCl (without alkali)	0·3
p-phenylenediamine HCl (with alkali)	0·4
Methyl-p-phenylenediamine (without alkali)	0·7
Phenylhydrazine	<1
Hydroquinone	1
2-hydroxhydroquinone	>1
Glycin	1·6
Hydroxylamine	2·0
Toluhydroquinone	2·2
Methyl-p-phenylenediamine (with alkali)	3·5
Benzyl-p-aminophenol	<5
Dimethyl-p-phenylenediamine HCl	5
p-hydroxydiphenylamine	<6
p-aminophenol	6
Chlorohydroquinone	6–7
p-amino-o-cresol	7
Dibromohydroquinone	8
p-amino-m-cresol	9
Dimethyl-p-aminophenol (sulphate)	10
Dichlorohydroquinone	11
Pyrogallol	16
Metol	20
Bromohydroquinone	21
p-methylamino-o-cresol	23
2 : 4-diaminophenol (with alkali)	30–40
Thiourea	50

It is easy to state, after this table, that the introduction of CH_3 into the nucleus of hydroquinone doubles the reducing power in the resulting toluhydroquinone. A methyl group substituting an amino hydrogen atom of p-phenylenediamine (methyl-p-phenylenediamine) increases the reducing power from 0·4 to 3·5—almost nine times greater; two methyl groups give dimethyl-p-phenylenediamine and the index of reducing power increases from 3·5 to 5. The introduction of halogens increases the developing energy hydroquinone = 1, chlorohydroquinone = 6, bromohydroquinone = 21.

Influence of temperature. Raising the temperature increases the developing potential (by a corresponding decrease in redox potential). The apparent sensitivity of an exposed emulsion is doubled if the temperature is increased, for example, from 15°C to 33°C.

50. Negative developers with a single developing agent

Developing solutions containing only one developing agent are less frequently used than solutions containing a mixture of two developing agents. They give, however, excellent results each having its own particular characteristics.

1. *Metol.* Metol (Elon, Genol, etc.) is found as fine white crystals which are insoluble in concentrated sulphite solutions: this is why it must be dissolved first. Metol has a high reduction potential which rapidly brings up the low exposure regions, that is the shadows, whilst it *generally gives low contrast* when it is used alone.

The impurities frequently present in metol can produce dermatitis. To cure this, it is recommended to soak the hands for more than an hour in hot water.

Water to	1000 cc
Metol	15 g
Sodium sulphite anh.	75 g
Potassium carbonate	50 g
Potassium bromide	1 g

Immediately before use take one part of this solution and one or two parts of water. Development time at 18°C, 4–6 minutes. The image appears quickly, after about 4–10 seconds.

2. *Pyrogallol.* Pyrogallol is found as colourless needles which are very soluble and *oxidize very rapidly in solution* (which becomes brown). It can also stain the gelatin and the fingers. Pyrogallol baths can only be used once. Stock solutions are therefore prepared with bisulphite or metabisulphite and a little bromide. Just before use they are mixed with a solution of sulphite and a solution of sodium carbonate. If the stock solutions are concentrated they are diluted with a large quantity of water. The developer obtained in this way changes rapidly. In preparing the concentrated stock solution of pyrogallol the latter must not be added until the metabisulphite has dissolved. The following formula (D1) gives vigorous developers whose energy is not reduced by dilution. The image appears slowly but the gamma can reach a high value if the time is extended. A yellowish residual organic stain image is formed at the same time as the silver image.

A.	Water to	1000 cc
	Sodium metabisulphite	10 g
	Pyragallol	60 g
	Potassium bromide	1 g
B.	Water to	1000 cc
	Sodium sulphite anh.	100 g
C.	Water to	1000 cc
	Sodium carbonate anh.	75 g

For development take:

Tank: 1 part of A, B and C+11 parts of water; (12 minutes at 18°C).
Dish: 1 part A, B and C+7 parts of water; (6 minutes at 18°C).

In this formula sodium metabisulphite can be advantageously replaced by the more stable potassium salt.

3. *Pyrocatechin*

A.	Water to	500 cc
	Sodium sulphite anh.	35 g
	Pyrocatechin	12 g
B.	Water to	500 cc
	Potassium carbonate	60 g

For use take 1 part of each solution.

4. *Glycin.* Glycin (Kodurol) is found as small mica-like plates slightly soluble in the absence of alkali or sulphite. Glycin must therefore be dissolved *after* the sulphite. Glycin gives developers which are very resistant to oxidation and suitable for prolonged use in a dish. A large quantity of stock solution can therefore be prepared. The more the developer is diluted, the softer the results. Glycin baths are very sensitive to potassium bromide and to temperature. Furthermore, when they contain too much sulphite there is a risk of producing dichroic fog. Potassium carbonate gives a more powerful developer than sodium carbonate.

		KL	Agfa
Water to	1000	1000	1000 cc
Sodium sulphite anh.	3	100	125 g
Glycin	3	40	50 g
Sodium carbonate anh.	6	80	—
Potassium carbonate	—	50	250 g
Dilution	Undiluted	+3 parts water	+4 parts water
Development time at 18°C	15–25	8–10	5–10 mins.

5. *p-Aminophenol.* p-aminophenol is a readily oxidized compound which needs an adequate amount of sulphite. The developers must be kept in well-stoppered bottles. The hydrochloride is more soluble than the free base, but as it is precipitated by alkalis there is no point in using it. *The caustic alkalis form very soluble phenates which can be kept in concentrated solution*: for 100 g of p-aminophenol, 21 g of caustic soda, 36 g of caustic potash or 6·4 g of

lithium hydroxide (rarely used) are needed for this. The p-aminophenol developers are sensitive to potassium bromide.

	A	B	C	D
Water to	1000	1000	1000	1000 cc
Sodium sulphite anh.	70	100	75	50 g
p-aminophenol base	8	10	10	8 g
Sodium carbonate anh.	60	50	—	— g
Potassium carbonate	—	—	—	50 g
Caustic soda	—	2·1	—	— g
Lithium hydroxide	—	—	4	— g

The formula A develops in 3–6 minutes. Formulas B and C are more active. If the concentration of C is doubled, a bath is obtained which develops in one minute.

51. Diaminophenol developers

Some developing agents have a sufficiently low redox potential in neutral or acid solutions to be able to develop without the addition of alkali. The presence of sodium sulphite is sufficient to bring about reduction.

For this, it is necessary that the developing agent molecule should contain at least one and preferably two, amino groups, as with diaminophenol.

Diaminophenol (or amidol) is used as the hydrochloride, found as a colourless or blue-grey crystalline powder which is very soluble. *It is a very powerful reducer which can develop in neutral or acid solution. Diaminophenol acts mainly at the bottom of the emulsion layer.*

In alkaline solution it is rapidly oxidized. Stock solutions can be prepared with bisulphite and before use are neutralized by adding a solution of carbonate. The following formulas are generally preferable.

Neutral Formula	Sodium sulphite anhydrous	100 g
	Diaminophenol	20 g
	Water to	1000 cc

This solution keeps in full, well-corked bottles. For use, take one part of solution to three parts of water. The image appears in about 12 seconds and development is continued for 4–6 minutes. In cases of overexposure add up to 20% of a 10% solution of potassium bromide.

Acid Formula	Sodium bisulphite	25 cc
	Sodium sulphite	20 g
	Diaminophenol	5 g
	Potassium bromide	2 g
	Water to	1000 cc

This bisulphite bath keeps better than the previous one.

52. Superadditivity of developers

Two developers are said to be superadditive when used together, if the sum of their simultaneous action is greater than the sum of their actions considered separately. The phenomenon of superadditivity is mainly apparent with short development times. The most common example is that of the *metol-hydroquinone* system.

This phenomenon was first noticed by Luppo–Cramer. Reinders and Beukers have observed that metol serves to *shorten the induction period* of development by lowering the potential barrier surrounding each grain of silver bromide. The hydroquinone takes no part until this has happened. T. H. James(3) has put forward the hypothesis that superadditivity is only possible if the two developing agents have *different electrical charges* (or *free valencies*). That with the low charge (like metol) reduces the potential barrier and starts off development. It is not until then that the developer with the higher charge (hydroquinone) can take part in the reduction.

Thus many developers, with a charge of 1 or 0, can be used with hydroquinone (charge 2) or better with sodium-hydroquinone-monosulphonate: these are metol, hydroxylamine, diaminodurene, and Phenidone. The two latter show stronger superadditivity than metol. R. W. Henn(4) has made many tests with various substituted p-aminophenols.

Levenson's theory. The preceding conception in which metol alone acts first has been criticized by G. I. P. Levenson.(5) According to him, the hydroquinone takes part in the reduction from the beginning of development, its action being catalyzed by the metol, confirmed by the fact that hydroquinone can only develop if it is adsorbed via an oxidation product (see Theory of development). *The hydroquinone regenerates the metol by reducing its oxidation product*, p-methyl-quinone-imine. This action is furthermore dependent on the conversion of the two oxidation products (of metol and hydroquinone) to the sulphonates, by the sulphite. Thus a change in the structure of hydroquinone such as the inclusion of a CH_3 groups tends to slow down the sulphonation of its oxidized form and reduces the superadditivity. Similarly, a change in the structure of metol, which, on the contrary, accelerates the sulphonation of the oxidized form also reduces the superadditivity.

To sum up, *a mixture of developers is superadditive when one of them can readily reduce the oxidized form of the other*, and when the sulphite reacts less rapidly on the former than on the latter.

Axford and Kendall have shown that at a pH of 8·2, hydroquinone is inactive but regenerates phenidone from its coloured oxidation products.

In the case of metol, Levenson has shown that it dissociates differently depending on the pH:(6)

$$\text{Metol}\quad \left\{\begin{array}{ll} \text{Cation OH—C}_6\text{H}_4\text{—HN}_2\,.\,\text{CH}_3{}^+ & \text{charge } +1 \\ \text{Hybrid O—C}_6\text{H}_4\text{—NH}_2\,.\,\text{CH}_3 & \text{charge } \ \ 0 \\ \text{Free base OH—C}_6\text{H}_4\text{—NH}\,.\,\text{CH}_3 & \text{charge } \ \ 0 \\ \text{Anion O}^-\text{—C}_6\text{H}_4\text{—NH}\,.\,\text{CH}_3. & \text{charge } -1 \end{array}\right.$$

The cation is formed from pH 8·3 but towards pH 10·4 there will be an equivalent of anions and free base plus hybrid.

53. Metol-hydroquinone developers

Metol-hydroquinone developers are used more frequently than others because of their versatility given by the phenomenon of *superadditivity*. The formula variations are infinite; however, experience has shown that it is better not to deviate too far from certain proportions if maximum sensitivity, average contrast, little fog, acceptable grain and good keeping qualities are required.

Universal metol-hydroquinone formula

The following formula is the most suitable one for the majority of emulsions—negative or positive. It produces optimum speed without excessive contrast or very coarse grain.

Water to	1000 cc
Metol	2 g
Sodium sulphite anh.	35 g
Hydroquinone	5 g
Sodium carbonate anh.	25 g
Potassium bromide	1 g

Development time at 18°C: 5 minutes for average contrast, 10 minutes for underexposed images. To reduce the contrast, dilute with an equal part of water. Increasing the metol with a corresponding reduction of hydroquinone also reduces contrast.

Among the other formulas we would mention D 72 which is in current use, and MQ.80 which used to be used for rack development of films.

	D 72	MQ.80
Water to	1000	1000 cc
Metol	3	2 g
Sodium sulphite anh.	45	18·75 g
Hydroquinone	12	0·5 g
Sodium carbonate anh.	62·5	12·5 g
Potassium bromide	2	0·75 g

D 72 is used diluted with an equal part of water. Development time, 5 minutes in a tank and 4 minutes in a dish. The sensitivity obtained is less than that given by the preceding formula and the grain is coarser.

Formulas for under-exposed images

	P.G.	D 82
Water to	1000	1000 cc
Metol	1·75	14 g
Sodium sulphite anh.	45	52·5 g
Hydroquinone	4·35	14 g
Sodium carbonate anh.	22	— g
Potassium bromide	0·9	9 g
Caustic soda	—	9 g
Alcohol (methylated spirit)	—	48 cc
Development time at 18°C	12 mins.	4–5 mins.

D 82 keeps for only a few days in stoppered bottles and for only two hours in a dish.

54. Pyro-metol developer

The pyro-metol developer whose preparation is quite complicated, can be used for negative development. It is used to obtain maximum sensitivity. The D 7 formula is typical:

A.	Water to	1000 cc
	Metol	7·5 g
	Sodium metabisulphite	7·5 g
	Pyrogallol	30 g
	Potassium bromide	4·2 g
B.	Water to	1000 cc
	Sodium sulphite anh.	150 g
C.	Water to	1000 cc
	Sodium carbonate anh.	75 g

This developer can be used two or three weeks.

For use take:

Dish: 1 part A, 1 part B, 1 part C and 8 parts water. Develop 7–9 mins.

Tank: 1 part A, 1 part B, 1 part C and 13 parts water. Develop 9–12 mins.

To maintain the volume of solution add 1 part of 1, 1 part of B, 1 part of C and 4 parts of water.

55. Phenidone developer

Ilford's *Phenidone* is a new developing agent disclosed by Kendall which can be used together with hydroquinone. It produces even greater superadditivity than metol. Used alone, on the other hand, it gives very low contrast.

Phenidone, which is 1-phenyl-3-pyrazolidone has a zero charge at low pH and a charge of 1 at a higher pH. It initiates development so rapidly that the induction period is practically nil.(7) It appears to form a positively charged intermediate oxidation product which helps to reduce still further the potential barrier and facilitates the adsorption of the developing agent ions which are negatively charged.

Axford and Kendall(8) have shown that the maximum development rate is reached when the developer contains 7% of Phenidone compared with hydroquinone. This rate is 50% faster than that of the metol-hydroquinone combination (which reaches its maximum rate with 28% metol), the two measurements being made at pH 10·4. Unfortunately, Phenidone tends to produce fog with high-speed emulsions. This disadvantage can be overcome by adding 0·15 g of benzotriazole per litre of developer.

The advantage of Phenidone over metol appears to be, apart from its greater development rate, a greater consistency of sensitivity and a high activity at relatively low pH values The latter property enables high contrasts to be obtained with X-ray materials in a less alkaline bath than is customary for metol hydroquinone, and even an equivalent effect to that of a hydroquinone caustic bath.

In the *preparation of Phenidone-hydroquinone solutions* the hydroquinone must be dissolved before the Phenidone, which is previously mixed with 2·5 times its weight of potassium metabisulphite. Phenidone does not appear to produce dermatitis like metol.

Universal formula ID 62(9)

Water to	1000 cc
Hydroquinone	12 g
Phenidone	0·5 g
Sodium sulphite anh.	50 g
Sodium carbonate	60 g
Potassium bromide	2
Benzotriazole	0·2 g

For development, add water in the following proportions:

Emulsion	Developer		Water	Development time at 20°C
Chloride paper	1	+	1	45–60 secs.
Bromide paper	1	+	3	1½–2 mins.
Films (dish)	1	+	3	2–4 mins.
Films (tank)	1	+	7	4–8 mins.

56. Combined developers

Metol can develop over-exposed images without alkali. If it is combined chemically with hydroquinone its activity is increased and the resulting product, *Metoquinone* (Lumière) develops normally in neutral solution.

Water to	1000 cc
Sodium sulphite anh.	35 g
Metoquinone	10 g
Potassium bromide	1 g

Metol has also been combined with chlorohydroquinone (*Chloranol*) and p-phenylenediamine with hydroquinone (*Hydramine*). These compounds are not used any more but *Meritol* (Johnson's) is made and is a combination of p-phenylenediamine and pyrocatechin. *Meritol* is used for fine-grain development(10) but the caustic soda formula (two bath) has been recommended for under-exposed negatives:

A.	Water to	1000 cc
	Sodium sulphite anh.	45 g
	Meritol	8 g
B.	Water to	1000 cc
	Caustic soda	6·3 g

For development treat for 3 minutes in A, then for 3 minutes in B. To reduce the contrast dilute A.

57. Developer for doubling speed

According to Renwick (1920) then Stauffer, Smith and Trivelli, certain *hydrazine* derivatives can make the under-exposed grains of an emulsion developable by a *contagious effect*. Miller, Henn and Crabtree(11) use a hydrazine derivative together with an anti-foggant in a developer such as D 19 having a high sulphite and bromide concentration.

A.	Water to	1000 cc
	Metol	2 g
	Sodium sulphite anhydrous	100 g
	Hydroquinone	9 g
	Potassium carbonate	50 g
	Potassium bromide	5 g
B.	Water to	30 cc
	Nitrobenziminazol nitrate or benzotriazole 2 : 1000	20 cc
	Hydrazine hydrochloride	1·6 cc

Add B to A immediately before use as the developer does not keep for more than a day.

The amount of hydrazine hydrochloride must be increased with the sulphite. Optimum pH 9·5. Semicarbazide hydrochloride also produces the same effect.

The peculiarity of this developer is that it only shows the maximum effect when the fog density is an high as 0·4–0·6, which would be inadmissible with a normal developer. A grainy image is produced.

M. Tajima(12) has disclosed D 72 diluted with an equal volume of water together with 14 mg of nitrobenziminazole and 3 g of a hydrazine salt.

The increase of sensitivity, although definite, has frequently been exaggerated by some writers. This 'contagious' development appears to be due to the formation of a semi-quinone which diffuses towards the other grains. This quinone becomes a hydroxyhydroquinone, the sulphite acting as a catalyst.(12b)

58. Compensating developers

The so-called compensating developers are used for the development of images which normally have a long density scale, a scale which they reduce by accelerating the appearance of the shadows and slowing down that of the highlights. A metol-hydroquinone developer with a high proportion of metol in slightly alkaline solution is used for this:

Water to	1000 cc
Metol	3 g
Sodium sulphite anh.	40 g
Hydroquinone	1 g
Borax	10 g

Development time: 12–20 mins. at 20°C.

A plain metol bath, slightly alkaline and containing a solvent, primarily alters the intermediate gradations:

Water to	1000 cc
Metol	15 g
Sodium sulphite anh.	25 g
Borax	10 g
Hypo	2 g

Another method to reduce the density range is to develop in a *tanning developer* with a low concentration of sulphite; this produces, at the same time as the silver image, a *residual coloured* organic image which particularly intensifies the lower densities. This residual image is produced by the oxidation products of the developer which are deposited in the absence of sulphite. The very unstable bath must be made up as two solutions:

A.	Water to	1000 cc
	Potassium metabisulphite	12 g
	Pyrocatechin	80 g
B.	Water to	1000 cc
	Caustic soda	35 g

For use take:

A	10 cc
B	10 cc
Water	200 cc

For under-exposure increase the quantity of caustic solution.

For over-exposure add 1 cc of 5% potassium bromide.

A *Windisch* formula uses:

A.	Water to	1000 cc
	Sodium sulphite anh.	5 g
	Pyrocatechin	16 g
B.	Water to	1000 cc
	Caustic soda	100 g

For use take:

A	5 cc
B	2–3 cc
Water	200 cc

Development time: 18–24 mins.

59. Tropical developers

There are several methods for developing at relatively high temperatures without producing reticulation of the gelatin.

1. Pre-hardening.
2. Hardening development.

3. Addition of sodium sulphate to a normal developer to prevent the gelatin from swelling.

Hardening developer. Diaminophenol can be used together with chrome alum:

Water to	1000 cc
Sodium sulphite anh.	35 g
Diaminophenol	5 g
Chrome alum (5 % solution)	100 cc
Potassium bromide	2 g

In the case of *very high temperatures* a developer containing *formaldehyde* or *glyoxal* can be used together with an *anti-foggant* (see ultra rapid development, para. 95).

Sodium sulphate developers: the addition of sodium sulphate to a developer enables development to be carried out up to 35°C without inconvenience owing to the reduced swelling of the sensitive layer. The necessary quantity of sodium sulphate depends on the temperature at which it is to be used. Average quantities for metol-hydroquinone developers of the D.72 (diluted with an equal part of water) and D 76 types:

Sodium sulphate anh.	50 g up to 26°C 100 g up to 32°C 150 g up to 36°C

In spite of the considerable increase in temperature, development time is only slightly reduced: at 32°C the reduction is only 30%.

Special developers containing sodium sulphate

	Agfa 55	DK.15
Water to	1000	1000 cc
Metol	15	6 g
Sodium sulphite anh.	75	90 g
,, sulphate anh.	50	45 g
,, metaborates	—	22·5 g
Potassium bromide	—	2 g
Development time	8–10 mins. at 30°C	3½ mins. at 30°C 6 mins. at 25°C 10 mins. at 18°C

A reduction in the metaborate to 5 g in DK15 reduces the contrast.

Equivalents of the various forms of sodium sulphate

Sodium sulphate anh. Na_2SO_4	100 g
,, ,, heptahydrate $Na_2SO_47H_2O$	190 g
,, ,, decahydrate $Na_2SO_410H_2O$ (Glauber's salt)	260 g

The Agfa formulary for photomechanical emulsions recommends the addition to the developer of 10–20 g of ***sodium nitrite*** to maintain the clarity of negatives above 25°C.

60. Bromide paper developers

Developers for positive emulsions are generally contrasty developers. They give strong blacks and develop rapidly. It is true that positive emulsions are fine grained which enables them to be readily reduced by the developer. The fog must be practically nil but this is due more to the emulsion layer than to the developer.

Any well-balanced developer can be used to develop positive images. If it is too dilute, good blacks cannot be obtained, and if it contains too much bromide the image will appear slowly.

The universal metol-hydroquinone developer given in para. 53 can be used to develop bromide papers. Development time 2–3 minutes at 18°C. The proportion of hydroquinone can, however, be increased while the metol is reduced in order to give a rapid increase in contrast. It must not be forgotten that development of positive images is generally taken to *gamma infinity*; therefore development is complete. The contrast, therefore, depends on the nature of the paper rather than on the time of development.

	D 72 Kodak	Agfa
Water to	1000	1000 cc
Metol	3	2 g
Sodium sulphite anh.	45	26 g
Hydroquinone	12	6 g
Sodium carbonate anh.	67·5	52 g
Potassium bromide	2	2 g
Dilution for papers	add 3 parts water	add 1 part water
Development time	1½–2 mins. at 21°C	2 mins. at 18°C
Lantern slides	add 1 part water 1–2 mins. at 21°C	—

61. Developers for contrasty emulsions

	D 154 for documents	Infra-red plates, microfilms	D 11 for high contrast lantern plates
Water to	1000	1000	1000 cc
Metol	1·25	2·25	1 g
Sodium sulphite anh.	22·5	72	75 g
Hydroquinone	6	8·75	9 g
Sodium carbonate anh.	30	48	25 g

Potassium bromide	0·5	4	5 g
Development time undiluted	2–3 mins. at 18°C 1–1½ mins. at 21°C	6–7 mins. at 18°C	5½ mins. at 21°C

Soft-working developer for photo-mechanical emulsions (Agfa)

Water to	1000 cc
Metol	1 g
Sodium sulphite anh.	40 g
Hydroquinone	6 g
Sodium carbonate anh.	21 g
Potassium bromide	1 g
Potassium metabisulphite	1·5 g
Citric acid	0·5 g

Develop 4–6 mins. at 18°C.

62. Developers for motion-picture positives

	D 16	[2]	Levenson (13)
Water	1000	1000	1000 cc
Metol	0·3	0·7	0·7 g
Sodium sulphite anh.	38	50	40 g
Hydroquinone	6	7	4 g
Sodium carbonate anh.	19	40	20 g
Potassium bromide	·9	2	1 g
Potassium metabisulphite	1·5	—	— g
Citric acid	0·7	—	— g

To replenish the D 16 formula: metol 0·3 g, sulphite 38 g, hydroquinone 9 g, carbonate 38 g, bromide 0·7 g, metabisulphite 1·5 g.

For *titles and variable area sound-recording negatives*, use formula 2. For variable-density tracks whose gamma is low, develop in soft negative developers.

63. Caustic developers for maximum contrast

The high alkalinity of *caustic soda* or *potash* developers gives them a very high energy which is shown as a rapid increase in the high densities. Caustic developers, generally using hydroquinone, utilize this property for the development of very high-contrast images with strong blacks such as positives for photomechanical processes (process-type emulsions).

Caustic developers have the disadvantage that they attack the gelatin and the skin; also their action must not be carried on for longer than necessary. Furthermore they do not keep well.

		D 8 Kodak	Agfa 1	Agfa 2
A.	Water to	1000	500	500 cc
	Sodium sulphite anh.	90	—	— g
	Potassium metabisulphite	—	5	12·5 g

	Hydroquinone	45	5	12·5 g
	Caustic soda	37·5	—	— g
	Potassium bromide	30	1	12·5 g
B.	Water to	—	500	500 cc
	Caustic potash	—	25	25 g
	Water to dilute	500	—	— cc
	Development time at 18°C	2 mins.	3–5 mins.	2–3 mins.

Wash carefully before fixing to avoid smears and dichroic fog. Fix in a hardening fixer.

64. Chloride paper developers

Chloride (gaslight) papers are made with two emulsion types: *black tone* and *bluish tone*. The emulsions giving black tones are generally coated on ivory cream bases, whilst the bluish-tone ones are coated on white base. The black-tone papers can easily give bluish tones by incorporating certain anti-foggants in the developer. Conversely, warm black tones can be obtained on bluish materials by modifying the developer.

Chloride papers develop very quickly, the image being completely formed at once, the density then increasing: this enables exposure errors to be corrected—a property of great use to printers of amateur negatives. This effect depends upon the quality of the emulsion.

Chloride papers tend to become *yellowish* particularly when kept for a long time. The manufacturers incorporate anti-yellowing agents to overcome this fault; these compounds can also be added to the developer. Nevertheless, it is recommended that development of chloride papers should not be continued longer than necessary. For the same reason the developer should not contain an excess of sulphite which dissolves the silver chloride (subsequently reduced by the developer to yellow colloidal silver).

Generally, the following developer formulas can be used for the development of both black and bluish chloride papers:

Universal M.Q. developer (para. 53): development time 60–90 secs. at 18°C.

Formula D 72 (para. 53): one part stock solution to two parts of water. Development time: 45–60 secs. at 21°C.

Phenidone formula (para. 55): one part stock solution and one part water. Development time 45–60 secs. at 20°C.

Special chloride paper formula:

Water to	1000 cc
Metol	2 g
Sodium sulphite anh.	25 g
Hydroquinone	5 g
Sodium carbonate anh.	25 g
Potassium bromide	0·5 g

Development time: 90 secs. at 18°C.

To *obtain bluish tones* from papers normally giving black tones, one of the following compounds should be added: *benzotriazole* or *6-nitrobenziminazole nitrate*. Concentration 0·1–0·25 g per litre. The best procedure is to add 25 cc per litre of a 1% aqueous-alcoholic solution of benzotriazole. Many other compounds have a similar effect—methylbenzoxazoles, azimidobenzenes, azimidonaphthalenes, methylnaphthothiazoles, quinine salts, formalcystine (1 : 1000). Salts of 5-halogen-2-aminopyridine and the 3 : 5-disubstituted compounds also produce bluish images.⁽¹⁴⁾

To overcome yellowing add 15 cc of a 1% aqueous solution of *Antiflavog* per litre of developer.⁽¹⁵⁾ This is a diphenyliodonium compound.

Development of warm black images on blue-black papers. The bluish tone does not appear in the presence of a high concentration of bromide. As the latter retards development, it is desirable to accelerate it by raising the temperature.

Water to	1000 cc
Metol	0·8 g
Sodium sulphite anh.	14 g
Hydroquinone	4 g
Sodium carbonate anh.	12 g
Potassium bromide	6 g

Development time 2½–3 mins. at 23–24°C. Compared with a normal developer, the contrast is increased, and the sensitivity reduced slightly.

65. Developers for warm tones with chlorobromide or chloride emulsions

The development of warm tones on papers and lantern plates made with silver chlorobromide or chloride is primarily dependant on the fineness of grain of these emulsions and upon their bromide/chloride ratio.

For a given emulsion, the tone becomes warmer, that is more red, as the developer is *diluted*, contains more bromide, and as development is reduced. This implies that for a given colour, a given contrast is produced, and therefore the emulsion contrast must be selected to suit. On the other hand, to compensate for the *loss of sensitivity*, the print must be overexposed, especially when development is shortened. As a general rule close control of the results is difficult.

Warm black formula D 166

Water to	1000 cc
Metol	1·15 g
Sodium sulphite anh.	25 g
Hydroquinone	8·5 g
Sodium carbonate anh.	25 g
Potassium bromide	12·5 g

Dilute with 3 parts of water.

Development time: 3 mins. at 18°C for chlorobromide papers.

Formula for brown tone (Agfa Portriga type emulsions):

Water to	1000 cc
Hydroquinone	24 g
Sodium sulphite anh.	60 g
Potassium carbonate	80 g
Potassium bromide	2 g

Dilute with 4 parts of water.
Development time: 4–7 mins. at 18°C.

Formula for sepia and red-brown tones with glycin: D.159.

This bath, which gives attractive warm tones, must be used with a harder emulsion than that used with D 166, to compensate for the apparent reduction in contrast:

Water to	1000 cc
Hydroquinone	7 g
Glycin	4 g
Sodium sulphite anh.	25 g
Sodium carbonate anh.	26 g
Potassium bromide	1 g

Dilute with 2 parts of water.
Development times: red tones 2½ mins.; brown tones 6 mins.

66. Special developers for warm-tone lantern plates

1. *Standard bromide formula*:

Water to	1000 cc
Sodium sulphite anh.	25 g
Hydroquinone	12 g
Sodium carbonate	24 g
Potassium bromide	4 g

Dilute wth an equal part of water.

Examples of relative exposure and development times:

Exposure	Development	Colour obtained
24 secs.	3 mins.	red
20 ,,	4 ,,	red-brown
16 ,,	5 ,,	brown
12 ,,	6 ,,	sepia
4 ,,	10 ,,	warm black

2. *Ferrocyanide developer*: often gives brighter colours. First prepare:

Water	1000 cc
Sodium sulphite anh.	40 g
Potassium ferrocyanide	30 g
Hydroquinone	10 g
Caustic potash	50 g

and add, to a litre of developer, the following quantities of *10% potassium bromide*:

Amount of bromide	Colour obtained	Developing time
100 cc	Purplish brown	10–15 mins.
180 cc	Purple	20–30 mins.
200 cc	Carmine	30–40 mins.

3. For *green tones* develop 2–3 minutes in:

Water to	1000 cc
Sodium sulphite anh.	10 g
Potassium ferrocyanide	30 g
Hydroquinone	4 g
Sodium carbonate anh.	15 g
Potassium bromide	0·2 g

The colour becomes yellowish if 35% of a 5 g per litre hypo solution is added.

4. Bright colours can be obtained by mixing *metol* with *tartaric acid* and *hypo*. A *red* image is obtained by developing for 6–8 mins. in the following solution:

Water to	1000 cc
Sodium sulphite anh.	19 g
Metol	2·5 g
Hypo	2·5 g
Tartaric acid	0·75 g

If the amount of tartaric acid is increased, together with the developing time, the colour passes through purplish red to violet, then to blue. With 4 g of the acid and a development time greater than 20 minutes, a blue image is developed. On the other hand, with only 0·25 g tartaric acid the image colour shifts towards the orange.

5. The addition of *ammonia* or *ammonium salts* to a hydroquinone bath accelerates the formation of red tones without a great reduction in contrast:

A.	Water to	1000 cc
	Sodium sulphite anh.	65 g
	Hydroquinone	14 g
	Potassium bromide	10 g
B.	Water to	1000 cc
	Ammonia S.G. 0·920	32 g
	Ammonium bromide	6 g

Mix 1 part A with 1 part B and develop 3 mins. at 18°C.

6. *Thiocarbamide* (thiourea) produces warm tones following the method which has been given by Mees. Three baths are prepared: A—metol 10, hydroquinone 5, sulphite anh. 50, carbonate anh. 36, water 2,000.

B—ammonium carbonate 50, ammonium bromide 50, water 500.

C—thiocarbamide 3, ammonium bromide 1, water 400.

The solutions A, B and C are mixed in the following proportions: brown tones, 14 : 18 : 1; blue-grey tones, 12 : 3 : 1; warm black tones, 10 : 5 : 1. The warm tones are obtained with long exposures and the contrast must be kept constant for each tone. The order of the colours is successively: yellow, purple, blue-grey and black.

Carrell has used thiourea for physical development (*Phot. Jl.*, 1947, p. 157) after iodide conversion. The stock solutions are as follows: silver nitrate + excess sulphite + hypo; M.Q. developer; thiocarbamide + ammonium bromide. Depending on the exposure and development time, blue, blue-black, purple-black, brown, purple, red-brown and warm black tones are produced.

It should be remembered that the colours and development times shown for all these warm tone formulas are given only as examples. The results are greatly dependent on the emulsion type.

The exact colour of lantern images is only seen after drying.

7. *Warm tone developer using reductone*. Willmanns and Schneider have claimed(16) that organic compounds containing the grouping OH . CH = C . OH—have developing properties and that they give brown or red images. Stewart(17) has used *glycoreductone*, isolated by Euler and Martius,(18) and prepared in the following way:

20 g of anhydrous sodium carbonate (or 22·5 g of the monohydrate) is dissolved with 50 g glucose in 300 cc of warm water. The solution is heated to 91–93°C for two-and-a-half minutes and then cooled rapidly. A second solution of 45 g of anhydrous sulphite, 12 g of hydroquinone and 4 g of potassium bromide in 400 cc of water is prepared. The two solutions are mixed and made up to a litre. This solution develops warm tones in about five minutes at 18°C.

67. Inorganic developers

1. A number of inorganic substances are capable of developing photographic images. They are not used in practice but can be of use in certain cases where organic developers are not available and also for laboratory research.

Gaseous *hydrogen* in the presence of colloidal palladium,(19) hydrazine NH_2—NH_2, *hydroxylamine*(20) NH_2—OH, *hydrogen peroxide* in an alkaline solution, and all salts which can pass from a lower to a higher valency, are reducers of silver halides. In the latter case the degree of reduction is limited by the reversible reaction and development ceases when an equilibrium is reached, for example with copper chloride

$$Cu^+ + Ag^+ \leftrightharpoons Cu^{++} + Ag$$

For development to take place normally, it is necessary to displace the equilibrium of the reaction by removing the higher valency ions completely as they are produced. This can be done by converting them into complex ions: thus a ferrous ion reduces a silver salt and itself is oxidized to the ferric state:

$$Fe^{++} + Ag^+ \leftrightharpoons Fe^{+++} + Ag$$

The ferric ions are sequestered by the addition of sodium fluoride (NaF) which converts them into a ferrifluoride ion $(FeF_6)^{---}$ in which the ferric ion is not reactive.

2. *Sodium hydrosulphite*

Sodium hydrosulphite, $Na_2S_2O_4$ or more exactly Na . O—S—O—O—S—O . Na is an energetic reducer. It has, however, the disadvantage that its solutions are unstable and the vapour is suffocating. Lumiere and Seyewetz have prepared a relatively stable dry mixture:

Sodium hydrosulphite anh.	100 g
Sodium bisulphite anh.	165 g
Potassium bromide, dry	35 g

To prepare the developer, 120 g of this powder is dissolved in a litre of water. This developer has a strong desensitizing action (200 times) which permits the use of a deep yellow light during development. With some emulsions a high fog level is produced.

68. Metal-organic complexes

Polybasic organic acids have the general formula $R(CO.OH)_n$, where R is an organic radical and CO.OH is the carboxylic acid radical. Among the bivalent acids the simplest of the series are *oxalic acid* CO.OH—CO.OH, *malonic acid* CO.OH—CH_2—CO.OH. Of the tribasic acids, *citric acid* CO.OH—CH_2—C.OH(CO.OH)—CH_2—CO.OH is the most common.

With polyvalent metals, such as iron, titanium, vanadium molybdenum, uranium, etc., these acids form complex anions which correspond to each valence, and in which the characteristics of the metal are completely masked. The general discussion of complexes will be deferred but the ions of interest in this connection are those with the constitution $[(R(CO_2)_n)_x\, My]^{z-}$ where

M is a metallic atom and the integers x and y depend upon the valency of the metal and the number of acid radicals in the ion, whilst the basicity of the complex ion is represented by the usual symbol $^-$, the number of such electrons being shown by ^{z}.

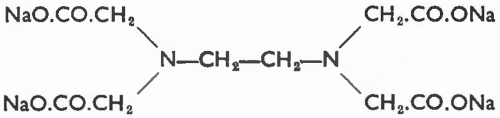
Thus iron, bivalent in the ferrous state Fe^{++} and trivalent in the ferric state Fe^{+++}, forms with the oxalate ion $(CO.O—CO.O)^{--}$ or $(C_2O_4)^{--}$, *ferro-oxalic* $[(C_2O_4)_2Fe]^{--}$ and *ferri-oxalic* $[(C_2O_4)_3Fe]^{---}$ ions respectively. With bases, ferro-oxalates and ferri-oxalates are formed.

The ferro-oxalic ion, being derived from the ferrous ion, is a reducing agent. It reduces silver ions, and is itself oxidized to the ferri-oxalic ion:

$$\underset{\text{ferro-oxalic ion}}{[(C_2O_4)_2Fe]^{--}} + \underset{\text{oxalic ion}}{(C_2O_4)^{--}} + \underset{\substack{\text{silver}\\\text{ion}}}{Ag^+} = \underset{\substack{\text{silver}\\\text{metal}}}{Ag} + \underset{\text{ferri-oxalic ion}}{[(C_2O_4)_3Fe]^{---}}$$

Sodium or potassium ferro-oxalates are therefore developers, whilst the corresponding ferri-oxalates are oxidizing agents. Similar behaviour is found with ferro-malonate $(CH_2 = C_2O_4)_2Fe\,K_2$ and ferro-citrates; the titano-oxalates whose valency changes from 3 to 4, and the uranium derivatives having valency changes from 4 to 6.

Many other complex substances studied by Rzymkowski show developing properties, particularly *cuprammonium oxalate, tartrate and citrate*⁽²¹⁾ and complexes of *iron* Fe^{++} and *titanium* Ti^{+++} with *nitrilotriacetic acid* and *ethylenediamine-tetracetic acid.*⁽²²⁾ The cuprammonium compounds can be obtained by mixing an ammoniacal solution of cuprous chloride with a solution of neutral potassium tartrate, oxalate or citrate. The iron and titanium complexes are produced by mixing the corresponding acid or its sodium salt with an ammoniacal solution of ferrous or titanous sulphate. The most interesting complexes are those from the tetrasodium salt of ethylenediamine-tetracetic acid, with the formula:



better known by the names Trilon B or F, Celon E, Versene and Sequestrene.

Titanium oxalate developer. This developer has the property of depositing, in proportion to the silver image, titanium oxide TiO_2 which can be used as a mordant for dyes. It is prepared by mixing the two following solutions:⁽²³⁾

Potassium oxalate 3%	550 cc
Titanium trichloride comml. soln.	50 cc

Ferrous oxalate developer. To prepare a ferrous oxalate developer, a *ferrous salt* is mixed with an excess of potassium oxalate in distilled water. As it does not keep, it must be prepared just before use. To prepare the developer, 3 parts of a 330 g per litre solution of potassium oxalate is mixed with one part of a 330 g per litre solution of ferrous sulphate and 20 drops of 10% potassium bromide solution should be added to each 100 cc of mixed solution. To accelerate development, 3 drops of 5% hypo is added to 100 cc of developer.

When the ferrous sulphate and potassium oxalate are mixed a precipitate of ferrous oxalate is formed, but this is redissolved in excess potassium oxalate (which gives a ferro-oxalic complex).

Aerial oxidation results in the precipitation of basic ferric salt. This disadvantage can be overcome by replacing the ferrous sulphate with *ferrous lactate* (Rzymkowski): 7 g of ferrous lactate in 100 cc of 25% potassium oxalate. The resulting red solution is neutral.(24)

A more stable bath is obtained using sodium glycolate:(25) 3 parts of 300 g per litre potassium oxalate, 1·5 parts of 350 g per litre sodium glycolate and 1 part of 350 g per litre ferrous sulphate.

The three ingredients can be mixed in the dry state, after each has been powdered separately and dried at 100°C under reduced pressure. The yellow powder obtained by mixing 91 parts of ferrous sulphate, 244 parts of neutral potassium oxalate and 155 parts of sodium glycolate, dissolves readily in water at a strength of 250 g per litre.

After development, the plate is treated in a hydrochloric acid stop bath, rinsed in distilled water, and fixed in a bath containing 1% calgon to avoid precipitating calcium oxalate in the gelatin.

T. H. James has studied dilute ferrous oxalate developers in a basic solution.(26)

69. Reversible developers. Development with vanadium salts

Normal developers are irreversible reducing systems. The study of superadditivity, however, has shown that, with some developer combinations, one is immediately regenerated from its oxidized form by the other. Some organic derivatives such as those from anthraquinone-β-sulphonic acid can be regenerated by electrolytic reduction.

The most suitable compounds for experiments on reversible systems are metallic ones. In 1894 A. and L. Lumiere(27) foresaw the use of vanadium salts Va^{++} as developers, Liesegang(28) the use of chromium, zinc and molybdenum salts. The first systematic study of the electrolytic regeneration of vanadium salts was carried out by Rutter in 1906.(29) Much later, Fuchs(30) used an electrolytically reduced chrome alum solution, and Kellner and Bennevitz(31) developed with nascent hydrogen liberated at a cathode. Rzymkowski(32) has finally disclosed since 1935 a series of photographic developers prepared electrolytically, by stressing the reversibility of metallic complexes such as potassium ferro-oxalate and titano-oxalate.

For a reversible system to be used as a developer bath, oxidized and reduced forms must be soluble, and the redox potential must be sufficiently low.

Vanadium developer. The complete reversible system represented by $V^{++}-e \leftrightharpoons V^{+++}$ has recently been studied by Roman(33) and used in practice. Bivalent vanadium bromide develops a positive emulsion very quickly; the resulting oxidation products are electrolytically regenerated at a lead cathode, following the scheme:

$$VO^{+++}+2H^{+}+e \rightarrow V^{+++}+H_2O$$
$$V^{+++}+e \rightarrow V^{++}$$

The developer must be kept in a high-pressure nitrogen atmosphere. A cell enables the intensity of regeneration to be controlled. Fortmiller and

James[34] have shown that the development velocity depends mainly on the concentration of vanadous ions.

Rasch and Crabtree[35] have used a developer made from a solution of vanadic anhydride in dilute sulphuric acid, in the presence of oxalic acid, which is electrolytically reduced to the vanadous salt. A specially constructed machine enables 1000 metres of 35-mm positive film to be developed in only 1 litre of solution, the liberated bromide being partially eliminated by diffusion into the cathode section of the cell. The image is developed in 20 secs. at 15°C and the sensitivity is doubled. The tendency to fog can be avoided by including some potassium iodide. The high acidity of the bath makes hardened emulsions necessary. Tests on negative emulsions have not, so far, been satisfactory.

70. Special developers

1. *Deep-acting developers.* The most effective are *acid diaminophenol* (*amidol*) (para. 51) and *p-phenylenediamine* developers. The addition of *safranine* favours depth development (Namias 1924).

2. *Solutions for developing the surface latent image*

Ferrous oxalate developer:[36]

A.	25% neutral potassium oxalate	
B.	Water to	300 cc
	Ferrous sulphate cryst.	25 g
	Citric acid	1 g

For use, mix equal parts of A and B and develop for 5 minutes at 18°C.

Sulphite-free glycin solution:[37]

Water to	1000 cc
Glycin	30 g
Sodium carbonate anh.	44·4 g

Develop 5 minutes at 18°C.

Isoascorbic acid developer:[38]

Water to	1000 cc
Metol	2·5 g
Isoascorbic acid	10 g
Sodium metaborate	35 g
Potassium bromide	1 g

3. *Solutions for developing the internal latent image.*

The internal latent image of silver bromide crystals can be developed by adding 1–4% hypo to a normal organic developer.

Hautot and Sauvenier's formula:

Water to	1000 cc
Metol	1·5 g
Sodium sulphite anh.	50 g

Hydroquinone	6 g
Sodium carbonate anh.	32 g
Potassium bromide	2 g
Hypo crystals	10 g

The following bath has also been used:

A.	Water to	800 cc
	Pyrocatechin	50 g
	Sodium metabisulphite	52 g
	Potassium bromide	100 g
	Potassium iodide	6 g
B.	Water to	200 cc
	Caustic soda	50 g

Develop for 3 minutes at 18°C.

71. Physical development

Physical development is the production of a visible image by depositing metallic silver on the development centres, from a solution containing a soluble silver salt and a reducing agent.

In normal chemical development it is the silver bromide crystals containing the development centres which are reduced, but here in contrast, the sensitive silver salt takes no part in the development process; the only reaction is between the developing solution and the development centres. Consequently, the first step can be to remove the silver halide, allowing development to be carried out in white light.

The developing solution consists of a solution of a silver salt—silver nitrate, or preferably silver sodium sulphite—and a reducing agent. The reducing agent is normally an ordinary developing agent such as hydroquinone, metol, p-aminophenol or p-phenylenediamine.

Even in the absence of a sensitive layer, the silver salt is reduced very slowly to produce colloidal silver. In the presence of the particles of metallic silver which constitute the latent image, however, the reduction takes place much more rapidly, depositing silver from the solution on the development nuclei to produce very fine silver grains which soon give a visible image which increases in density.

With such a fine-grain image, a much greater resolving power can be achieved by physical development. On the other hand, there is a loss of speed which necessitates an increase of 2–4 times in exposure. The images are flat and frequently foggy. Furthermore, development is very slow, often taking several hours.

1. *Development before fixation.* It is necessary to reduce the soluble silver salt in the solution but not the insoluble halide. This can be done merely by raising the redox potential of any kind of developer to a value not exceeding 120 mV, by reducing the pH (that is by acidifying the solution). At this potential the soluble silver salts are still reducible. An acidified developer is

therefore used (pyrogallol, sulphite and acetic acid, for example) to which is added 10% of a 10% silver nitrate solution, or silver sodium sulphite.

The following solutions are prepared:

A.	Distilled water	60 cc
	Sodium sulphite anh.	12 g
B.	Distilled water	20 cc
	Silver nitrate	3·2 g

Pour B into A with stirring. Then add 70 cc water followed by 32 g hypo. This solution of silver sodium sulphite will keep. Just before use, 800 cc of water containing 3·3 g diaminophenol (amidol) is added.

2. *Development after fixation.* The plate is first fixed in 6% hypo. After washing, it is developed in a mixture of the following solutions, a suitable ratio being 1 part of A to 5 parts of B.

A.	Distilled water	1000 cc
	Sodium sulphite anh.	180 g
	10% silver nitrate	75 g
B.	Water	1000 cc
	Sodium sulphite anh.	30 g
	p-phenylenediamine	20 g

Other developing agents can be used together with the silver sodium sulphite solution (solution A).

If the silver nitrate is replaced by mercuric nitrate, a solution of mercury sodium sulphite is formed, which gives a mercury image similar to the silver image. The mercury developer is more stable, but less active than the silver developer.

3. *Quinhydrone physical developer.* This developer disclosed by Rzymkowski(39) is a powerful intensifier.

A.	Distilled water to	100 cc
	Citric acid	12 g
B.	Alcohol 90% to	100 cc
	p-benzoquinone	2 g
C.	Distilled water to	100 cc
	Hydroquinone	2 g
D.	Distilled water to	100 cc
	Silver nitrate	10 g

Mix in the order A : 3 cc; B : 7·5 cc; C : 7·5 cc; D : 4·5 cc and make up to 100 cc with distilled water.

4. *Development after iodizing.* To prevent reduction of the silver halide, it can be converted to silver iodide by bathing for a few minutes in 1% potassium iodide containing 2·5% anhydrous sulphite. After rinsing, develop for 30–40 minutes.

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Chapter VII

FINE-GRAIN DEVELOPERS

72. What is 'grain' in a photographic image?

Everyone knows that the photographic image is made up of a *dispersion* of silver particles in a thin layer of gelatin. The average diameter of these particles in negatives is 1–3μ; and depending whether there are many or few, the image appears dark or light. The image is therefore discontinuous like a more or less coarse mosaic.

It is obviously always beneficial to have images whose grain appears as fine as possible. Now it is best to see how and to what extent fine grain is possible, without upsetting the other important aspects. It is also advisable to correct certain false preconceived ideas which are widely held, but whose correctness has not been established.

A negative emulsion has coarser grain as it is made faster. *An emulsion of extreme sensitivity and very fine grain cannot be obtained.* The individual grain diameter is not however the only factor, and we will see the part that the other ones play.

The commonly used methods of determining graininess are by judging either a photomicrograph of the negative or, more frequently, an enlarged print. Now it is very easy to be deceived by one or other of these methods.

By enlarging parts of each step of sensitometer strips on a coarse-grain fast emulsion and a slow fine-grain one, using a microscope (Fig. 6a) the difference of average grain size is readily seen. However, the most striking point is that the *grains*, at first not numerous in the *clear parts of the negative* (corresponding to the shadows of the subject) multiply as the density increases, and *aggregate* to form *large black veins* leaving *big empty spaces* (half-tones of the subject). The texture of this mottling is finer with medium speed emulsions.

In the *dense areas of the negative* (which are the subject highlights), the grains are so numerous that they cover the major part of the surface of each zone examined, but they leave *empty spaces* between them, which contract in the very high densities. These empty spaces form *holes* which are smaller as the emulsion grain is finer.

Let us make a positive print, which as far as practical results are concerned is the final product:

The clear parts of the negative, containing the dispersed black grains give, on printing, the shadows of the positive (Fig. 6b). The black grains *become white patches* which, as the negative density increases, become bigger, to give

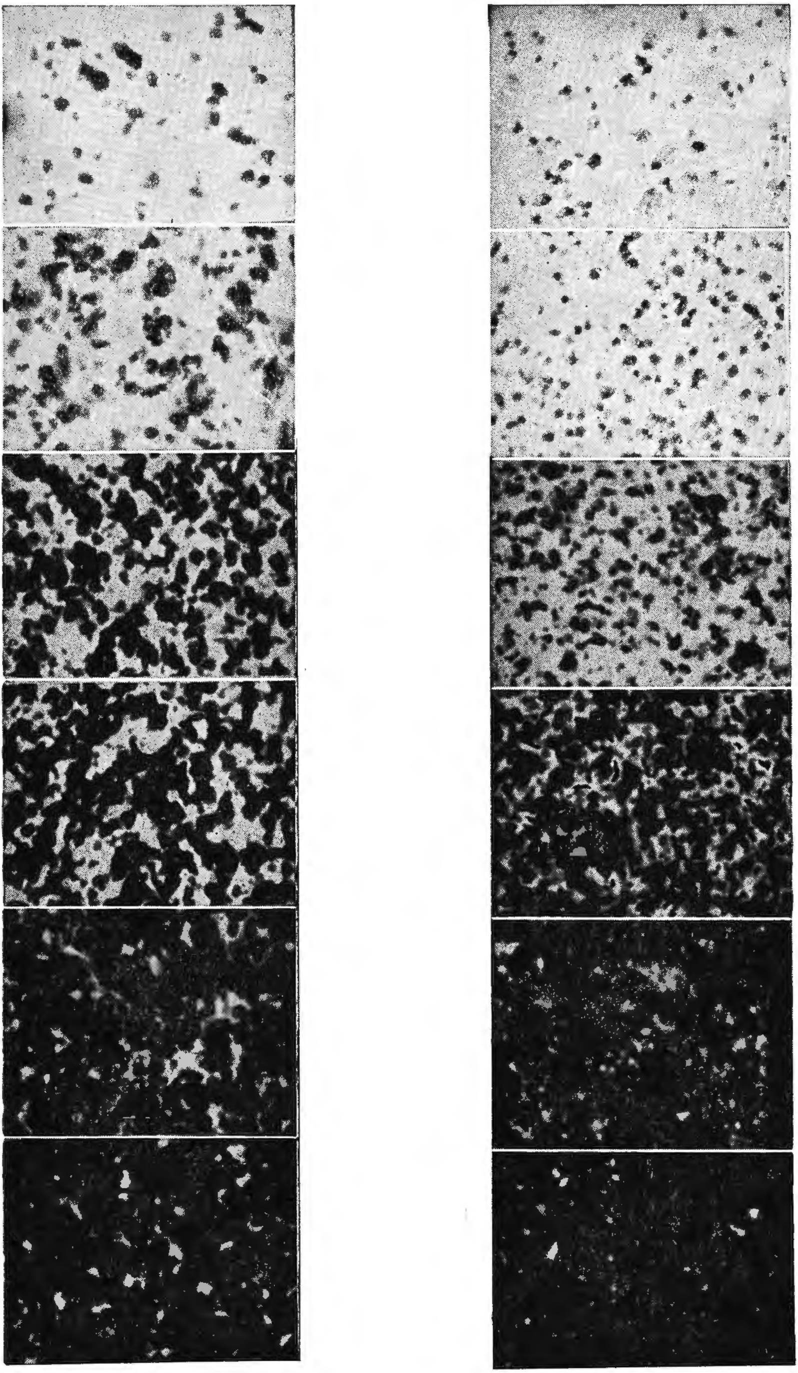


FIG. 6A. Photomicrographs of developed areas of increasing density on two emulsions, one coarse-grained, the other fine-grained. Enlargement, 850X.

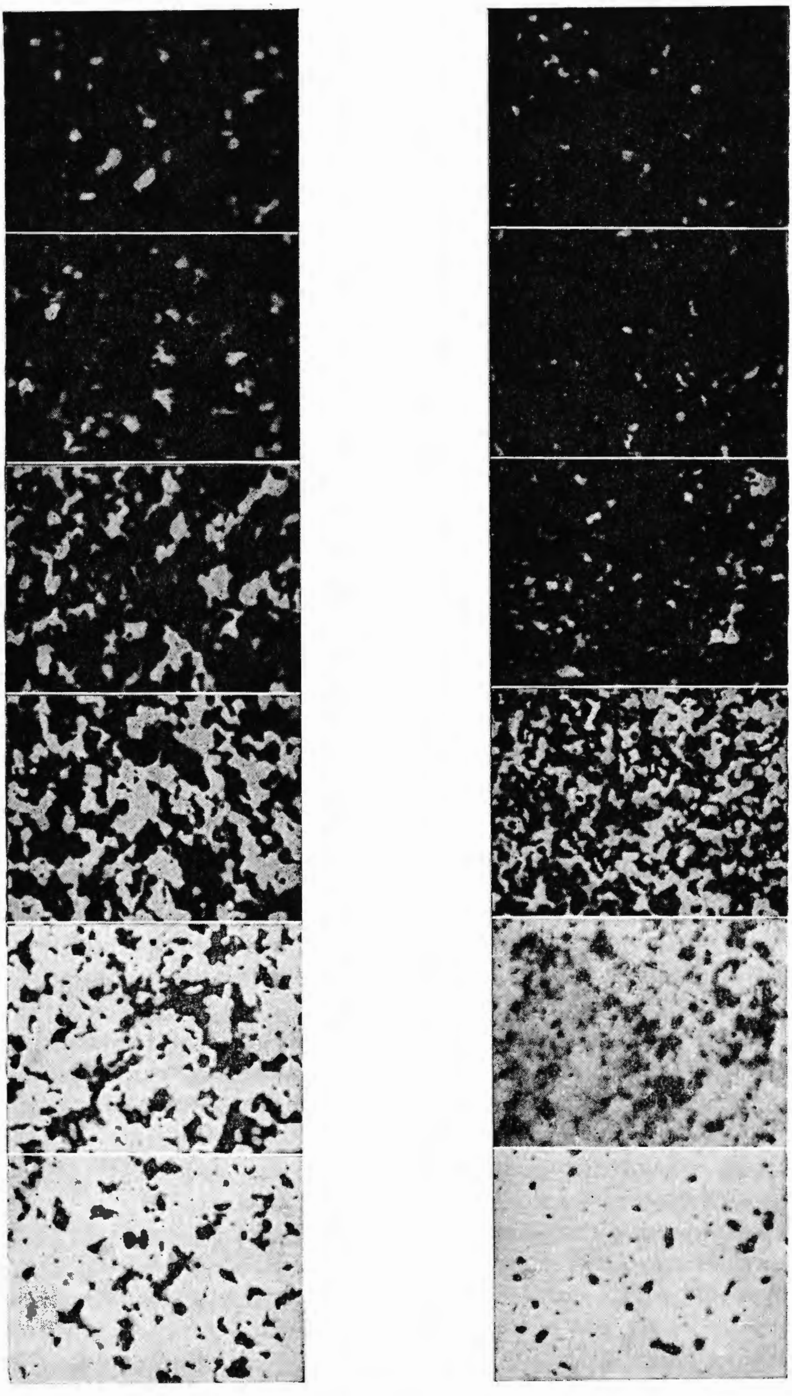


FIG. 6B. Positive prints corresponding to the two negative wedges (enlarged to 850 diameters) of Fig. 6A. The light negative areas with isolated silver grains naturally give dark positive areas whilst the dark negative areas give the clear areas in the print, whose 'grains' are in fact the spaces between the silver grains of the corresponding negative images.

mottled areas in the positive half tones. Finally, in the highlights of the print (printed from the high negative densities) black dots are found which correspond to the spaces between the grain clumps of the negative.

Now, *where is the grain most obvious, in the enlargement?* Not obvious in the highlights, it becomes more apparent as the density increases, with a maximum in the *middle densities*. Beyond there, the black patches on a white background are replaced by white patches on a black background, which become smaller and less noticeable.

We can therefore draw the following primary conclusions:

1. The grain which we see on a positive print is not the grain of the negative emulsion, but the image of the *holes* left between the *grain aggregates*, these holes being considerably larger than the grains themselves.

2. In the shadows of the print, white patches are seen which correspond to the grain aggregates and not the individual grains.

3. The *half-tones* are formed of large mottled black and white areas whose pattern is more likely to be finer as the initial grain size is smaller. However, the individual small size of the grains of the negative is not enough to ensure apparent fine grain in the print; a regular *topographical* dispersion of the grains in the gelatin during the manufacture of the material is essential. This is not easy, as the precipitated crystals generally form chain aggregates. It is these chains which lead to the formation of the large veins of reduced silver seen with the microscope. By varying the conditions under which a single emulsion was prepared, the writer obtained different dispersions, with the same average grain diameter. This shows that the *dispersed state of the crystals affects the final apparent graininess on the print.*

4. Comparison of a fine- and a coarse-grain emulsion is only of value at *equal densities*. The mottled structure of the areas of different density can lead to errors of judgment.

5. This leads to the *printing* of positives which has an influence on grain. The masses and spaces of the negative image are not sharply defined. Their density decreases at the borders. This results in a variation in their apparent diameter by diffusion depending on the exposure given during printing, in turn depending on the general density of the negative. This effect can be estimated from the examples in Fig. 6c.

(*a*) *For dense negative areas* giving the light areas in the print, the grain *increases* with printing exposure.

(*b*) For *light negative areas* giving the shadows in the print, the grain *decreases* with printing exposure.

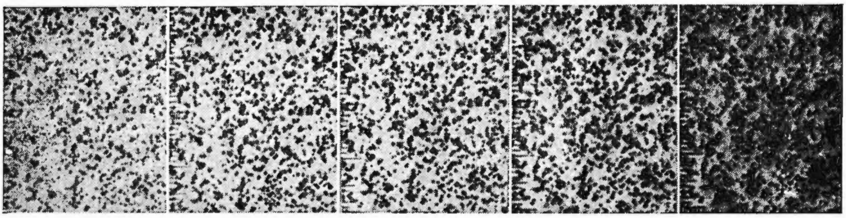
(*c*) For the *middle negative densities* giving the half tones, the grain is at a *maximum with the optimum exposure*. It is reduced by underexposure (enlargement of the whites) and by overexposure (enlargement of the shadows).

In consequence, therefore, of the printing factors, that is on the choice of subject, we are obliged to use the dense or clear negative areas and underexpose or overexpose, print of different apparent graininess will be obtained in which chance plays a considerable part.

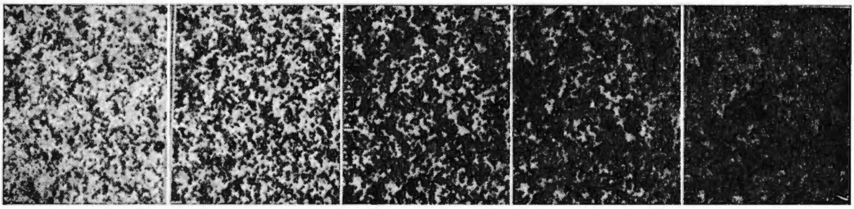
73. Effect of the developer on grain

Of the various factors which, as we shall see, affect the grain of the photographic image, we will study first the developer and the development procedure.

The effect of the developer is great, but it is not always enough to counterbalance the effect of initially coarse grain, of a bad crystalline dispersion or unfavourable printing conditions.



(i) Print with increasing density of a dense negative area. The sensation of graininess increases with increasing exposure.



(ii) Print with increasing density of a medium density negative area. The graininess is at a maximum in the area of optimum exposure (in the centre).

FIG. 6C. Effect of exposure during the printing of a positive on the 'apparent grain' of the image. The negative was enlarged 300X.

A fine-grain developer cannot restore the loss of definition caused by a coarse-grain emulsion. We would add, furthermore, that the effectiveness of M.Q.-borax, and metol-sulphite developers has been greatly overrated, and contrary to the general belief, they are not at all suitable for certain types of ammoniacal emulsions. In general, care must be taken before generalizing on the good results which can be obtained with some negative materials.

What is the *mechanism* which produces finer developed grain than that produced by normal development.

Fine-grain developers generally contain a *solvent* for silver bromide: this solvent can be excess *sulphite*, *potassium thiocyanate*, or the developing agent itself, e.g. p-phenylenediamine. It is unlikely that the solvent works by simply breaking the bromide crystal into small pieces as was thought at one time. The silver grains are as we know, spongy clusters of filaments which are extruded during the reduction process carried out by the developing agent, a process which is affected by a large number of factors such as the adsorption of the developing agent onto the halide crystal. The shape, the size and the constitution of the developed grains are in the first place dependent on the nature of the developing agents, which is shown in Fig. 6d.

By *reducing the alkalinity*, the energy of the developer is reduced, development takes place more slowly and the mass of filaments thus formed is more fragile In the presence of a solvent, which during this time etches the crystal surface, the latter can become detached from the parent mass to form separate grains, often with their own side branches.

Simultaneously, the crystals undergo *physical development*, by deposition of silver around the centres, due to soluble silver complexes formed by the solvent (see end of para. 40). Unfortunately, the importance of that physical process has not yet been estimated.

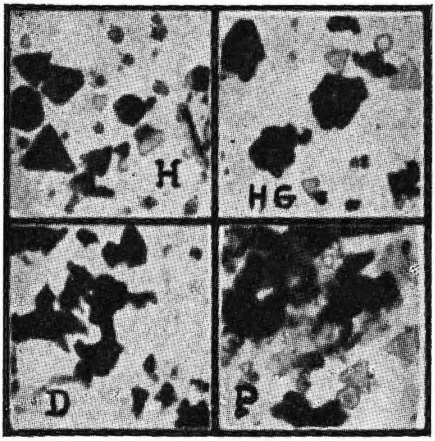


FIG. 6D. Action of different developers on the grains of the same emulsion (after Trivelli)

H: hydroquinone;
HG: metol-hydroquinone;
D: diominophenol;
P: paraphenylene-diamine.

There are two types of fine-grain developer:

(*a*) *Pseudo fine-grain developers* of the M.Q. borax or metol-sulphite types, whose effectiveness is questionable. In the most favourable cases they only produce a slight reduction in grain. On the other hand the loss in sensitivity is nil or negligible. The solvent action is of slight importance, it results only from the long immersion in the developer.

(*b*) *True fine-grain developers*: principally those containing thiocyanate or p-phenylenediamine. They have a strong solvent action towards the silver bromide, which has the result of reducing the emulsion sensitivity, necessitating an increase in exposure of 50–100%.

Before passing to the description of the different baths used, we note that the development gamma varies between 0·6 and 0·8. Many workers prefer the higher value. In fact, the choice depends on the contrast of the subject photographed. A flat subject is preferably developed to $\gamma 0{\cdot}8$ and a harshly lit subject to 0·65. The shape of the characteristic curve also intervenes, and can completely falsify tone values. We will return to this important point in the chapter on sensitometry.

Fine-grain images are warmer toned and more transparent than coarse-grain ones. Their visual contrast is frequently lower than their true contrast. This must be taken into account when judging their results.

74. Borax developers

M.Q. borax developers are widely used for the development of amateur and ciné negatives. The development time is long and the *contrast is low*. As amateur films are generally treated alike whatever their make, considerable differences between them are found: emulsions with a high gelatin ratio or ammoniacal types usually give flat results if the time is adjusted for a make of neutral emulsion.

D 76 type formula

	Working solution	Replenishment solution
Water to	1000	1000 cc
Metol	2	3 g
Sodium sulphite anh.	100	100 g
Hydroquinone	5	7·5 g
Borax	2	20 g

Development time at 18°C: films 8–16 minutes in dish, 10–20 minutes in tank. Ciné films: 10–25 minutes in tank. These times are for $\gamma = 0{\cdot}8$; for $\gamma = 0{\cdot}65$ reduce times to 60%. At 24°C and $\gamma = 0{\cdot}8$ reduce to 65%.

Development time is doubled after treating 0·25 m^2 of film that is 7·5 m of 35 mm film. Also, replenisher can be added gradually to maintain the level of the solution, but it is not recommended to add more than 1/5th of the initial volume; it is better to change the bath.

The activity of D 76 in a tank increases the first day, then drops rapidly. Levenson⁽¹⁾ has shown that the increase in activity is due to the oxidation of some hydroquinone which liberates caustic soda from the sulphite; thus the hydroquinone is used up.

Development with D 76 is more rapid if the *borax* is replaced by *sodium metaborate* (DK 76). The development times for various quantities of alkali are as follows:

Quantity per litre	Borax	Metaborate
2 g	20 mins.	10 mins.
10 g	15 mins.	7½ mins.
20 g	10 mins.	5 mins.

Buffered borax developer formula D 76d. The addition of boric acid to a D 76 developer increases its resistance to pH variations (buffer effect). Also it produces lower gammas. This bath has mainly been used for the development of ciné and sound recording negatives (variable density) which only need a low gamma.

Water to	1000 cc
Metol	2 g
Sodium sulphite anh.	100 g
Hydroquinone	5 g

Borax	8 g
Boric acid crystals	8 g

With a new bath add 0·25 g potassium bromide.
Development time 10–15 mins. at 18°C.

75. Pyro, p-aminophenol, and Phenidone developers

Pyro developer.(2) If the hydroquinone in D 76 is replaced by pyrogallol, and the borax is increased to maintain the pH at 7·6, a developer is obtained which not only gives the same graininess as D 76, but higher contrast due to the formation of a secondary organic image, from the oxidation of pyrogallol, which intensifies the main image. The sensitivity appears higher than with D 76.

Water to	1000 cc
Metol	2 g
Sodium sulphite anh.	100 g
Pyro	2 g
Borax	6 g

Development time 15 mins. at 20°C for Super XX film.

p-Aminophenol developer I.D 44

Water to	1000 cc
Metol	4 g
Sodium sulphite anh.	60 g
p-Aminophenol hydrochloride	5 g
Glucose	20 g
Sodium hexametaphosphate	1 g
Salicylic acid	0·5 g

Exposures must be doubled.

Phenidone developer. Axford and Kendal have proposed(3) the following phenidone developer for relatively fine grain:

		Replenisher	
	Working solution	Continuous	Intermittent
Water to	1000	1000	1000 cc
Sodium sulphite anh.	100	100	100 g
Hydroquinone	5	8	6·5 g
Phenidone	0·2	0·24	0·22 g
Borax	3	9	4 g
Boric acid	3·5	1	0·25 g
Potassium bromide	1	—	— g

Development time: 7–11 mins. at 20°C.

Continuous regeneration requires 365 cc per square metre of film. Note the small amount of Phenidone in the formula, sufficient to promote superadditivity, because ***hydroquinone regenerates Phenidone from its oxidation product.***

76. Plain metol developers

These simple formula developers contain a single developing agent. The results which they give vary with various emulsions; also the published information on the fineness of grain must be taken with reserve.

Metol formula D 23. Metol, in simple sulphite solutions has little tendency to fog, which at a pH of 7·6 enables development to be carried out up to 30°C.

Water to	1000 cc
Metol	7·5 g
Sodium sulphite anh.	100 g

Development time at 20°C, about 25 mins.

Metol formula D 25. The preceding bath is acidified with metabisulphite, and its activity is reduced. It therefore develops more slowly and is said to give finer grain than D 76, but with only 50% of the emulsion speed.(4)

Water to	1000 cc
Metol	7·5 g
Sodium sulphite anh.	100 g
Potassium metabisulphite	15 g

Average development time 22 mins. at 25°C.

77. Simple pyrocatechin developer

Burki and Jenny(5) have stated that *ammonium sulphate* added to a pyrocatechin developer gives warm-toned colloidal silver. They have prepared a fine-grain developer by adding a phosphate *buffer* to keep the pH between 9·7 and 10. The sensitivity is reduced by 50%.

Water to	1000 cc
Sodium sulphite cryst.	15 g
Pyrocatechin	3 g
Disodium phosphate cryst.	2 g
Trisodium phosphate cryst.	14 g
Ammonium sulphate	14 g

78. Thiocyanate developer

This developer gives quite fine grain, intermediate between that given by D 76 and that from p-phenylenediamine. The loss of sensitivity is 40%.

DK 20 formula	Working solution	Replenisher
Water to	1000	1000 cc
Metol	5	7·5 g
Sodium sulphite anh.	100	100 g

Sodium metaborate	2	20 g
Potassium thiocyanate	1	5 g
Potassium bromide	0·5	1 g

Development time 15–25 mins. at 18°C in dish or 12–20 mins. in tank.

79. p-phenylenediamine developers

p-Phenylenediamine developers⁽⁶⁾ give very fine grain. They have the disadvantages of being slow and toxic; they must therefore be handled with great care. They stain the skin brown. Loss of sensitivity is 50%.

p-Phenylenediamine alone

Water to	1000 cc
p-Phenylenediamine (base)	10 g
Sodium sulphite anh.	50 g

Development time: average 25 mins.

p-Phenylenediamine-glycin, preferable to the above.

Water to	1000 cc
p-Phenylenediamine (base)	10 g
Glycin	8 g
Sodium sulphite anh.	90 g

Development time: 12–20 mins. depending on the initial emulsion grain.

Developers with better solubility and reduced toxicity are obtained by substituting one of the amino hydrogens with a sulphone group of the types $—SO_2NH_2$,$—SO_2NHR$, $—NH—SO_2R$ (F.P. 866,339—1941).

A satisfactory compound of this type is *N-β-methyl-sulphonamidoethyl-4-aminoaniline* $NH_2—C_6H_4—NH—CH_2—CH_2—NH—SO_2—CH_3$. It can be used in the following bath:

Water to	1000 cc
Sulphonamido-p-diamine	5 g
Sodium sulphite anh.	30 g
Sodium carbonate anh.	30 g

Unfortunately, these compounds are not available commercially, except for some colour motion picture films.

p-Phenylenediamine-metol formulas

	Super Micros	T.P.1
Water to	1000	1000 cc
p-Phenylenediamine (base)	5	15 g
Metol	10	8 g
Sodium sulphite anh.	60	60 g
Hydroquinone	—	0·5 g
Trisodium phosphate	5	5 g
Potassium bromide	1	0·5 g
Development time at 18°C	6–9 mins.	10–12 mins.
Loss of sensitivity	60%	50%

80. Developers using combined p-phenylenediamine

We have already seen (para. 56) that developing agents can be reacted together to give combined developers such as, for example, metol and hydroquinone and p-phenylenediamine and hydroquinone. The compound of *p-phenylenediamine* and pyrocatechin gives a fine-grain developing agent, Johnson's *Meritol.*

Water to	1000 cc
Meritol	16 g
Sodium sulphite anh.	90 g

Developing time: 13–24 mins. at 18°C.

Loss of sensitivity 50%.

Used with metol the grain is less fine, but the loss of sensitivity is only 25%.

Water to	1000 cc
Meritol	13·5 g
Metol	2·5 g
Sodium sulphite anh.	90 g

Development time: 8–12 mins. at 18°C.

Once used, the solutions do not keep.

Taylor(7) was able to prepare *compounds of p-phenylenediamine with diglycocoll derivatives*, which in alkaline sulphite solutions are fine-grain developers. For example, p-phenylenediglycocoll obtained by condensing p-phenylenediamine with monochloracetic acid.

81. o-Phenylenediamine developers

Windisch compounded a developer using o-phenylenediamine and metol which gave images with grain intermediate between p-phenylenediamine and D 76. The W 665 formulas are given below:

	W 665	W 665N
Water to	1000	1000 cc
o-Phenylenediamine (base)	11·6	7 g
Metol	11·6	11 g
Sodium sulphite anh.	90	70 g
Hydroquinone	—	1 g
Potassium metabisulphite	10	7 g
Potassium bromide	—	0·5 g
Development time at 18°C	12–18 mins.	12–15 mins.
Loss of sensitivity—50%		

82. Atomal developer

The Agfa 'Atomal' fine-grain developer uses hydroxyethyl-o-aminophenol.(8)

A.	Warm water	800 cc
	Hydroxyethyl-o-aminophenol	6 g
	Pyrocatechin	10 g
	Hydroquinone	4 g

B.		
	Sulphite anh.	100 g
	Sodium carbonate anh.	25 g
	Potassium bromide	1 g
	Sodium metaphosphate	1 g

Add B to solution A and make up to 1 litre.
Development time: 10–15 mins.

83. Miscellaneous fine-grain developers

A series of fine-grain developers comprises certain basic heterocyclic compounds such as 6-amino-1 : 2 : 3 : 4-tetrahydroquinaldine.

By combining a *pyridine nucleus* with *chlorohydroquinones* a developing agent is obtained(9) which can be used for the preparation of fine-grain developers. Negative substituents in the molecule help in this. For example, from 2 : 3-dichlorhydroquinone, *hydroquinone-pyridine chloride* is obtained which can be used in a concentration of 7 g per litre together with 60 g anhydrous sulphite and 15 g anhydrous carbonate. With positive substituents (methyl), on the contrary, very vigorous developing agents are obtained, for example 2 : 3-dimethylhydroquinone-pyridine, which can be used in normal developers.

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2. Smethurst P. C.: *Brit. Jl. Phot.*, 1951, 410; *Sci. Ind. Phot.*, 1951, 418.
3. Kendall J. D.: *Brit. Jl. Phot.*, 1954, 81; Axford A. and Kendall J. D.: *Brit. Jl. Phot.*, 1954, 138–140.
4. Henn and Crabtree: *Phot. Soc. Amer. Jl.*, 1944, 727.
5. Burki and Jenny: *Camera*, 1943, 55.
6. For a study of phenylenediamine development see: Fortmiller L. J. and James T. H.: *Phot. Soc. Amer. Jl.*, 1951, 102; *Sci. Ind. Phot.*, 1952, 100.
7. Taylor G.: B.P. 481,681 (1936).
8. F.P. 636,478 and add. 35,793 (1928).
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Chapter VIII

USE OF DEVELOPING SOLUTIONS

84. Methods of development

The simplest and oldest development method is to immerse the exposed sensitive material in a quantity of developer sufficient to cover it completely. The surface of the material can be either horizontal or vertical. In the former case the operation is carried out in a dish, and in the latter, a tank. The stagnant accumulation of development by-products in a tank where a large volume of liquid remains stationary is greater than in a dish. This is why tank development generally takes longer.

When the liquid is circulated, or the material agitated, the development time can be greatly reduced. This takes place in the development of motion picture materials in a continuously running machine; here, the film, guided by rollers passes successively through the development, fixing and washing tanks.

It is, however, sometimes necessary to perform all these operations—development, fixing and washing—in the same vessel without disturbing the material. This takes place, for example, in some radar ultra-rapid processing units.(1) The vessel in this case is very small and is equipped with a pump to change the baths rapidly.

Another method which is becoming widely used is *spray development.* The developer is applied as flat conical jets from nozzles.(2) Oxidation is obviously accelerated, but as the volume of the bath is small it is frequently renewed. The system is more economic if the pH of the bath is $\leqslant 9$.

Katz and Esthimer(3) have speeded up development up to three times by applying a *turbulent liquid* to the development surface, that is, a rapidly circulated liquid.

Application of a *viscous developer* is used in the treatment of optical sound tracks in some colour processes. The developer is thickened with carboxymethylcellulose or with methylcellulose. If the picture area is treated in the same way, one would imagine that the bromide liberated in the high densities would soon prevent the small quantity of developer from functioning. According to Rudkin, this disadvantage can be overcome by adding colloidal silica or kieselguhr.(4)

Finally, it is possible to develop with a *sponge* which is kept moving over the image to avoid uneven treatment. This method is often used for processing large bromide prints.

85. Development time

The development time is influenced by many factors: emulsion type, developer formula, dilution and working method, required gamma, temperature and agitation.

Negative development takes a long time with fine-grain developers—10 to 20 minutes. With ordinary developers the time is 5 to 10 minutes. Motion picture positive is developed in 3 to 4 minutes.

The contrast increases with development time until a limit is reached dependent on the emulsion type and the developer composition.

Fine-grain emulsions develop much more quickly than coarse-grain high-speed ones. The speed of development also depends on the crystalline form of the silver bromide and the gelatin ratio of the photographic layer.

As a general rule in continuous professional work *the development time must be periodically modified to compensate for the changes in contrast* due to variations in the composition of the bath, changes which can reach or even exceed ±10% of the required gamma.

86. Development temperature

Temperature influence is represented by an Arrhenius equation which has been studied by James.(4b) The normal development temperature is 18–20°C, but it is possible that development must be carried out at temperatures lower or higher than this. In this case the normal time must consequently be increased or decreased. Inadequate temperature control of the bath always results in irregular development.

Below 18°C the activity of hydroquinone decreases much more rapidly than that of metol, which, in effect, varies the composition of an M.Q. developer towards a less contrasty bath. The reverse takes place at temperatures above 18°C.

Generally, the development time should be doubled or halved for a difference of 8°C less or more. As an example, here are the relative times for three different developers:

	D 76	D 72, 1 : 1	D 11
13°C	17 mins.	8¼ mins.	6 mins.
15·5°C	13 „	6½ „	5 „
18°C	10 „	5 „	4 „
21°C	7¾ „	4 „	3¼ „
24°C	6 „	3 „	2½ „

We have already seen that in the presence of *sodium sulphate*, which prevents the gelatin from swelling, the development time at 24°C is practically the same as at 18°C. It is the same with an unhardened film developed at 18°C and the same film pre-hardened and developed at 24°C. Above 24°C the time must be reduced:

Temp.	27°C	29°C	32°C	35°C	43°C
Take	85%	70%	60%	50%	25% of the normal time

To develop at low temperatures without too great an increase in time,(5) 5–15% urea can be added to swell the gelatin and speed up development by 25%. The oxidation of the developer is accelerated, giving warmer tone images.

87. Agitation

Developer agitation is an important operation which has a considerable influence on the image characteristics. The rapid elimination of by-products can bring about a considerable reduction in the time taken to complete the image; this takes place by development with a turbulent liquid.

Agitation by intermittent jets of gas(6) at a pressure of 0·35 kg/cm^2 is preferable to mechanical agitation or simple circulation. Changes in the developer are negligible if nitrogen is used.

The development of low densities is governed chiefly by the *reaction speed* of the developer, but that of high densities depends on the *diffusion* of the developer in the emulsion layer. This is important in case of short developing times. The use of hydroquinone prepared with radioactive carbon C^{14} permits the phenomenon to be observed.(6c)

88. Equipment materials

Development is carried out in dishes or tanks made from materials inert to the developer. *Pyrex glass* and porcelain are suitable only for small apparatus. Enamelled iron(6b) is often used for dishes, and *stoneware* for tanks; the former is readily chipped, whilst the latter is very heavy and awkward. *Stainless steel* and *plastic materials* are best.

Stainless steel must not contain more than 0·08% carbon otherwise an iron carbide is formed during welding which leads to corrosion.(7) Welding is preferably done electrically in an inert atmosphere with a jet of cooling water on the opposite side. The sheets must be annealed and polished. Treatment with nitric acid diluted with 2·5 parts of water for 30 minutes at 50–60°C removes the superficial impurities (this operation must be carried out where there is adequate ventilation and gloves must be used).

Muehler and Crabtree have given the following test for *molybdenum stainless steel*, the only resistant one: put a drop of concentrated nitric acid onto a clean area of the vessel or sheet, then a drop of concentrated hydrochloric acid. Leave for 30 seconds. Transfer the reacted drops to a porcelain crucible with a micropipette. Add 10 drops of distilled water then 4 drops of 10% potassium thiocyanate. Stir, then add 5 drops of stannous chloride solution (dissolve 6·5 g stannous chloride in 5 cc hot hydrochloric acid then make up to 25 cc with water). If an orange-red coloration is produced the steel is molybdenum stainless type 316, but if only pale green then the steel is type 304 without molybdenum.

Developing tanks are often made from *polyvinyl chloride* which can be hot-air welded. At one time *ebonite* was used, but chlorinated rubber is better. *Teflon* (polytetrafluoroethylene), which has very high chemical resistance can also be used. In the absence of other materials, *wood* can be used, but if possible it should be impregnated with paraffin wax, bitumen or bakelite, or it will be necessary to sterilize it periodically with a toxic solution of 1 : 1000 pentachlorophenol.

The developing apparatus fittings (pump, pipes, taps) should be stainless steel, lead, ebonite or P.V.C.

Non-metallic equipment can be *cleaned* with the corrosive solution of dichromate in sulphuric acid:

Water	1000 cc
Potassium dichromate	80 g
Sulphuric acid conc.	50 g

Dissolve the dichromate in warm water. Cool, then *slowly, and with stirring*, add the acid to the solution. *Warning*: never pour water into the sulphuric acid: this can splash acid into the air.

After cleaning retain the chromic acid solution, and wash with plenty of water.

Metallic apparatus is cleaned with damp pads and fine chalk or pumice powders or even household cleaners. Remove rust marks with 10% nitric acid or sodium nitrate.

The bath is contaminated during development with foreign matter brought in by the films and by the air, and with particles of gelatin, colloidal silver and insoluble calcium salts. The sludge which is produced necessitates careful filtration of the circulated bath, using clean filters. The sludge is deposited on the inside of tanks and in the pipes. Periodic cleaning in 1% hydrochloric acid for 3–4 hours is advisable.(8) Neutralization with 2% soda and washing follows.

89. Sulphide fog

Water frequently contains *sulphur-producing bacteria* which attack the sulphite of a developer left in a deep tank. They form *sodium sulphide* which results in a *yellow fog* of silver sulphide. After a few films have been developed, this fog disappears due to exhaustion of the sulphide.

Hypo-contaminated clips can also produce this fog.

Bacterial reduction (*proteus vulgaris*) of sulphite (or hypo) of used developers was noted by Dundon and Crabtree.(9) It produces a slight grey deposit or dichroic fog with a metallic lustre on the gelatin surface of films. This deposit is not firmly fixed; it can be removed with a pad damped with alcohol, or by immersing in a 10% solution of ammonium thiosulphate containing 0·5% acetic acid, or failing that, in an acid-hardening fixer. It consists of silver sulphide Ag_2S covered with metallic silver. It can be reproduced artificially by adding 0·2–10 mg per litre of sodium sulphide to the bath. Its natural occurrence is encouraged by the presence of particles of gelatin (rich in sulphur compounds such as cysteine), red antimony sulphide rubber, or atmospheric hydrogen sulphide.

The sulphide fog can be avoided by adding to the bath 30 cc per litre of 1% cadmium chloride.

To neutralize the sulphide, add 0·1 g per litre lead acetate dissolved in a little water. The resulting precipitate is allowed to settle.

To prevent the action of sulphide bacteria Henn and Crabtree(10) recommend resorcinol (0·1–0·5%) and pentachlorophenol (0·005–0·01%) (poisonous). Rogers(11) proposed derivatives of 3 : 6-diaminoacridine: acriflavine, proflavine and dyestuff 914 (I.C.I.) in a concentration of 1·25 mg per litre.

Whatever method of elimination is used, cleaning the tanks with warm water containing 5% trisodium phosphate is recommended.

90. Aerial oxidation of developers

Aerial oxidation of developers takes place spontaneously without use. During development, the two oxidation processes—aerial and by silver bromide—take place concurrently. In aerial oxidation it is primarily the hydroquinone which is affected, the products being hydroquinone-monosulphonate, sodium sulphate, sodium hydroxide and various brown tanning substances (5 %).

The amount of *sodium sulphate* which is produced can be used to determine the degree of aerial oxidation, as this substance is not produced during oxidation by silver bromide. One molecule of oxygen, O_2, forms one molecule of sodium sulphate Na_2SO_4 from sodium sulphite Na_2SO_3, the other half of the oxygen being used in the formation of a molecule of sodium hydroxide. The sodium sulphate is estimated by adding barium nitrate, and weighing the barium sulphate $BaSO_4$, which is precipitated.

In developing machines, aerial oxidation is encouraged by circulating pumps, filtration systems, film perforations and by air forced in for agitation.

Oxidized baths give much lower gammas.

Aerial oxidation fog is accelerated by *copper* in concentrations of 2 mg per litre (except with the non-alkaline D 76). The action of the copper can be neutralized with 0·1 % phenosafranine and sequestering agents: Versene, Sequestrene, Trilon B or F.

Keeping properties of developers. Developers keep for 24 hours in dishes, 15–30 days in tanks, and 3–6 months in well-stoppered bottles.

	Tank	Stoppered bottle
D 72	15 days	3 months
D 76	30 days	6 months
DK 20	30 days	6 months
D 11	30 days	6 months

Caustic soda developers do not keep.

91. Exhaustion of developing solutions

Take, for example, a metol-hydroquinone solution containing sulphite, carbonate and 1 % potassium bromide. *The reduced silver bromide liberates an equivalent quantity of soluble bromide,* whilst the silver is deposited in the gelatin layer. The silver iodide produces soluble iodide. *The developing agents are used up in proportion to the amount of film developed.* To reduce 1 g of silver bromide, 0·36 g of hydroquinone or 0·8 g of metol are needed and they decompose 0·55 g sulphite, forming *monosulphonates* and small quantities of disulphonates. The halide dissolved by the sulphite is reduced to colloidal silver which coagulates to muddy materials removed by filtration.

The progressive destruction of the developing substance leads to a reduction of image contrast; the accumulation of bromide slows down development although, after a certain limit is reached, the iodide in solution is taken up by the sensitive layer.(12)

With an unreplenished developer the necessary development time increases in proportion to the exhaustion. After an area of 0·5 m^2 has been developed the time is doubled with an M.Q. carbonate bath. It is doubled after only 0·25 m^2 in D 76 which is spent after 0·37 m^2. It is the same with the thiocyanate containing DK 20.

In the case of papers, D 72, diluted with an equal volume of water can develop 1·5 m^2.

92. Continuous development

In the development of film on continuous machines the composition of the developer must be kept constant for months on end. Let us see what happens during the treatment of 35 mm film.

When the developed film leaves the developer, *it takes with it a certain amount of developer* (observed to be in the region of 30 cc/metre) which is completely lost. In the same film 0·05 g of metallic *silver* per metre (5 g/100 m) is produced, and a corresponding quantity of *soluble bromide* is left in the solution. The proportions of metol and hydroquinone which are *used up* have already been given. Knowing the quantity of film developed in an hour (1800 metres for example) it is easy to calculate the approximate weights of materials involved.

Consequently, on one hand the concentration of active constituents is reduced, whilst the concentration of unwanted by-products is increased. Hydroquinone, metol and sulphite are used up, whilst bromide, sulphonates and sodium sulphate are produced, and the pH is altered by the liberation of hydrobromic acid and sodium hydroxide.

Use is made of the carry-over of solution in regenerating the bath by maintaining the solution level with a *new solution of special composition* (replenisher).

If, after an hour, for example, a quantity h of hydroquinone is used in each litre (by oxidation by silver bromide and by the air) and if the volume of liquid lost is L, a similar volume L of new solution containing $\mathrm{Vh}+\mathrm{L}(\mathrm{H}-\mathrm{h})$g of hydroquinone must be added. V is the total volume of developer and H the initial hydroquinone concentration per litre. Similarly with the other constituents, metol and sulphite. Taking a smaller unit of time, more accurate amounts can be calculated.

Calculations are more complicated in the case of the by-products formed in the same bath. The solution is continually enriched with more and more unwanted substances. The loss of the volume L of developer in each unit of time removes a certain amount, but as this is again diluted with the bulk of the liquid, the quantity removed is less than the quantity produced.

Suppose that *s*g hydroquinone-sulphonate are produced per litre per hour. At the end of the hour L litres of old developer are removed and replaced by L litres of a new developer. After this operation there are $\mathrm{s}(\mathrm{V}-\mathrm{L})/(\mathrm{L})$g of sulphonate per litre. $(\mathrm{V}-\mathrm{L})/\mathrm{V}$ is the proportion of solution kept after each operation. If we represent it by r, the amount of substance remaining after the first replenisher addition is sr. After the second hour, there is $s+sr$ g of sulphonate of which it remains $(s+sr)\times r = sr+sr^2$. And after the nth operation, we shall have $sr+sr^2+sr^3 \ldots sr^n$, which can be written: $s(r+r^2+r^3 \ldots r^n)$ Actually the variation does not take place each hour, but continuously at each instant dt. One can therefore apply the Evans formula⁽¹³⁾

$$x = k - (k - a)e^{-Lt/V}$$

where x represents the concentration (per litre) of the substance under consideration at time t (minutes) a is the initial concentration of the substance in the bath, k the concentration of substance formed at each moment, assumed to be dissolved in the volume L (per minute) and e is the Naperian logarithm base.

There then comes a time when the concentration of the unwanted substance formed is so high that the amount disposed of in the volume L of the solution carried over equals the amount formed. At this moment the bath is in *equilibrium*; the unwanted material is removed as quickly as it is formed. The function x represented by the Evans formula is an exponential function which consequently tends towards a limit which is precisely this equilibrium. But there are several different equilibriums for each of the substances concerned. Take, for example, the example of soluble bromide given by Evans.

The initial concentration in the developer is l g per litre therefore $a = l$. Let L = 10 litres/minute, and the total volume of liquid, V = 40,000 litres, feeding several machines. If a total of 300 metres of film per minute is developed under these conditions an average of 15 g of silver and 15 g of sodium bromide are produced per minute.

As $l = 10$L we have $k = 15/10 = 1{\cdot}5$ g of bromide. The equation becomes

$$x = 1{\cdot}5 - (1{\cdot}5 - l)e^{-\frac{10}{40{,}000}t} = 1{\cdot}5 - 0{\cdot}5e^{-\frac{t}{4{,}000}}$$

At t = ∞ it is seen that $x = 1{\cdot}5$ g: at the equilibrium the bromide concentration is, in fact, constant. To reach a concentration of 1·4 g per litre (starting with the initial concentration in a fresh bath) the time necessary is given by substitution in the preceding formula:

$$t = \frac{2{\cdot}3V}{L}\log_{10}\frac{(k - a)}{(k - x)}$$

giving t = 9,200 minutes, or about six days. The new bath is, then, almost at the equilibrium for bromide after six days' continuous use.

The calculation which has just been made for the bromide can be applied to all of the bath constituents. In each case an equilibrium is reached.

The study of continuous development must be completed by:

1. Analytical estimation of the substances present at various determined times.
2. The measurement and adjustment of pH.
3. The development of sensitometric strips.
4. The working out of suitable different replenishers for when the machine is in use or idle (surface oxidation only in this case).

93. Faults due to development

Certain faults of developed images are due to improper development conditions.

Patches: uneven development due to poor circulation of the bath. They are particularly prevalent when the development is short in an energetic bath.

Clear parallel lines going in the opposite direction to the film movement (streamers) or downwards if it is in a static vertical position: due to by-products streaming from high density areas which slow down development in the adjoining area.

Development too slow: spent developer, temperature too low or an accidental excess of bromide.

Development too fast: developer too concentrated or too warm.

Fog: over-development, developer too warm or lacking bromide (assuming that it is not emulsion or light fog), accidental presence of an organic fogging agent provided, for example, by red rubber or a nearby chemical store.

Yellow fog: bath, or sensitive material, sulphide contaminated—chloride paper defective or developed too long.

Pressure marks: from slides or rollers; irregular circulation of by-products.

Clear circular spots. Air bells on the surface of the sensitive material at the time of immersion. They are also caused by the perforations, circulating pumps and air agitation jets.

Dust can be stuck to the dry film or may come from a badly filtered bath.

Oil marks from the mechanism of the machine.

Reticulation: developer too warm or caustic, followed by a cold rinse.

Certain faults are due to the emulsion: *absorbent spots* due to static electricity (effluvia), *grey mottle* on papers, *white points* with dark centres or *black points* with halos, due to dust falling on paper during baryta treatment or on the emulsion during coating.

94. Development accelerators

There are six ways to increase the development rate of a particular emulsion. The first three depend on the same principle—the increase of developer energy.(14)

1. *Concentration* of the developer (to an optimum value).
2. Increase of *alkalinity*.
3. Raising the *temperature*.
4. *Swelling* the gelatin by adding urea to the bath (para. 86).
5. Reduction of the potential barrier surrounding the silver bromide grain by including a *cationic surface active agent*(15) such as laurylpyridinium chloride in a concentration of 0·1 g per litre. The maximum density is also increased. The access of developer ions is increased due to the reduction in negative surface charge by this product.(16)
6. Addition (or pre-treatment) of 0·1 g per litre of a dye such as neutral red, safranine, methylene blue, methyl violet, janus green, pinakryptol yellow,(17) 3 : 3′-diethyl-oxa- and thia-carbocyanine chlorides, etc. This can at the same time produce fog and colour desensitizing or sensitizing.

According to James, the dye acts as a surface active agent to reduce the potential barrier. Levenson(18) on the contrary, has put forward the idea that their action is more like that of a developing agent analogous to metol in superadditive developers, based on the fact that the leuco derivatives of the dyes are powerful developers.

95. Ultra-rapid development

We have just seen that the rate of development is dependent on the concentration of developer, on the pH, on the temperature and on the presence of accelerators. It also depends to a great extent on the rate of agitation, that is, on the rapid renewal of the liquid.

In caustic solutions at high temperatures, development is particularly rapid. Under these conditions it is advisable to add an antifoggant, and also formalin or glyoxal if the emulsion has not been ***previously hardened.***

The following formula is widely used:

Water to	1000 cc
Alcohol	100 cc
Ethylene glycol	100 cc
Metol	15 g
Sodium sulphite anh.	50 g
Hydroquinone	15 g
Caustic soda	15 g
Potassium bromide	8 g

This bath can be used concentrated, or diluted with 500 cc of 10% ethylene glycol. Thus diluted it develops in 4 seconds at 60°C.(19) It is advisable to add 0·5 g of benzotriazole as an antifoggant.

Fix in 10% hypo containing 50 cc bisulphite, heated to 60°C. Do not add alum as it decomposes at this temperature.

The above formula can also be used without the addition of glycol. The latter is a hygroscopic compound and enables the material to be dried after rapid fixing and washing without crystallization of the substances still present in the film.

If the emulsion is not hardened, add 5–10% formalin.

Another bath which develops in 30 secs. at 40°C contains:

Water to	1000 cc
Metol	27 g
Sodium sulphite anh.	80 g
Hydroquinone	27 g
Caustic soda	40 g
Potassium bromide	40 g
Benzotriazole	1 g
Formalin	35 cc

Pyrocatechin formula:

A	Water to	1000 cc
	Pyrocatechin	100 g
	Sodium sulphite anh.	100 g
B	Water	1000 cc
	Caustic soda	60 g
	Potassium bromide	100 g
C	Formalin	200 cc

Omit the formalin with hardened emulsions.
Development time: 40 secs. at 30°C. A few seconds at 60°C.

Phenosafranine formula:

A	Water to	1000 cc
	Sodium sulphite anh.	25 g
	Hydroquinone	50 g
	Phenosafranine 1 : 5000	25 cc
B	Water to	1000 cc
	Caustic soda	300 g
	Potassium bromide	10 g

Treat for 5 seconds in A, then 1 second in B.

According to Crabtree and Russel, a well hardened emulsion can be developed in 1 second at 65°C in D 8 developer (hydroquinone-caustic-excess bromide). Jaenicke also disclosed a sensitive layer impregnated with hydroquinone, dried and exposed, which gives an image in 1 second by simply treating in strong alkali.

Development is stopped by immersing in a stop bath heated to 50°C containing a buffering agent like sodium acetate. If the emulsion is lightly coated, fixing can be omitted.

To develop with maximum speed, the solution must be rapidly streamed down as a thin layer, on the surface of the sensitive material. Equipment to do this has been made.(20)

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4b. James T. H.: *Phot. Sci. Techn.*, 1955, 81–90.
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Chapter IX

THE DEVELOPING AGENTS

96. The developing functions of cyclic compounds

A compound is a reducer with respect to exposed silver bromide when its redox potential is lower than 120 mV at a predetermined pH, and when it can be adsorbed to the crystal surface.

Whilst the chemical constitution of the reducer is unimportant in itself when the preceding condition is fulfilled, it is nevertheless true that these conditions are essentially dependent on the constitution.(1) To be of practical use, a developing agent must, in other respects, have certain characteristics which simplify its use: solubility, keeping qualities, absence of stain, reasonable power at a moderate pH, non-toxicity, simplicity of preparation to be economical, etc. No developing agent possesses all of these properties together.

Developing agents having an aliphatic (non-cyclic) structure are known, but have no place in current use. Only a few aromatic (or cyclic) developers are made on a large scale and made available to photographers.

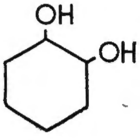
Organic compounds capable of developing fall into two groups, the *hydroxy* compounds and the *amines*; they can be hydroxy and amino at the same time = *aminophenols*.

In all cases, at least *two functional groups, hydroxyl or amino*, must be present; in other words, the nucleus must contain two —OH groups, two $—NH_2$ groups or one —OH group and one $—NH_2$ group.

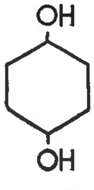
OH and NH_2 are, by convention, termed *developing functions*.

In addition, for the developing functions to be active, they must be present in the *ortho* or *para* positions relative to each other.

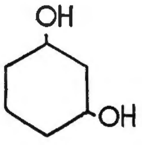
Thus o-dihydroxybenzene and p-dihydroxybenzene (also known as pyrocatechin and hydroquinone) are developers, whilst m-dihydroxybenzene (resorcinol) although a reducer, does not develop, or only with great difficulty.



o-dihydroxybenzene
(pyrocatechin)



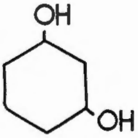
p-dihydroxybenzene
(hydroquinone)



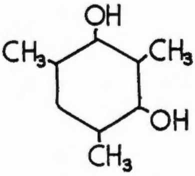
m-dihydroxybenzene
(resorcinol)

The same is true of m-aminophenol and m-phenylenediamine.

The reason for this anomaly lies in the fact that the meta compounds are more prone to exist in the keto form, with one of the phenolic hydrogen atoms migrating to an adjacent nuclear methine group, C . OH becoming C : O. This molecular rearrangement is most pronounced in phloroglucinol $C_6H_3(OH)_3$ in which the three hydroxyl groups are all meta to each other. If the migration of the hydrogen atoms is prevented by nuclear substituents, the meta compounds have developing properties. When the nuclear carbon atoms adjacent to the hydroxyl groups carry methyl, CH_3, substituents, the hydroxyl groups retain their hydrogen atoms; mesoresorcinol is a developer.



resorcinol
(non-developer)



mesoresorcinol
(developer)

The mechanism of reduction by the di- and tri-hydroxybenzenes is, therefore, essentially a transformation from the phenolic to the *quinonoid* state in which the phenolic function C—OH becomes a cyclic ketone function C = O with liberation of hydrogen ions:

$$\underset{\text{Hydroquinone}}{OH{-}C_6H_4{-}OH} \rightarrow \underset{\text{quinone ion}}{[O = C_6H_4 = O]^{--}} + \underset{\text{Hydrogene ion}}{2H^+}$$

It has already been shown how quinone combines with the sulphite present in the developer to form a *sulphonate*.⁽²⁾

We have said that resorcinol develops only slightly—if at all. In fact, it can be made to develop very slowly. James and Levenson⁽³⁾ used a solution containing 11 g resorcinol and 28 g caustic potash per litre, for 4 hours at 25°C in an atmosphere devoid of oxygen. A yellow residual image was formed at the same time.

HYDROXYBENZENES

97. Hydroquinone

Hydroquinone, $C_6H_4(OH)_2$ (p-dihydroxybenzene) was disclosed as a developer by Abney in 1880. It occurs in needle-shaped orthorhombic prisms, melting point 169°C. It is more readily dissolved in hot than cold water, and is soluble in alcohol and ether.

It is identified by sulphomolybdic acid; 80 cc of 15% ammonium molybdate and 20 cc of 30% sulphuric acid give a dark blue coloration when boiled with hydroquinone. Pyrocatechin and the phenolic acids are first removed by precipitation with 10% lead acetate.

Preparation. Quinone, prepared by oxidizing aniline, is reduced to hydroquinone with sulphur dioxide.

$$C_6H_4O_2+SO_2+H_2O \rightarrow C_6H_4(OH)_2+H_2SO_4$$

One part of aniline is dissolved in 8 parts of dilute sulphuric acid and 3 parts of sodium dichromate are added in small portions. After the solution clears, the temperature is raised to 35°C and the quinone is extracted with ether, and purified by steam distillation. The yellow crystals which are obtained are treated with sulphur dioxide in alkaline solution. The resulting hydroquinone is extracted with ether. It is purified by dissolving in water, decolorizing with activated carbon, and crystallizing after a short treatment with sulphur dioxide. Other reducing agents can be used—bisulphite(4) or ferrous sulphate,(5) or the reaction can be carried out under reduced pressure.(6) Following another procedure(7) the reduction is stopped when the pH is between 5 and 9; the reaction is finished after adding a primary amine which precipitates the hydroquinone produced.

Hydroquinone can be prepared by the following scheme: 16 g aniline are poured into a flask containing 400 cc water and 80 g sulphuric acid cooled in iced water. About 40 g of finely ground dichromate is slowly added until the green precipitate formed is redissolved. The resulting solution is poured into a vessel containing 200 cc of ether; after shaking and standing 30 minutes, the ether layer is separated, and the ether is evaporated off. Quinone crystals are left. These crystals are dissolved in a little water on the water-bath, and an excess of saturated sulphur dioxide solution (about 150 cc) is added. The quinone is reduced to hydroquinone. Heating is continued in an evaporating basin until the water is removed and the hydroquinone crystallizes. The product is recrystallized from boiling water (20 g to 100 cc). By cooling to 10°C, 17 g of the purified product is deposited. The remaining 3 g can be recovered from the mother liquor by evaporation.

Aniline can be oxidized with manganese dioxide and sulphuric acid. The quinone is then reduced with iron powder. Using the method of von Bramer and Zabrisbie of the Tennessee Eastman Corp., the yield of purification is increased by steam distilling rather than crystallizing.(8)

Instead of starting with aniline, benzene C_6H_6 can be oxidized by electrolysis in an acid medium.(9) To reduce quinone to hydroquinone, Kikuchi and Masago(10) used as catholyte 300 cc of 2% H_2SO_4 containing 5 g of quinone and 0·5 g ammonium vanadate (catalyst) and as anolyte, 30 cc of 2% H_2SO_4. Lead electrodes. Temp. 50°C; D.C. 3A/dm^2 at 6–7·5V; time 3 hours.

Also, by treating p-bromophenol with an alkali between 75 and 150°C, hydroquinone is produced.(11)

$$Br\,.\,C_6H_4OH + KOH \rightarrow C_6H_4(OH)_2 + KBr$$

Fasciati(12) treated p-dichlorophenol with oleum, then with soda lye in the presence of copper.

98. Hydroquinone derivative developers

2-Chlorohydroquinone (Adurol) which occurs as colourless needles or tablets M.Pt. 103°C. It is soluble in water and alcohol. $ClC_6H_3(OH)_2$.

Schering's *bromohydroquinone* and *2 : 3-dichlorohydroquinone.*

The halogens generally increase the energy of the developer when substituted in the nucleus, especially bromine.

Toluhydroquinone $CH_3C_6H_3(OH)_2$ and *xylohydroquinone* $(CH_3)_2 . C_6H_2(OH)_2$ are the hydroquinones derived from toluene and m-xylene.

1 : 2 : 5-Trihydroxybenzene is a developer, although phloroglucinol (the 1 : 3 : 5 compound) does not develop, its hydroxyl groups are in the meta position to each other.

Nitro groups, being oxidizing groups, completely neutralize the developing properties of hydroquinone when they are introduced into the nucleus.

The following alkyl and acylamino derivatives of hydroquinone were disclosed as developers in 1936 by L. Schinzel(13): 2 : 5-dimethyl and 2 : 5-diethylhydroquinone; 2 : 5-diphenoxyhydroquinone, 2 : 5-di-p-phenetylhydroquinone, 2 : 5-dibenzoylaminohydroquinone, 2 : 5-diacetaminohydroquinone, 2 : 5-diphenyl-3 : 6-dibenzylhydroquinone.

Hydroquinone-pyridine derivatives: Buchta, Barnett, then Diels succeeded in replacing the chlorine of chlorhydroquinone with pyridine. It now seems preferable to react quinone and pyridine in the presence of acetic acid.(14) By adding HCl, yellow needles are obtained, M.Pt. 225°C.

The hydroquinone-pyridine derivatives are more soluble than hydroquinone (for they form hydrochlorides), often produce less fog and are not so prone to aerial oxidation.

To prepare a developing solution, 7 g of this product are used with 30 g sulphite and 70 g carbonate (per litre).

The energy is increased by introducing positive substituents into the hydroquinone nucleus, e.g. *2 : 3-dimethylhydroquinone-pyridine* which yields very energetic developers (K. Kumetat):(15)

Water to	1000 cc
2 : 3-dimethylhydroquinone-pyridine	7 g
Sodium sulphite, anhydrous	60 g
Potassium carbonate cryst.	35 g
Potassium bromide	4 g

99. Pyrocatechin

Pyrocatechin, used by Eder and Toth in 1880 is an o-dihydroxybenzene isomeric with hydroquinone. It crystallizes in orthorhombic prismatic needles which melt at 104°C, and is readily soluble in water, alcohol and ether.

Pyrocatechin is prepared by reacting caustic soda with o-chlorophenol in an autoclave at 300°C.

$$\underset{\text{o-chlorophenol}}{ClC_6H_4(OH)} + \underset{\text{caustic soda}}{3NaOH} \rightarrow \underset{\substack{\text{sodium}\\\text{o-diphenate}}}{C_6H_4(ONa)_2} + \underset{\text{water}}{2H_2O} + \underset{\substack{\text{sodium}\\\text{chloride}}}{NaCl}$$

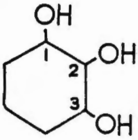
Copper salts are catalysts in this reaction. The sodium salt is reacted with sulphuric acid to liberate the pyrocatechin, which is extracted with ether (removed by distillation at reduced pressure).

Pyrocatechin is also obtained by fusing o-dichlorobenzene with caustic potash and also by heating guaiacol(16) with hydrochloric acid in an autoclave at 140°C.

Adrenalin: hormone derived from pyrocatechin, *l*-adrenalin with the formula $C_6H_3(OH)_2 . CH(OH)—CH_2 . NH . CH_3$, is a developer. J. Rzymkowski(17) used the following bath: adrenalin 4 g, caustic soda 4 g, potassium bromide 1 g, water to 1000 cc.

100. Pyrogallol

Pyrogallol was disclosed by Regnault and Archer in 1851; it is a *1 : 2 : 3-trihydroxybenzene* (diphenol) with the formula:



It is in the form of colourless needles melting between 131·5 and 132·5°C, soluble in water, alcohol and ether. In alkaline solution it rapidly absorbs oxygen from the air, and turns brown. When poured into lime wash, a characteristic red colour is produced.

Pyrogallol is formed by the action of caustic potash solution on dibromosalicylic acid, but in practice it is prepared by thermal decomposition of *gallic acid.*

$$\underset{\text{Gallic acid}}{C_6H_2(OH)_3COOH} \rightarrow \underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + \underset{\text{Carbon dioxide}}{CO_2}$$

Gallic acid, the monocarboxylic acid corresponding to pyrogallol is itself obtained from the tannin of *gall nuts*. The crushed gall nuts are extracted with a mixture of 5 parts ether, 0·6 parts alcohol and 0·2 parts water. After 24 hours, the liquid is drawn off and separates into two layers. The lower layer, yellow and syrupy is extracted with ether, and the extract is evaporated under reduced pressure. The yellowish white powder which remains is composed of tannin. The tannin solution together with a dilute acid is heated to 70–80°C for 24 hours. The tannin is hydrolyzed to gallic acid which is deposited from the filtered solution. It is purified by decolorizing with animal charcoal and recrystallizing from alcohol. The hydrolysis can also take place by means of 'penicillium glaucum' or 'aspergillus niger', both of which contain a diastase, tannase, which attaches the elements of a molecule of water to the tannin.

To convert the gallic acid to pyrogallol, it is heated to 200°C together with two parts of water. The carbon dioxide is released at intervals. The resulting solution is decolorized with animal charcoal then, after concentration, is left to crystallize. The gallic acid can also be distilled with powdered pumicestone in a current of carbon dioxide which carries away the resulting pyrogallol.

The esters of pyrogallol are developers. These include *l-methyl* and *l-ethyl-pyrogallols* disclosed by Schuster(18) and Stockelbach's(19) *1-tert-butyl* and *diethyl-pyrogallols.*

A further trihydroxy-benzene, methylated directly in the nucleus was disclosed by Schinzel(20)—2 : 4 : 6-trimethyl-1 : 2 : 3-trihydroxybenzene.

101. Naphthols

Many naphthols have been used successfully as photographic developers:

1 : 4-Dihydroxynaphthalene $C_{10}H_6(OH)_2$, 1 : 5-dihydroxynaphthalene, 1 : 5-dihydroxynaphthalene-6-sulphonic acid (Andresen 1889),(21) 4-methoxy-1-naphthol $OH . C_{10}H_6 . OCH_3$ and 4-ethoxy-1-naphthol,(22) 2-phenyl -1 : 4-dihydroxynaphthalene $C_6H_5 . C_{10}H_5(OH)_2$ (Schinzel 1936).

102. Hydroxyanthracenes

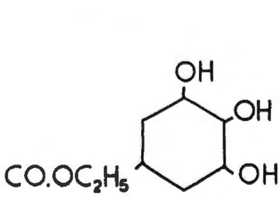
Schinzel(23) has also desclosed the following compounds as developers:

1 : 2-dihydroxyanthracene
1 : 4-dihydroxyanthracene
1 : 2-dihyroxyanthracene monomethyl ester
1 : 4-dihydroxyanthracene monomethyl ester

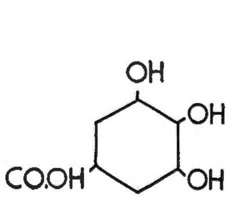
103. Influence of aldehyde, carboxyl and ketone groups

The introduction of an aldehyde group —*CH* = *O* into the benzene ring of the developer has no appreciable influence on the developing power; thus *protocatechuic aldehyde* $C_6H_3(OH)_2CHO$, a hydroquinone derivative, is a normal developer.

The *carboxyl group* —COOH, characteristic of organic acids, has a more pronounced influence. If the carboxyl group is directly substituted in the nucleus in the para position, developing power disappears. Thus gallic acid, a pyrogallol derivative, does not develop, nor does the pyrocatechin derivative, protocatechuic acid $C_6H_3(OH)_2 . COOH$. This is explained by the assumption that the carboxyl group and the hydroxyl group, in the para positions to each other, are transformed into anhydride groups in the presence of alkalis. This results in the loss of a developing function —OH, that remaining in the ortho position being insufficient. By esterifying the carboxyl group this conversion to the anhydride is prevented, and consequently the developing power is not lost; thus ethyl gallate develops whilst gallic acid does not:

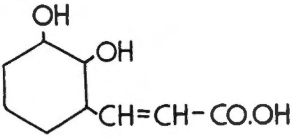


Ethyl gallate
(develops)



Gallic acid
(does not develop)

If the acid group, instead of being directly substituted in the nucleus is separated by an acyclic chain the developing properties are retained. This is the case with caffeic acid, a pyrocatechin derivative.



Caffeic acid
(develops)

The ketone group —CO— has no appreciable effect on the developing power. Thus 1 : 4-dihydroxy-3-acetophenone $(OH)_2 . C_6H_3—CO—CH_3$, 1 : 2 : 3-trihydroxy-5-acetophenone and 1 : 2 : 3-trihydroxy-5-benzophenone $(OH)_3 . C_6H_2—CO—C_6H_5$, are developers.

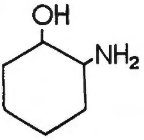
On the other hand, this property disappears in trihydroxybenzophenone if the phenyl radical, C_6H_5, contains a hydroxyl group, for this produces an anhydride conversion effect which destroys one of the OH developing functions.

AMINOPHENOLS

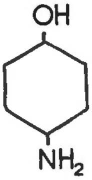
104. Properties

The aminophenols are compounds which contain both an amino $—NH_2$ group and a hydroxyl —OH group. They only have developing properties when the $—NH_2$ and —OH groups are ortho or para to each other. The m-aminophenols(24) generally do not develop. It is, furthermore, necessary that the hydroxyl group is not blocked by an alkyl radical —OR.

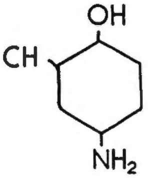
The simplest members of the series are: *o-aminophenol* (hydrochloride) melting point of base 170°C, soluble in water; *p-aminophenol,*(25) hydrochloride or oxalate, whose base melts at 183°C, crystallizes in prisms, soluble in water, soluble with difficulty in alcohol and ether, also called p-amidophenol.



o-aminophenol



p-aminophenol



p-aminocresol

p-Amino-o-cresol or 5-amino-2-hydroxy-toluene as the sulphate is also a developer. It is the p-aminophenol of toluene. The introduction of a methyl $—CH_3$ or ethyl $—C_2H_5$ into the ortho nuclear position relative to the hydroxyl, increases the developing power. Also known are 2-amino-3-hydroxy-toluene and 2-hydroxy-3-amino-1 : 4-dimethylbenzene.(26)

Sulphonic acid groups on the other hand reduce the developing power; thus p-aminophenol-3-sulphonic acid $HSO_3 . ClH_3 . (OH)_2$ is a much weaker developer than the parent compound.

The effect of introducing a *carboxylic acid group* is not as great; o-aminosalicylic acid $NH_2 . C_6N_3(COOH) . (OH)$ is a good developer. Similarly with p-aminosalicylic acid (Hauff's *Neol*) which crystallizes in sublimable needles, soluble with difficulty in cold water.

If an *alcohol group* $—CH_2OH$ is substituted in the 2- position of the nucleus instead of carboxyl, *Edinol, o-hydroxymethyl-p-aminophenol* hydrochloride⁽²⁷⁾ is obtained, a compound readily soluble in water but only slightly in alcohol.

By substituting a phenylamine (anilino) group $—C_6H_4NH_2$ in the 3-position of p-aminophenol, diaminohydroxy-diphenyl⁽²⁸⁾ $(OH)(NH_2) . C_6H_3—$ $—C_6H_4NH_2$ is formed, known as *Diphenal* and related to benzidine. It occurs as long velvety needles melting at 148°C, almost insoluble in cold water, but soluble in alcohol.

2-Hydroxy-3-aminobenzylamine $(OH)(NH_2)C_6H_3CH_2—NH_2$ is another type of aminophenol disclosed by Einthorn.⁽²⁹⁾

The diphenyl nucleus $C_6H_5—C_6H_5$ is capable of providing a large number of developing agents, many of which were used by Trumbull⁽³⁰⁾ (1934), these are the:

p-hydroxyphenyltoluidines $OH . C_6H_4—C_6H_3(CH_3)(NH_2)$
p-hydroxyphenylanisidines $OH . C_6H_4—C_6H_3(OCH_3)(NH_2)$
p-hydroxyphenylphenetidines $OH . C_6H_4—C_6H_3(OC_2H_5)(NH_2)$

R. W. Henn⁽³¹⁾ disclosed that the introduction of a phenyl group in a p-aminophenol reduces the activity by half, whilst with o-aminophenol the activity is considerably increased.

The replacement of the hydroxyl group —OH by a mercapto group —SH destroys the developing properties.

105. Preparation of the aminophenols

The aminophenols are prepared in three different ways:

1. Action of *ammonia* on *dihydroxybenzenes* under pressure in an autoclave:

$$C_6H_4(OH)_2 + NH_3 \rightarrow NH_2C_6H_4OH + H_2O$$

Hydroquinone therefore yields p-aminophenol. The ammonia can be replaced by ammonium chloride.

2. Action of *ammonia* on a *chlorophenol* in the presence of copper sulphate,⁽³²⁾ in an autoclave at 140°C.

$$Cl . C_6H_4OH + 2NH_3 \rightarrow NH_2C_6H_4OH + NH_4Cl$$

The chlorophenols are produced by the controlled reaction of chlorine on phenols.

3. *Reduction of nitrophenols* to aminophenols:

$$NO_2C_6H_4OH + 3H_2 \rightarrow NH_2C_6H_4OH + 2H_2O$$

Many methods of reduction can be used:

With tin and hydrochloric acid; with thiosulphuric acid⁽³³⁾ $H_2S_2O_3$; with powdered zinc and sodium bisulphite⁽³⁴⁾ at 50–50°C; with aluminium amalgam in dilute alcoholic suspension at the boil (the filtrate being subsequently treated with CO_2); with stannous chloride $SnCl_2$ which gives the chlorostannates of the aminophenols which are insoluble in hydrochloric acid, and from which the tin is removed by precipitation with hydrogen sulphide. Nitrophenols can also be reduced electrolytically⁽³⁵⁾ in an alkaline solution using a nickel cathode, or by reduction of nitrophenol vapour with hydrogen using pumice stone impregnated with reduced copper as a catalyst, at a temperature of 265°C.⁽³⁶⁾

The nitrophenol corresponding to the aminophenol can be obtained by nitration of phenol; one part of phenol is treated with a cooled mixture of two parts of nitric acid and four parts of water. The oil which separates as the top layer is washed and then steam distilled. Only the o-nitrophenol passes over, the para compound is in the residue from which it is extracted with boiling water. The lower the temperature of nitration the more of the para isomer is formed.

o-Nitrophenol can also be prepared by heating a mixture of 25 parts phenol, 25 parts ethyl nitrate, $C_2H_5 . NO_3$, 80 parts of water and 160 parts of sulphuric acid at 150°C. After 5 hours the upper layer is removed and distilled.

Other methods of preparing *p-nitrophenol* are: boiling p-nitraniline with concentrated caustic soda; heating p-nitrochlorobenzene $NO_2 . C_6H_4 . Cl$ with sodium carbonate. The product is purified by dissolving in boiling water, neutralizing with carbonate, evaporating, and recrystallizing from hot concentrated hydrochloric acid. M.Pt. 114°C.

Hydroxyalkylaminophenols. The hydroxyalkylaminophenols such as Edinol, hydroxymethyl-p-aminophenol hydrochloride, are prepared like the simple p-aminophenols by introducing a chloroalkyl group such as $—CH_2Cl$ by means of formaldehyde. For example, p-nitrophenol reacts with formaldehyde, H . CHO, in the presence of hydrochloric acid to give chloromethyl-p-*nitro* phenol

$$OH . C_6H_4 . NO_2 + HCHO + HCl \rightarrow OH . C_6H_3(CH_2Cl)(NO_2) + H_2O$$

The chloromethyl compound is hydrolyzed by water to hydroxymethyl-p-*nitro*phenol $OH . C_6H_3(CH_2OH)(NO_2)$.

The latter is converted to hydroxymethyl p-*amino*phenol by the methods already given, for example, with tin and hydrochloric acid.

106. Aminonaphthols

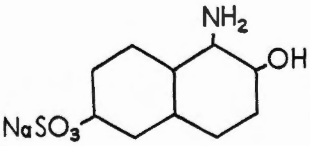
The naphthols, as do the phenols, give aminonaphthol developing agents. It is in all cases essential that the two developing functions are located in the same ring of the naphthalene nucleus.

They are generally used as *sulphonates* in order to increase their solubility; the activity of the parent aminonaphthol is but slightly diminished by the introduction of the sulpho groups. Aminonaphthols are not commercially available.

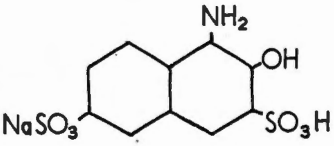
Eikonogen is the sodium salt of 1-amino-2-naphthol-6-sulphonic acid(37) and crystallizes with 2½ molecules of water. It occurs in the form of rhombohedral plates and loses its water of crystallization at 110°C. It is more soluble in warm than cold water, but is very slightly soluble in alcohol and ether. In acid solutions the free sulphonic acid precipitates.

Diogen is similar to the previous compound but differs by having a second free sulphonic acid group in the 3-position; it is therefore 1-amino-2-naphthol-3-sulpho-6-sodium sulphonate. Diogen crystallizes in colourless needles, slightly soluble in cold water, but readily soluble in alkaline sodium sulphite solutions. Other known derivatives include 4-amino-1-hydroxy-3-naphthoic acid (Hauff) 3-amino-2-naphthol-7-sulphonic acid (Andresen), etc.

The *preparation of the aminonaphthols* is similar to the aminophenols; methylamine can be reacted with 1′ : 2-dihydroxynaphthalene under pressure. Another method is to react sodamide with a naphthol sulphonic acid



Eikonogen



Diogen

The more common method is to reduce the corresponding azo derivative. Thus, diazotized aniline $C_6H_5N = NCl$ is coupled with Schaeffer's acid or β-naphthol-6-sulphonic acid to form benzene-azo-β-naphthol-6-sulphonic acid. The latter is reduced with stannous chloride to give 1-amino-2-naphthol-6-sulphonic acid or Eikonogen, by losing a molecule of aniline

$$C_6H_5N = N\text{—}C_{10}H_5(OH)(SO_3H) + 2H_2$$
$$\rightarrow C_{10}H_5(NH_2)(OH)(SO_3H) + C_6H_5NH_2$$

If the same procedure is followed using β-naphthol-3 : 6-disulphonic acid, 1-amino-2-naphthol-3 : 6-disulphonic acid is produced, whose sodium salt is Diogen.

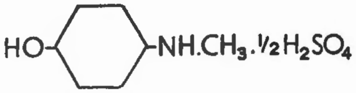
N-SUBSTITUTED AMINOPHENOLS

So far only the simple aminophenols having the amino group intact have been considered. It is possible, though, to replace one of the hydrogen atoms of this group with an alkyl radical, an alkyl carboxylic or sulphonic acid, a phenyl radical, etc. Although any substitution of the hydroxyl group destroys the developing power,(38) substitution in the amino group on the contrary, increases this power.

The simplest of the series of N-substituted aminophenols are the *methyl-p-aminophenols*.

107. Metol or p-methylaminophenol

Disclosed by Hauff,⁽³⁹⁾ p-methylaminophenol (*sulphate*) has the structure:



it is known under the trade names *Metol*, *Genol*, *Elon*, *Planetol*, etc.

It occurs as a white powder, of needle or prismatic crystals, and decomposes on heating. Metol is readily soluble in water, but only with difficulty in alcohol and ether. The free base is slightly soluble in cold water and very soluble in alcohol and ether, M.Pt. 87°C.

Also used are p-dimethylaminophenol $OH.C_6H_4N(CH_3)_2$ oxalate, p-benzylaminophenol $OH.C_6H_4NH.CH_2C_6H_5$ hydrochloride, and o-methylaminophenol hydrochloride.

Ortol consisted of a mixture of o-methylaminophenol and hydroquinone.

Dimethyl-o-aminophenol, corresponding to pyrogallol, was perhaps the essential constituent of *Pyrophane* prepared by condensing pyrogallol with dimethylamine $NH(CH_3)_2$. It developed without alkali.

From toluene, $C_6H_5CH_3$, many interesting developers are derived.

$$\left.\begin{array}{l}\text{6-methylamino-3-hydroxytoluene}\\ \text{2-methylamino-3-hydroxytoluene}\\ \text{3-methylamino-2-hydroxytoluene}\end{array}\right\} CH_3NH.C_6H_3(CH_3)(OH)$$

The methyl group can be replaced by an alcohol or acid group, giving for example, 3-methylamino-2-hydroxybenzoic acid $CH_3.NH.C_6H_3(COOH)(OH)$ derived from salicylic acid.

The aminophenol nucleus can be halogenated; by doing so in this case the 4- or 5-chloro-2-methylaminophenol (Hauff)⁽⁴⁰⁾ and the 4 : 6-dichloro-2-methylaminophenol (Schneider and Williams)⁽⁴¹⁾ are obtained.

It can also be substituted by an alkoxy group R—O—, as in 5-methoxy-2-methylaminophenol⁽⁴²⁾ $CH_3O.C_6H_3(OH)(NH.CH_3)$.

Reddelein and Muller⁽⁴³⁾ used developers in which the alkyl substituent of the amino group is further substituted by an alcoholic hydroxyl —OH group:

$$\left.\begin{array}{l}\text{p-hydroxyethyl-aminophenol}\\ \text{o-hydroxyethyl-aminophenol}\end{array}\right\} OH.C_2H_4.NH.C_6H_4OH$$

3-methyl-4-hydroxethylaminophenol $OH.C_2H_4.NH.C_6H_3(OH)(CH_3)$
2-chloro-4-hydroxyethylaminophenol $OH.C_2H_4.NH.C_6H_3(OH)(Cl)$

The most interesting are the *p-hydroxyethylaminophenol*, almost as powerful as metol, but less easily oxidized and more soluble, and *o-hydroxyethylaminophenol*, a fine-grain developer known by the name *Atomal* (Agfa), and prepared by reacting ethylene oxide with o-aminophenol.

Diphenylamine gives the following derivatives:

4-Hydroxydiphenylamine $OH.C_6H_4.NH.C_6H_5$ (Hauff 1891) and 4 : 4-dihydroxydiphenylamine $OH.C_6H_4.NH.C_6H_4.OH$ (Schering 1907).

108. Glycin or *p-hydroxyphenylglycin*, $OH.C_6H_4.NH.CH_2COOH$ p-

aminophenol derivative in which an amino hydrogen atom has been replaced by the alkyl radical of glycolic acid $HO.CH_2.COOH$, acid-alcohol. Glycin disclosed by Bogisch in 1891, is in the form of mica-like plates and is decomposed on heating. It is slightly soluble in water and alcohol, but dissolves in alkaline sulphite solutions (forming the sodium salt of the acid radical). It is a slow but powerful developer, very resistant to aerial oxidation and producing no fog.

By replacing the carboxylic acid group of glycin with sulphonic acid $—SO_3H$, *Eurekine* was obtained with the formula $OH.C_6H_4.NH.CH_2SO_3H$, and was used as the sodium salt. This compound is ready soluble in cold water and warm alcohol, crystallizes in long needles and decomposes on heating.

The substitution of a *phenyl group* in the amino group diminishes the developing energy, but if the phenyl group contains a $—NH_2$ or $—OH$ group the energy is restored and surpasses that of the parent substance. This is the reason why the following are active developers:

p-dihydroxydiphenylamine $OH.C_6H_4.NH.C_6H_4.OH$
p-aminohydroxydiphenylamine $OH.C_6H_4.NH.C_6H_4.NH_2$

With the *aminonaphthols* the following developers are obtained:

4-methylamino-1-naphthol-6-sulphonic acid, 1-amino-4-hydroxy-2-naphthoic acid (Hauff 1891), 3- or *4-phenyl-amino-1-naphthol* $C_6H_5NH.C_{10}H_6OH$ (Trumbull 1934),⁽⁴⁴⁾ *4-acetamino-1 : 2-dihydroxynaphthalene* $CH_3.CO.NH.C_{10}H_5(OH)_2$, *2 acetamino-3-chloro-1 : 4-dihydroxynaphthalene, 2 : 8-di-acetamino-1 : 4-dihydroxynaphthalene* (Schinzel 1939).⁽⁴⁵⁾

109. Preparation of N-substituted aminophenols (Metol and others)

The N-substituted aminophenols can be obtained by reacting an alkylamine $R.NH_2$ or R_2NH with a dihydroxybenzene at 200°C under pressure; thus metol is prepared by reacting methylamine CH_3NH_2 on hydroquinone.⁽⁴⁶⁾

$$C_6H_4(OH)_2 + CH_3NH_2 \rightarrow OH.C_6H_4.NH.CH_3 + H_2O$$

At the Eastman Kodak plant at Rochester, a 40% aqueous solution of methylamine is reacted with hydroquinone for 4 hours in an autoclave at 170–180°C in the presence of sodium bisulphite. Caustic soda is then added to give the sodium salt. By treating with hydrochloric acid, crude metol is obtained. By redissolving in a basic medium, the base can be recrystallized. It is then converted to the sulphate.⁽⁴⁶ᵇ⁾

Similarly dimethylamine $(CH_3)_2NH$, and mono- and diethylamine can be reacted with the o- or p-dihydroxybenzenes.

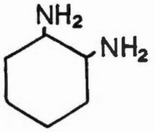
Metol can also be prepared by methylation of p-aminophenol $OH . C_6H_4 . NH_2$ by means of methyl sulphate. The quantity of the latter must not exceed the theoretical amount otherwise some dimethyl derivative will be formed. The p-aminophenol sulphate which is formed at the same time, is separated by acidifying the solution with a little acetic acid and then precipitating with benzaldehyde, the metol remaining in solution. The solution is then concentrated to give needle crystals which are then recrystallized.

The derivatives of *p-hydroxyphenylglycin* are prepared by fusing chloracetic or bromacetic acid with the corresponding aminophenol, in the presence of an alkali. By thermal decomposition (145°C) in solvents such as ketones(47) or a mixture of cyclohexane and chlorobenzene (Agfa)(48) metol base, which is then converted to the sulphate, is produced industrially.

DIAMINES

110. Simple diamines

o- and p-dinitrobenzene $C_6H_4(NO_2)_2$ give, on reduction, the two diamines, *o-phenylenediamine* and *p-phenylenediamine*, both of which have developing properties.



o-phenylenediamine

p-phenylenediamine

In practice, p-phenylenediamine is mostly used, as the hydrochloride. This is readily soluble in water, but slightly soluble in alcohol. The phenylenediamines are strong bases. They are oxidized to quinonoid compounds.

Preparation: the phenylenediamines are prepared by reduction of nitrobenzene(49) or nitraniline(50) $NO_2 . C_6H_4 . NH_2$.

The latter are obtained by nitration of acetanilide $C_6H_5NH . CO . CH_3$, in sulphuric acid solution for the para derivative, or in acetic acid for the ortho compound. The separation of the three nitranilines o-, m-, and p- is carried out by fractional neutralization in the order o-, m-, then para.

The *toluylene diamines* $CH_3C_6H_3(NH_2)_2$ derivatives of toluene $C_6H_5CH_3$ are obtained in a similar way.

A different procedure is to treat p-chloronitrobenzene with ammonia in alcoholic solution, the product being readily reduced to p-phenylenediamine.

In the naphthalene series, three diamines were disclosed by Andresen (1889): *1 : 2-naphthalenediamine*, *2 : 3-naphthalenediamine* and *1 : 4-naphthalenediamine* sulphonated in the 6- or 7- position.

111. Substituted diamines

The alkyl derivatives of the p-phenylenediamines are good developers especially the unsymmetrical *N-dimethyl* and *N-diethyl-p-phenylenediamines* $R_2N \cdot C_6H_4NH_2$, also called dimethyl and diethylaminoanilines. *Colour development* is based on the use of these compounds. They are prepared by reducing the *p-nitroso* or *p-nitrodialkylanilines.*(51) The alkylanilines which are to be nitrated or nitrosated are themselves prepared by alkylation of aniline with an alkyl chloride, such as methyl chloride, or an alkyl sulphate, or by reacting aniline hydrochloride with an alcohol.

The splitting of *dialkylaminoazobenzenes* $R_2N \cdot C_6H_4N = NC_6H_4NR_2$ also produces dialkylaminoanilines.

The number of substituted p-phenylenediamines which possess developing properties is very great; the *methyl, dimethyl, ethyl, diethyl, butyl, 2-methyl-N-diethyl* derivatives were used by Hauff(52) in 1891. Fischer(53) disclosed the *dipropyl* and *3-methyl-N-diethyl* derivatives, and Kodak,(54) *diethylamino-o-phenylenediamine, 3-bromo-p-phenylenediamine* and supplementary alkoxy substituents as in *2-amino-5-diethylaminophenetole* $C_2H_5O \cdot C_6H_3(NH_2)N(C_2H_5)_2$. Mention must also be made of the p-phenylenediamines with acid substituents in one of the NH_2 groups: 4-amino-N-methylaminobenzene-ω-sulphonic acid; 4-amino-N-benzylaminobenzene-4′-sulphonic acid;(55) and *4-aminobenzene-iminodiacetic* acid(56) $NH_2 \cdot C_6H_4N : (CH_2COOH)_2$.

The alkylaminoanilines with the structure $NH_2 \cdot C_6H_4 \cdot NHRY$ where Y is a sulphone derivative such as $—SO_2NH_2$, $—SO_2NHR$ or $—NH—SO_2 \cdot R$ are more soluble than the ordinary alkyl derivatives and are more suitable for fine-grain development.

Such is N-β-methylsulphonamidoethyl-4-aminoaniline(57)

$$NH_2—C_6H_4—NH \cdot CH_2 \cdot CH_2NH \cdot SO_2 \cdot CH_3$$

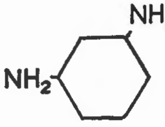
These sulphone compounds are prepared by reacting a primary amine with an alkyl sulphonyl chloride or a chlorosulphonic ester. F.P. 1,080,501 discloses the use of sulphobenzoic anhydrides.

If the benzene nucleus of a substituted p-phenylene diamine is replaced by a naphthalene nucleus, the *alkyl-naphthylenediamines* are produced, the simplest of which, disclosed by Hauff(58) *ass. diethyl (or dimethyl)-1 : 4-naphthylenediamine* $(C_2H_5)_2N \cdot C_{10}H_6NH_2$, monomethyl-1 : 4-naphthylenediamine, etc.

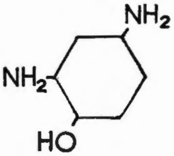
DIAMINOPHENOLS

112. Diaminophenols

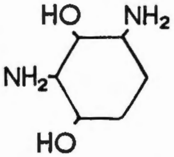
These are used as the hydrochloride (Amidol).(59) Diaminophenol can be considered as the o-hydroxy compound of m-phenylenediamine (non-developer). It is an energetic developer but is rather unstable. It is preserved by adding boric, lactic or glycolic acid.



m-phenylene diamine



diaminophenol



diaminoresorcinol

diaminocresol

By introducing a second —OH group in the diaminophenol nucleus, *diaminoresorcinol* is obtained in which the OH and NH_2 groups are each in the meta position to each other (non-developing position) but which together give a powerful developer. *Diaminocresol*⁽⁶⁰⁾ $OH . C_6H_2(CH_3)(NH_2)_2$ has also been used.

Diaminophenol hydrochloride is found as colourless needles which decompose on heating. It is very soluble in water, slightly soluble in alcohol. It has already been seen that diaminophenol is used without alkali.

Among the other diaminophenols disclosed by various authors, are the following: *4-hydroxyethylamino-2-aminophenol* $OH . CH_2CH_2NH . C_6H_3(NH_2)(OH)$, *2-hydroxyethylamino-4-aminophenol* and *4-hydroxyethylamino-2-acetaminophenol* (Reddelein and Muller);⁽⁶¹⁾ *5-dimethylamino-2-methylaminophenol* $(CH_3)_2N . C_6H_3(CH_3NH)(OH)$, *4-amino-6-methyl-2-methylaminophenol* and *6-amino-4-methyl-2-methylaminophenol* (Schneider and Wilmanus).⁽⁶²⁾

The following derivatives of diphenylamine⁽⁶³⁾ $C_6H_5 . NH . C_6H_5$ have been suggested: *4-hydroxyphenyl-4-toluidine* $OH . C_6H_4 . NH . C_6H_4 . CH_3$, *4-hydroxyphenylanisidine* and *phenetidine* $OH . C_6H_4 . NH . C_6H_4 . OR$, 4-amino-4-hydroxydiphenylamine-2-sulphonic acid $(SO_3H)(NH_2)C_6H_3 . NH . C_6H_4 . OH$ and 4-hydroxy-4-dimethylamino-diphenylamine.

113. Preparation of diaminophenols

The aminophenols are prepared by reducing the corresponding *dinitrophenols*. To do this, a mixture of red phosphorus and iodine in aqueous suspension can be used⁽⁶⁴⁾ or tin and hydrochloric acid:

1 : 2 : 4-dinitrophenol is reduced by four times its weight of tin and twelve parts of hydrochloric acid giving the stannic chloride double salt, from which the base can be separated by treatment with soda.

A third method is the elctrolytic reduction of one part of m-nitraniline $NO_2 . C_6H_4 . NH_2$ or m-dinitrobenzene $C_6H_4 . (NO_2)_2$ in 7 parts of concentrated sulphuric acid.

The base crystallizes in needles M.Pt. 78–80°C, and is converted to the hydrochloride.

Diaminoresorcinol is prepared by reducing dinitroresorcinol $(NO_2)_2C_6H_2(OH)_2$ with tin in hydrochloric acid. The nitro derivative itself is obtained by treating a 10% ethereal solution of resorcinol with nitrous fumes.

In the *naphthalene* series, the most common members are: *1 : 2-diamino-8-naphthol-3 : 6-disulphonic acid* (Andresen 1889), *2 : 8-diamino-1-naphthol-3 : 6-disulphonic acid*, *2 : 8-diamino-1-naphthol-3 : 5-disulphonic acid*, and *2 : 8-diamino-1-naphthol-5-sulphonic acid.*(65)

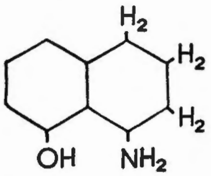
114. Polyamines *1 : 2 : 4-Triaminobenzene* is a developer, and also symmetrical *triaminophenol* hydrochloride known as *Reducine.*

From diphenylamine, $C_6H_5 . NH . C_6H_5$, the following are obtained: *2 : 4-diaminodiphenylamine* $(NH_2)_2C_6H_3 . NH . C_6H_5$ and *2 : 4 : 4′-triaminodiphenylamine* $(NH_2)_2 . C_6H_3 . NH . C_6H_4NH_2$.

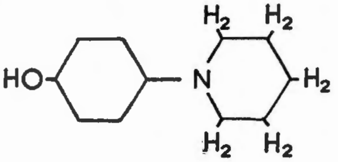
HETEROCYCLIC BASES

115. The Heterocyclic bases(66) are capable of providing a large number of developing agents. Their practical use is always limited by their price, which is considerably more than the simpler benzene derivatives, with no compensating advantages. The following compounds have been suggested:

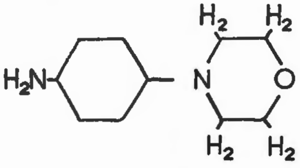
o- and p-dihydroxyquinolines (Lumiere and Seyewetz 1892).
o-hydroxyalkylhydroquinolines (Lembach and Schleicher 1895).(67)
dihydroxytetrahydroquinoline (A.G.F.A. 1896).(68)
o-hydroxyalkylhydroquinolines (A.G.F.A. 1896).
o-diaminoquinoline (Lumiere and Seyewetz 1892).(69)
8-methoxy-6-amino-1 : 2 : 3 : 4-tetrahydroquinoline (I.G.F. 1938).
6-amino-1 : 2 : 3 : 4-tetrahydroquinoline (I.F.F. 1938).
8-methoxy-6-amino-1 : 2 : 3 : 4-tetrahydroquinaldine (I.G.F. 1938).
4-hydroxy-N-phenylpyrrole (Reed 1933).(70)
4-hydroxy-N-phenyltetrahydropyrrole (Reed 1933).
4-amino-N-phenylpiperidine (Fischer 1914).(71)
4-amino-N-phenylpiperazine (Fischer 1914).
1-phenyl-3-methyl-4-amino-5-pyrazolone (I.G.F. 1937).(72)
1-phenyl-2 : 3-dimethyl-4-sulphamino-5-pyrazolone (Scheitlin 1909).(73)
2 : 6-dihydroxy-4 : 5-diamino-pyrimidine (I.G.F. 1938).(74)
6-hydroxy-2 : 4 : 5-triamino-pyrimidine (I.G.F. 1938).
2 : 4 : 5 : 6-tetraminopyrimidine (I.G.F. 1938).
6-amino-2 : 4 : 5-trihydroxypyrimidine (I.G.F. 1938).
5-aminodihydro-2-methylindole (I.G.F. 1938).
3-amino-4-oxo-2-iminotetrahydrothiophene (I.G.F. 1937).(75)
6-amino benzothiazoline (I.G.F. 1938).
amino and hydroxymorpholines (Reed 1933).(76)



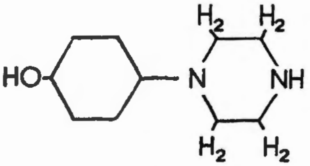
8-hydroxy-1 : 2 : 3 : 4-tetrahydroquinoline



p-hydroxy-N-phenyl piperidine



p-amino-N-phenyl morpholine

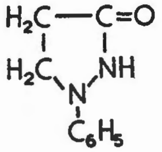


p-hydroxy-N-phenyl piperazine

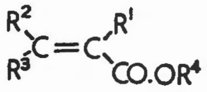
8-Hydroxy-1 : 2 : 3 : 4-tetrahydroquinoline is known as *Tetra-Q* (Dillon and Searle: U.S.P. 2,596,978) (1940). *6-Amino-1 : 2 : 3 : 4-tetrahydroaldine* gives fine-grain images.

116. Phenidone

Phenidone is 1-phenyl-3-pyrazolidone



which was synthesized in 1890.(77) It was not proposed as a developer until 1940, by Kendall, and was used after a new and simpler method of preparation had been worked out: reaction of a hydrazine compound RNH—NH$_2$



with an ester or an acrylic nitrile, in the presence of an alkaline catalyst.(77b)

Phenidone occurs as colourless crystals slightly soluble in cold water but very soluble in solutions which are not neutral. By oxidation in alkaline solution, inactive 1-phenyl-3-pyrazolone is produced.(78)

Phenidone can be used with hydroquinone. Maximum rate of development is obtained using 7% of phenidone with respect to the hydroquinone. Fog is produced with high-speed emulsions, but can be avoided by including an antifoggant (e.g. 0·15 g per litre benzotriazole).

117. Combined developers

A developing agent with an acid function (polyhydroxybenzene) is able to combine chemically with a developing agent containing a basic function, aminophenol or p-phenylenediamine to produce a neutral substance which will *develop without alkali*. The hydroxyl function is neutralized by the amino group. The principal combinations which are used in practice are:

Metoquinone: combination of metol and hydroquinone. White powder slightly soluble in cold water, soluble in alcohol.

Chloranol: combination of metol and chlorhydroquinone. More soluble than metoquinone. Resistant to aerial oxidation, keeps well in sulphite solution.

Hydramine: equimolecular combination of p-phenylenediamine and hydroquinone. Was found as pellets more soluble in warm than cold water, soluble in alcohol.

A commercial product is available which is a combination of p-phenylenediamine and pyrocatechin—*Meritol*—and is used as a fine-grain developer.

The solubility of these compounds is notably greater in alkaline solutions.

118. Aliphatic developers

The developing agents of the aliphatic (non-cyclic) type are mainly derived from the *aldols* and the *hydroxyacids*.

The *aldehydes* are reducers. They can be used as their *bisulphite compounds* for development in alkaline solution.

The *sugars*, polyhydric alcohols with an aldehyde or ketone group also develop in alkaline solution. M. Abribat(79) successfully used *glucose*, *mannose*, *arbinose*, *xylose*, *lactose*, *galactose*, and *dihydroxyacetone* at a pH varying from 6 to 11. Thus with glucose (previously heated in alkali with the air excluded) the redox potential at pH 7·2 is -200 mV and -420 mV at pH 11.

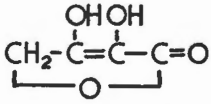
The *aldols* and hydroxy acids having an *ethylene linkage* are energetic developers; *Reducton* disclosed by von Euler(80) had the formula

$$\mathrm{HO\,.\,CH = C\,.\,OH{-}CH : O}$$

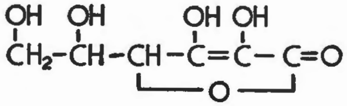
It is an aldehyde and ethylene-dihydric alcohol and is used with carbonate and sulphite.

The *hydroxyacids* HO—R—CO . OH give, when a molecule of water is removed, inner esters called lactones in which the hydroxy and carboxyl groups are linked by an atom of oxygen forming, therefore, a closed ring. Now the *ethylenic lactones*, derivatives of the hydroxy acids with a double bond are powerful developers. Examples:

Lactone of hydroxytetronic acid (Michiel)(81) and the lactone of *ascorbic acid*, isomer of vitamin C.



Lactone of hydroxy-tetronic acid



Lactone of ascorbic acid

The developing and reducing properties are due to the presence of the two hydroxyl groups situated on each side of a double bond, and to the presence of the lactonic chain which some authors consider as a heterocyclic nucleus.

Another interesting developing agent is *ethyl aminoacetoacetate*(82) $NH_2 . CH_2 . CO . CH_2 . CO . OC_2H_5$.

Ascorbic acid developers see T. H. James' paper: *Jl. Am. Chem. Soc.*, Jan. 1944, p. 91.

1. According to M. Abribat the exceptions to the redox potential rule are explained only by too low a solubility, or rather, by too low a concentration of developing agent around the grains.
2. The hydroxylamine sulphonic acids have been advocated as development regulators and solarization preventers. F.P. 600,532.
3. *Phot. Soc. Amer. Jl.*, Feb. 1944, 136–137.
4. U.R.S.S. 32,493 (1933).
5. U.S.P. 2,006,324 (1935).
6. U.S.P. 1,998,177 (1934).
7. U.S.P. 1,908,817 (1933).
8. *Ind. and Eng. Chem.*, 1952, 1730–1735.
9. B.P. 450,572 (1934); *Bull. Soc. Fr. Chim.*, 1923, 449–459.
10. *Jl. Soc. Sci. Phot., Japan*, Aug. 1951, 11–16 and *Sci. Ind. Phot.*, 1952, 191.
11. U.S.P. 1,934,632.
12. Fasciati A.: *Thesis*, Zurich 1945, 55 pages.
13. *Das Lichtbild*, Aus. 12-XI-1935, p. 173, and B.P. 498,869.
14. Buchta: *Ber.*, 1937, **70**, 2339.
15. Kumetat K.: *Zeits. Wiss. Phot.*, Oct. 1948, 113–119.
16. Guaiacol is pyrocatechol-monomethyl-ether $OH . C_6H_4 . OCH_3$.
17. Rzymkowski J.: *Die Pharmazie*, Aug., 1948, 346–349.
18. U.S.P. 2,017,295 (1933).
19. U.S.P. 2,037,742 (1934).
20. B.P. 498,869.
21. B.P. 5,207.
22. Homolka, 1914.
23. Canadian P. 380,587 (1939).
24. 2 : 4 : 6-trimethyl-m-aminophenol, however, was disclosed by Homolka, in 1914, as a developer.
25. Disclosed by Andresen in 1888.
26. Hauff: B. P. 15,434 (1891).
27. Schering: F.B. 382, 367 (1907).
28. B.P. 20,690 (1891).
29. G.P. 167,572 (1905).
30. U.S.P. 1,969,243.
31. Henn R. W.: *Phot. Soc. Amer. Jl.*, Nov. 1953, 149.
32. Diepolder: *Ber.*, 1904, **42,** 2,920—F.B. 397,524 (1908).
33. Goldberg: *Oesterrichen Chem. Ztg.*, 1900, **3,** 470.
34. Sidgwick and Callow: *J.C.S.*, 1924, **125,** 522.
35. Auwers and Eisenlohr: *Ann.*, 1909, **369,** 223.
36. Brown and Carrick: *J.A.C.S.*, 1919, **41,** 434.
37. Disclosed by Meldola in 1881.
38. Phenylhydrozine $C_6H_5 . NH . NH_2$ and phenylhydroxylamine $C_6H_5 . NH . OH$ although possessing no phenolic function are developers.
39. B.P. 15,434 (1891).
40. B.P. 27,931 (1896).

41. U.S.P. 2,060,594 (1936).
42. Schneider and Williams: U.S.P. 2,060,595 (1936).
43. U.S.P. 1,758,892 and 1,799,568 (1930 and 1931).
44. See also Harger: *J.A.C.S.*, 1919, **41,** 270.
45. U.S.P. 1,969,243.
46. B.P. 498,869 and U.S.P. 2,286,796.
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47. Norman S.: U.S.P. 2,101,750 (1935).
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49. Rinne and Zincke: *Ber.*, 1874, **7,** 869. Mignonac: *Bull. Soc. Fr. Chim.*, 1910(**4**), **7,** 154. Martin: *Organic Syntheses*, 1939, **29,** 70.
50. Hofmann: *Proc. Roy. Soc.*, 1863, **12,** 639. Brown and Carrick: *J.A.C.S.*, 1919, **41,** 436.
51. Wurster: *Ber.*, 1879, **12,** 522–528. Meyer: *Ber.*, 1903, **36,** 2978.
52. B.P. 15,434.
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Chapter X

DEVELOPER ANALYSIS

119. Importance of analysis

The properties of a developer depend on the relative concentrations of its constituents. We know that these proportions are continually changing during the useful life of the developer, not only during development, but also when not in use, due to aerial oxidation.

Constant estimation of all the compounds in the developer is necessary to maintain constant activity when continuous machines are used. The analyses are first necessary to determine the constitution of the developer, then to control the smooth running of the process, and detect accidental changes.

The frequency of analysis is obviously dependent on the amount of work done in the bath. Those used for continuous negative development must be analysed every day. The bromide should even be estimated every four hours in the case of positive films which pass through in large quantities. Finally, the pH must be measured frequently—every two hours for example.

It should be emphasized that developer analysis requires extreme care; and if the results are required as quickly as possible, the operations must be suitably organized with adequate apparatus and personnel. Otherwise the figures have no real value, for they will not correspond to the present condition of the developer.

Some methods enable a rough estimation of the state of the bath to be made quickly, but the results obtained are not accurate. These are principally the methylene blue test and the ferricyanide test.

Methylene blue test. 20 cc of a 1 : 15,000 solution of methylene blue in a test tube are shaken with 3 cc of developer. Normally, a fresh developer will declorize the dye in about 3 minutes, a used developer in 15–20 minutes, and two hours or more if the bath is exhausted.

Ferricyanide test (1). A standard ferricyanide solution is added to a 5 cc sample of developer diluted with 10 cc water. The test sample turns yellow, then orange and finally red-brown after a few minutes. The addition is stopped at the orange tint: 4 mols. of ferricyanide is equivalent to 1 mol. of metol or hydroquinone. The orange tint is generally very difficult to differentiate, which takes away all the accuracy of the test.

120. Selective extraction of hydroquinone and metol from developers

As metol-hydroquinone developers are the most widely used, these two developing agents are the ones most frequently estimated.

The estimation of developing agents includes a preliminary stage: the extraction of the pure substance. The direct titration of a used developer does not distinguish between the oxidized and the non-oxidized product. To estimate, for example, quinone in the presence of hydroquinone, a special technique based on the formation of hydroquinone-α-dithiosulphuric acid must be used, disclosed by Rzymkowski, which can be removed with an ion exchanger, Wofatito, M.(2)

The extraction of the organic developing agents contained in a developer can be carried out with an *organic solvent* which has no action on the corresponding quinones. At the same time, the hydroquinone and metol must be separated. This is made possible by the fact that metol remains in aqueous solution if the pH is far removed from 8, which enables the hydroquinone to be extracted first, in acid solution, then the metol, after neutralizing.

Atkinson and Shaner's method.(3) A 5 cc sample is put into the extraction apparatus (made up of a dropping funnel attached to a U-tube whose end is bent down again, and which has a restricting capillary tube at its lower bend). A few drops of 0·04% thymol blue in aqueous alcohol is added, followed by hydrochloric acid, until the solution is red (pH 2). Then sodium chloride is added until a slight excess remains, in order to reduce the solubility of the hydroquinone. The funnel tap is opened, and pure *ether* is run through at such a rate that the developer is not carried through the tube. After 100 cc of ether has passed into the receiver, water is poured into the funnel to recover the remaining solvent. The ether extract is transferred to a 500 cc flask of thick glass containing 200 cc hot water and 1 cc of concentrated hydrochloric acid; the ether is removed by evacuating. The acid aqueous solution obtained in this way is used for estimating the hydroquinone.

A second sample of developer is taken and sufficient hydrochloric acid is added to adjust the pH to 8 (beginning of yellow colour of thymol blue). The metol and hydroquinone are then extracted as above, and the aqueous solution of the two developers is titrated.

In the absence of the special extraction apparatus, an ordinary separating funnel can be used, using a small portion of the ether for the first extract, running off the aqueous layer into another funnel and again extracting with a fresh portion of ether. Three operations are necessary for total extraction. The ether extracts are combined. In this case it is advisable to use larger samples of the developer.

Stott's method.(4) 25 cc of developer is put into a 150 cc separating funnel, and a few drops of thymol blue is added. 25 cc of 50% sulphuric acid is added until the solution turns red, and 1 cc extra is added. The solution is then shaken vigorously with 50 cc of *ethyl acetate* and left. The aqueous layer is transferred to a second funnel and the operation is repeated. The two extracts are combined, and contain the hydroquinone, whilst the aqueous layer is retained to extract the metol. The sulphur dioxide in the ethyl acetate resulting from the acidification of the sulphite is neutralized by shaking with 25 cc of a solution containing 100 g per litre anhydrous sulphite, 10 g boric acid and 1 g caustic potash. The aqueous layer which separates is discarded, and the ethyl acetate extract is analysed.

The aqueous layer which still contains the metol is in turn poured into a separating funnel, thymol blue added, followed by 2N caustic until a blue colour is obtained ($pH > 9{\cdot}6$). Three successive extractions are made with 25, 15 and 10 cc of ethyl acetate. The three extracts are combined and are then ready for metol estimation.

Stott's operating method has been slightly modified by Levenson(5) to reduce the causes of errors: thymol blue is replaced by phenolphthalein and in the metol extraction, after neutralizing with caustic to a pink colour, it is decolorized again with sodium bicarbonate, following a suggestion by Gloyns.

121. Non-selective extraction of metol and hydroquinone

Non-selective extraction has the advantage of enabling both developers to be estimated in the same extract. As the solvent used is insoluble in salt-containing solutions, but soluble in pure water, it is unnecessary to evaporate after extraction.

Baumbach's method.(6) 25 cc of developer is put into a 250 cc separating funnel, and neutralized with hydrochloric acid until yellow to thymol blue. 15 g of potassium bromide and 25 cc of *methyl acetate* are then added and the mixture is shaken for 3 minutes. After leaving for at least 3 minutes the aqueous layer is run off and again extracted with 25 cc of methyl acetate. The aqueous layer is then discarded and the two acetate extracts are mixed. The organic solution is dried by being passed several times through layers of drying agent, then 150 cc water is added and the solution is titrated.

Shaner and Sparks method.(7) Instead of extracting with ordinary separating funnels, the Atkinson and Shaner extractor is used, whilst the more readily obtained *methyl ethyl ketone* (M.E.K.) is used as the solvent. The course of the operation is similar to Baumbach's: 10 cc of developer is put into the extractor with 0·5 cc of 0·04% thymol blue and enough 50% sulphuric acid to turn the indicator yellow. The solution is saturated with powdered potassium bromide, and 50 cc of M.E.K. is run through and collected at the exit tube in a graduated vessel.

Brunner, Means and Zappert's method.(8) Baumbach's method has been modified as follows: 25 cc of developer is placed in a separating funnel. Two drops of thymol blue is added, then 50% sulphuric acid until the solution is yellow (pH 8–8·5). 12 g potassium bromide and 25 cc *isopropyl acetate* are then added, and the funnel is shaken for 3 minutes, and the separated aqueous phase is run off into a 50 cc beaker (the solvent must fill the tube in the tap). The solvent is then run into a dry beaker, and the aqueous layer is returned to the funnel and again extracted with 25 cc isopropyl acetate (which has been used to rinse the beaker). The first solvent extract is transferred successively into three dry beakers, then into a fourth 400 cc one. The empty beakers are rinsed with the second extract, which is finally added to the first.

122. Estimation of hydroquinone in the separated extract

There are two methods of estimating the hydroquinone extracted from a developer: by titration with iodine or with ceric salts.

The *iodometric method* is to oxidize the hydroquinone with iodine solution in the presence of bicarbonate and starch solution which turns blue with excess iodine. The blue coloration must persist for one minute. It is more accurate to add excess iodine and back titrate with standard thiosulphate in the presence of an acetic acid–sodium acetate buffer. The blue colour is less persistent if the developer extract contains less than 0·02 M.

Bogdanof's procedure.(9) Twenty cc 2 M sodium acetate solution, 0·6 cc 4 M acetic acid and then the developer extract are added to 25 cc standardized iodine solution. After adding 1 cc of starch solution, the excess iodine is back-titrated with thiosulphate. If the hydroquinone is extracted from 25 cc of developer with treatment of the ether extract with 50 cc 2 M sulphuric acid, the final aqueous solution is made up to 200 cc, neutralized to methyl orange and 25 cc is taken for titration.

Atkinson and Shaner's procedure. The hydroquinone extract obtained by one of the methods already described is titrated with 0·01 M iodine in the presence of starch until there is a blue colour. The sulphur dioxide is neutralized in this way, but the hydroquinone does not react in acid solution. One hundred cc of a buffer containing 3% disodium phosphate and 1% sodium metaborate (pH 7·5) is added. The solution is then titrated with 0·01 N iodine until a persistent blue colour is obtained, or excess iodine is added and back-titrated with standardized thiosulphate.

Cerium colorimetric estimation. Sasai and Mizusawa.(9b) After extracting the metol and hydroquinone at pH 8·4, sulphuric acid and diphenylamine are added, and the solution is titrated with 0·05 N *ceric sulphate* until a blue-violet colour is obtained. A second extraction at pH 2 only removes the hydroquinone. Formalin is added to prevent the SO_2 from reacting, and the titration is carried out as above. The solvent used is ethyl acetate.

Cerium potentiometric estimation of hydroquinone. The estimation of hydroquinone with ceric sulphate (oxidizing agent) using potentiometric control was disclosed in 1935 by Furman and Valas, then recommended by Bogdanof: the developer extract in aqueous acid solution (50 cc of M H_2SO_4 to 25 cc developer) is freed from ether, and a further 150 cc of acid is added before titrating with a ceric sulphate solution.

The course of the reaction is followed with a pH meter fitted with a platinum or glass electrode and a calomel helf cell. The curve of the potential against the number of cc of reagent is plotted, whose inflection point shows the neutralization point. Agitation must be vigorous during the whole operation.

Stott's potentiometric method. Ten cc of the ethyl acetate hydroquinone extract prepared by the same writer's method (para. 120) is slowly added to 200 cc water acidified with 2 cc of 50% sulphuric acid. The mixture is vigorously shaken to dissolve the solvent, then the electrodes are introduced and titration is carried out with 0·01 N ceric sulphate. This is prepared from a 0·1 N stock solution (in dilute H_2SO_4) diluted before use with water containing 5 cc of 50% H_2SO_4 per litre. Temperature control is unnecessary, especially if comparison is made with a known amount of pure dried hydroquinone. The weight in g per litre of the hydroquinone is given by 0·22 × volume in cc of ceric solution, or more accurately $H = 0{\cdot}22\ (x - 0{\cdot}05)$ (Levenson).

123. Estimation of metol in separate extract

The metol is estimated in the same way as the hydroquinone, with iodine or ceric sulphate.

For iodometric estimation the amount of the product should be less than 0·02 M so that the end point will be clearly visible. The acid extract solution is neutralized to methyl orange before titrating. If p-aminophenol is also present, this is estimated at the same time.

Atkinson and Shaner estimate the metol + hydroquinone mixture obtained from 5 cc of developer neutralized to pH 8 with thymol blue (yellow colour). Knowing the weight of hydroquinone from a prior test, the metol can easily be calculated.

Stott's potentiometric method. The extract of the metol in ethyl acetate (para. 120) is poured into a 50 cc burette whose tip is immersed in a beaker filled with 400 cc water acidified with 4 cc of 50% sulphuric acid. Twenty-five cc of the solution is slowly run in with stirring. When dissolved, it is titrated with ceric sulphate, as for hydroquinone. The amount of metol in g per litre is given by $0{\cdot}069 \times n$ cc of ceric solution. Levenson, using 20 cc of extract removed with a pipette, obtained the weight of metol from the following expression, where K is an error coefficient and H is the weight of hydroquinone

$$M = 0{\cdot}088\, n\, K - 0{\cdot}003\, H$$

124. Estimation of metol and hydroquinone in a single extract

Baumbach's method (see para. 121) enables both the metol and the hydroquinone to be estimated in an extract containing the two compounds: the metol base is first titrated with a strong acid potentiometrically, then the sum of metol + hydroquinone with iodine.

The extract containing the developing agents, obtained by the method already given, is mixed with three volumes of water and one part of methyl acetate or isopropanol to reduce the polarity of the liquid (the inflection of the curve is less distinct, but still visible). The metol is then titrated with 0·1 M hydrochloric acid, despite the presence of the hydroquinone, after introducing the platinum and calomel or glass and calomel electrodes.

A buffer solution of 10% disodium phosphate is then added until the pH has reached 6·5 to 7, followed by 1 cc of starch solution before titrating with 0·1 N iodine. The metol and hydroquinone are converted to methylquinoneimide and quinone. In this way the weight of metol + hydroquinone is obtained. By difference, the quantity of hydroquinone is known.

Shaner and Sparks' procedure. The extract of metol-hydroquinone obtained from 10 cc of developer using methyl-ethyl-ketone (para. 121) is poured into 10 cc water. Sufficient methanol is added to make the ketone miscible, then the electrodes are immersed. The metol is titrated with 0·1 M hydrochloric acid. The amount of metol in g per litre is obtained by dividing the product of volume of HCl × strength × molecular weight of metol [172] by the volume of the sample.

The metol + hydroquinone sum is then determined, after adding enough disodium phosphate to raise the pH to 8, and 1 cc of starch solution, with 0·1 M iodine. If n is the volume in cc of the iodine solution, θ its I_2 content, v the volume of the test, M the weight of metol per litre, the concentration of hydroquinone in g per litre is:

$$55(n\,\theta/v) - 2\,M$$

Accuracy: metol 3–5%, hydroquinone 1·5–4%.

Brunner, Means and Zappert's procedure. The metol + hydroquinone extract in isopropyl acetate (see para. 121) is mixed with 100 cc water and 50 cc methanol. Potentiometric titration with 0·05 M hydrochloric acid is then carried out with glass and calomel electrodes. The inflection point is given by the pH v volume of HCl curve. The weight of metol is

$$\mathrm{M} = 6{\cdot}88\,\mathrm{v}\,\theta$$

where v is the volume of the hydrochloric acid and θ its strength.

Five cc of a mixture of equal volumes of water and H_2SO_4 is then added, and two drops of an 0·025 M solution of ferroin (ferrous complex of o-phenanthroline). The solution is titrated with 0·1 N ceric sulphate with mechanical agitation until the pink colour turns to a yellow-green which persists for 30 seconds. The weight of hydroquinone in g per litre is given by:

$$\mathrm{H} = 2{\cdot}2\left[\mathrm{V}'\Theta' - \left(\frac{\mathrm{M}}{3{\cdot}44}\right)\right]$$

To obtain a sharper inflection point in the potentiometric titration curve, Idelson⁽¹⁰⁾ replaced the water by acetic acid as a solvent for the metol and the acid (which is sulphuric or perchloric), as normally weak bases behave as strong bases in acetic acid. The disadvantage of this method, is that a precipitate is formed during the second titration with ceric sulphate.

125. Simultaneous spectrophotometric determination of metol and hydroquinone

Rees and Anderson⁽¹¹⁾ have worked out an interesting method of simultaneous spectrophotometric analysis of metol and hydroquinone, based on the fact that the absorption spectra of the two developers have characteristic ultraviolet absorptions if the dilution is great enough. Good results are obtained with 1 cc of developer in 100 cc of a pH 5 sodium acetate buffer solution. Both pH and temperature must be carefully adjusted.

Metol: Absorption maximum at 270 mμ.

Hydroquinone: Absorption maximum at 290 mμ + slight absorption due to metol.

Accuracy: in the order of a few mg. per litre.

126. Estimation of other developers

p-Aminophenol, glycin, amidol and *p-phenylenediamine* are estimated in the same way as metol. Pyrogallol is treated like hydroquinone.

Colorimetric determination of p-aminophenol. The amount of p-aminophenol can be determined colorimetrically by converting it to a dye with one of the two following methods used by Ballard:⁽¹²⁾

(*a*) Diazotization with sodium nitrate, then coupling with resorcinol.

(*b*) Reaction with dimethylaminobenzaldehyde. If metol is also present, the determination must be made with a spectrophotometer to separate the two coloured constituents.

Glycin estimation. The glycin is converted to nitrosamine with nitrous acid, following the method of Brune, Rieyer and Schultze.⁽¹³⁾ Pour 50 cc of developer into a solution of 20 cc water and 5 g barium chloride $BaCl_2 . 2H_2O$ to first precipitate the sulphite and carbonate. Filter through sintered glass, wash three times with 15 cc boiling water, and after cooling, add 2 cc of hydrochloric acid diluted with 2 cc water. Then titrate with a known solution of sodium nitrite with stirring. To find the end-point of the reaction put a drop of liquid onto a porcelain plate with a drop of starch iodide solution and continue until a permanent blue colour is obtained. 2·42 mg of glycin is converted by 1 mg of nitrite.

Estimation of pyrogallol. Pyrogallol is extracted with ether or other solvent, from the acidified developer, like hydroquinone. If the latter is also present, the extract is redissolved in water, acidified with acetic acid, and the pyrogallol is precipitated with lead acetate, filtered, dried and weighed. 1 g of the insoluble lead salt is equivalent to 0·333 g of pyrogallol.

Estimation of Phenidone. Oxidize with iodine in acid solution.

Estimation of dialky-p-phenylenediamines: see para. 562.

127. Estimation of sulphite

The sulphite is estimated with iodine in acid solution (to prevent developer oxidation). Run the developer from a burette into a flask containing 20 cc of 0·5 M iodine solution and 5 cc concentrated hydrochloric acid, until decolorizing is *almost* complete. Add 2 cc starch and continue titrating to a faint blue.

Bune, Reiyer and Schulze⁽¹⁵⁾ take 20 cc of developer and dilute to 100 cc. A 10 cc sample is poured into a solution of 5 g crystalline barium chloride in 5 cc water. The precipitate is collected on a sintered glass filter, and is washed four times with 15 cc boiling water. The filter is then placed over a 600 cc beaker and 20 cc 0·1 N iodine and 5 cc HCl with 5 cc water is put in the filter. After 3 minutes, 300 cc water is poured through the filter. The SO_2 reacts with iodine which is back-titrated with thiosulphate. One cc of iodine solution is equivalent to 6·3 mg sulphite.

Another technique is to precipitate the sulphite and carbonate with barium chloride, then to convert the sulphite to sulphate with hydrogen peroxide. The carbonate is decomposed on the water-bath with a known quantity of methyl red. If borate is present, add minnitol and follow the reaction with the potentiometer. (Pope, C. I.: *J.S.M.P.T.E.* 1955, **64**, 420).

Bisulphite. Bisulphite reacts with iodine in the same way as sulphite. The sulphite/bisulphite ratio is determined empirically by pH comparison of the test developer with that of a developer prepared according to the analytical results.

128. Estimation of carbonate

The carbonate in a developer is estimated by liberating carbon dioxide with an acid in a stream of air, passing through a chromosulphuric solution to remove SO_2, before absorbing with soda-lime, which often produces errors.

It is generally preferable to titrate potentiometrically using a pH meter fitted with a calomel reference electrode and a platinum electrode, or if this is not available, a glass electrode. The second inflection point gives the end point of the reaction, the first corresponding to the formation of bicarbonate.

The procedure is as follows:(16) 10 cc of developer, diluted with 100 cc water is titrated with 0·1 N HCl with the electrodes in position. Agitation must be violent as dissolved oxygen affects the result. The weight in g per litre of carbonate is given by 1·06 n, n being the volume in cc of hydrochloric acid solution.

Another method is to titrate in the presence of a coloured indicator made up of 0·1 g methyl orange and 0·25 g indigo carmine in 100 cc water. The green alkaline solution becomes grey at the neutral point, and then violet in acid solution.

129. Estimation of borates

As borate estimation is rather tedious it is often preferable to determine only the pH. The estimation is made in the following way:(17) One hundred cc of developer at pH 8 is extracted three times with 50 cc ether to remove the developing agents. The aqueous phase is then acidified with a few cc of HCl to eliminate the CO_2 and SO_2. The remaining traces of sulphite are oxidized with hydrogen peroxide. The solution is neutralized to bromocresol green (Blue at pH 5·2) with caustic soda, 50 cc glycerin is added, and then it is titrated with N/10 caustic soda in the presence of phenolphthalein. When the pink colour is obtained, its permanence is checked by adding more glycerin and heating. One cc of soda solution corresponds to 0·00618 g of H_3BO_3.

The borate ion can be detected by the red coloration of curcuma paper in acid solution, or by the green colour of a flame test on the dry extract mixed with alcohol and sulphuric acid.

The presence of boric acid and borates cannot be directly distinguished. An approximate idea can be obtained by pH comparison of the test developer made up according to the analysis.

130. Measurement of developer pH

The knowledge of the pH of the developer(18) is of interest for the control of its activity, although it is less important than the knowledge of the alkali content. It has only the advantage of being obtained by rapid measurement. Colorimetric determination is only approximate; a *glass electrode* potentiometric instrument is required. If this is not of a special type, a correction must be used above pH 9·5, due to the presence of sodium ions. The relative values are, however, generally adequate.

To standardize the instrument, it is advisable to use a buffer with the same sodium ion concentration as the developer to avoid errors due to the influence of sodium ions. For example (Levenson): sodium carbonate anh. 5 g, sodium bicarbonate 5 g, sodium chloride 58·5 g water to 1 litre. The pH of this solution is 9·3. The calomel reference electrode can advantageously be replaced by a more accurate one having the constitution Ag/AgCl/KCl (N/10)

The relationship between pH value, carbonate concentration and gamma is:(19)

pH	10·38	10·14	10·12	10·11	10·10	10·08	10·10
Carb.	68·0	38·7	37·0	35·8	22·4	18·0	18·0
γ	2·86	2·82	2·77	2·75	2·72	2·70	2·70

It is seen that slight variations in pH correspond to considerable differences in carbonate, and that the corresponding variations in γ are moderate.

131. Estimation of various constituents

Sodium sulphate. In a used developer, 10–20% of the sulphite is converted to sulphate, mainly by aerial oxidation. If more than 5% is found in a fresh developer, it is probably due to its deliberate addition to reduce the swelling of the gelatin.

To estimate the sodium sulphate, it is precipitated with barium chloride after acidifying the developer with HCl to decompose the sulphite and carbonate, which would otherwise also precipitate. The resulting barium sulphate will coagulate after boiling for one minute. It is then filtered, washed, dried and weighed in a tared Gooch crucible.

Potassium thiocyanate. To estimate the thiocyanate, put 25 cc developer, 180 cc distilled water and 60 cc sulphuric acid in a 400 cc beaker. Insert a silver and a calomel electrode and titrate potentiometrically (with a pH meter), using N/10 silver nitrate, which first precipitates the halides.

Orthophosphates give a yellow precipitate of ammonium phosphomolybdate(20) with an acidified developer, after prior precipitation of the iodides, bromides and chlorides with silver nitrate.

Sodium citrate. The sodium citrate in certain developers is precipitated with barium chloride at the same time as the sulphite, sulphate and carbonate. The washed precipitate is redissolved in an acid to separate the insoluble sulphate. The resulting solution is boiled to eliminate CO_2 and SO_2 and the citric acid is re-precipitated with a barium salt.

Other substances. A developer may contain alcohol, formalin (detected after distillation), ammonia, a desensitizing dye, a wetting agent, a sequestering agent such as hexametaphosphate, tetraphosphate, pyrophosphate, or ethylenediamine-tetraacetic acid. For the detection and estimation of these compounds, refer to general analytical works.

132. Bromide estimation

Two principal methods are used with many variations: oxidation of the bromide or precipitation with silver nitrate. The former is little used for developer analysis, but could be adopted.

(*a*) Kapur, Verma and Khoshla(21) oxidize the bromide with a mixture of chromic and nitric acids. The liberated bromine is collected in carbon tetrachloride, then potassium iodide is added. The liberated iodine is titrated with thiosulphate.

(*b*) Lane(22) liberates the bromine by adding chlorine water in the presence of sulphuric acid, and estimates it colorimetrically with a photoelectric instrument.

(*c*) Farkas and Lewin(23) treat the solution with hypochlorite at a pH between 9 and 9·4. Hypobromite is formed which is reduced by a basic solution of phenol, and the excess hypochlorite is estimated.

(*d*) Atkinson and Shaner(24) precipitate the bromide with silver nitrate in nitric solution, and in the presence of metanil yellow and a known excess of bromide.

(*e*) Baumbach(25) titrates the bromide potentiometrically with silver nitrate in acid solution with a silver and a calomel electrode. The addition of barium nitrate or alum gives better agreement between the inflection and equivalence points.

(*f*) Laitinen, Jennings and Parks(26) titrate with silver nitrate using a turning platinum electrode (current measurement).

Atkinson and Shaner's method. 15 cc concentrated nitric acid, 4 cc of 0·2% metanil yellow and 10 cc of 10% potassium bromide (to ensure an adequate bromide concentration) are added to 100 cc developer in a 300-cc flask. This is titrated with a 1·427% silver nitrate solution. The colour is blue at the beginning, and red at the end of the titration. The bromide concentration in g per litre is given by n – 100/10, where n is the volume in cc of silver nitrate required.

Potentiometric method. Evans, Hanson and Glasoe(27) have disclosed a potentiometric method in which the sulphur dioxide is first eliminated by boiling in acid solution, before adding sodium acetate.

When a mixture of silver iodide, bromide and chloride is precipitated the inflection points of the e.m.f.—vol. $AgNO_3$ curve do not correspond exactly with the points of chemical neutralization. Better agreement is obtained when barium nitrate or alum is added. However, in current practice the accuracy is adequate without this addition.

25 cc of positive developer (or 100 cc negative developer) are mixed with 75 cc distilled water, 0·5 cc bromocresol green and sufficient concentrated sulphuric acid to turn the solution yellow, plus a further 0·5 cc, and finally 100 cc distilled water. The silver and calomel electrodes are immersed in the solution together with a mechanical stirrer. Silver nitrate solution is then added drop by drop, but at a fairly fast rate until the potentiometer indicates 70 mV, then more slowly, waiting after each addition until equilibrium is reached. At about 120 mV the titration is complete, and it is unnecessary to draw the curve. Titration time 10 minutes. Maximum error 3%.

The silver electrode is prepared by electrolytic deposition of silver on a platinum wire, from an argenticyanide solution.

133. Iodide estimation

The iodide, precipitated as silver iodide with silver nitrate, is oxidized with chlorine. It is converted to iodate which is estimated *polarographically* by the technique of Evans, Hanson and Glasoe.(28) Another equally laborious method of Levenson's, is to first eliminate the reducing agents, then extract the iodine with cyclohexane and estimate it *colorimetrically.*(29)

The procedures of these two methods are so lengthy that we refer the reader to the original papers.

134. Estimation of impurities

Traces of *copper* in a hydroquinone developer can produce aerial fog. It is therefore advisable to estimate this metal. Evans, Hanson and Glasoe have determined it *polarographically* in the presence of 2% of a 60% solution of ethylenediamine which doubles the amplitude of the curve. Levenson used a *colorimetric method.*(31) The developer is shaken with a solution of zinc diethyldithiocarbamate in butyl acetate. The copper salt collects in the solvent layer, which it colours brown.

Lambert used the catalytic autoxidation of resorcinol by copper:(32) the green coloration of autoxidized resorcinol solutions increases linearly in density with the copper content.

Sulphide can be rapidly estimated with the polargraph, following the instructions of Evans, Glasoe, and Hanson.(30)

135. Analytical reactions of developing agents

The developing agents, as received, or extracted from a developer, can be identified by the characteristic reactions in the following table.

1. *Ultra-violet examination*

Substance	Fluorescence In sulphite solution	 Powder
Hydroquinone	Very light red-violet	light violet
Pyrocatechin	weak violet	none
p-Aminophenol HCl	none	weak violet
Glycin	violet	weak whitish
Amidol	none	weak whitish
p-Phenylenediamine	violet	none
Dimethyl-p-phenylenediamine	blue	none

2. *Ferric chloride* $FeCl_3$ gives the following reactions:

Hydroquinone	Brown colour
Pyrocatechin	Dark green colour
Pyrogallol	Blue colour changing to brown
p-Aminophenol HCl	Brown precipitate
Metol	Red-brown colour—slow
Metoquinone	Brown colour then precipitate
Glycin	Red-brown colour turning green and violet
Diaminoresorcinol	Violet colour turning brown.
Amidol	Blood-red colour
Eikonogen	Reddish-brown colour

3. *Potassium ferricyanide* $K_3Fe(CN)_6$ also gives characteristic reactions.

Pyrogallol	Dark red colour
p-Phenylenediamine	Green-brown colour turning brown with dark green precipitate
p-Aminophenol	Brown precipitate
Metol	Yellowish red colour
Glycin	Yellow colour
Amidol	Red colour turning brown

4. With *nitric acid*

Hydroquinone	Dark red colour becoming yellow
Pyrocatechin	Reddish-yellow colour
Pyrogallol	Dark red colour
p-Aminophenol	Yellow colour
Metol	Dark red colour
Metoquinone	Yellow colour
Glycin	Reddish yellow colour

5. The *alkali carbonates* colour amidol-sulphite solutions blue, and those of diaminoresorcinol, yellow-brown. With *caustic alkalis* the same solutions turn bordeaux red and blue respectively. With alkaline solution Eikonogen gives a golden yellow colour.

6. Plauman(33) has given the following system for *the identification of a commercial developing agent.*

Seven different tests are made on a 5% solution of the unknown, each taking 50 cc (see table, p. 144).

1. Addition of a few drops of 20% carbonate.
2. One or two drops of 5% ammonium vanadate.
3. A few drops of 5% caustic potash.
4. Addition of 10% ferricyanide, then a few drops of 20% carbonate.
5. Addition of 10% ferricyanide alone.
6. Addition of 10% ferrous sulphate.
7. Addition of 2% ferric chloride.

We would add a characteristic reaction of metol: a drop of its ether solution is put on filter paper followed by a drop of 16% hypochlorite. A definite bright blue-green colour is produced.

135b. Chromatographic analysis

Sasai, Mizusawa and Otoka(33b) have worked out a system for identifying developers by chromatography on paper. The developer, deposited on the latter is treated with a mixture of water, acetic acid and n-butyl alcohol (or ethyl acetate). The diffusion times are respectively 5–8 hours and 3½–5 hours. After drying, the paper is sprayed with a 2% ammoniacal solution of silver nitrate. The migration distance distinguishes the developers.

A similar technique was used by Mariani and Martinelli.(33c) A 35 × 35 cm sheet of paper is wrapped around a cylinder, and 3 mm³ of a 1% aqueous solution of the developing agent is placed at the beginning. After drying at 45°C the paper is damped with solvent from a spray and again dried.

The best solvent is made up of 15% water, 80% n-butyl alcohol and 5% acetic acid. The patches are then treated with N/10 ammoniacal silver nitrate which makes them grey, black or grey-violet.

136. A.S.A. standards of purity for developing agents

Metol: must dissolve completely in cold water to the extent of 4 g per 100 cc with 5 drops 10% H_2SO_4. One gramme of product must dissolve completely in 3 cc concentrated HCl. The fraction soluble in absolute alcohol or ether must not exceed

IDENTIFICATION TABLE FOR DEVELOPING AGENTS

	Insoluble in	Test 1 Carbonate	Test 2 Am. vanadate	Test 3 Potash	Test 4 Ferricyanide and carbonate	Check test
Hydroquinone	—	Yellow → brown	No change	Yellow → brown	Golden yellow → brown	Test 7—deep green
Pyrogallol	—	Yellow → brown	Blue	Yellow → brown	Brown	Test 6—Blue Add 1 → blue-violet
Pyrocatechin	—	No change	Violet	Green-brown	Green → green-brown	Test 6—Green Add 1 → red-violet
p-aminophenol H Cl	Ether	No change	Blue-green	Violet	Decolorized	—
Amidol	Ether	Blue	Red	Yellow-brown	—	Test 5—Red
Metol	Alcohol Ether	Yellow-brown	Olive green → violet	Yellow-brown	Yellow-brown → deep red-brown	Test 7—Weak red
p-phenylene-diamine H Cl	Alcohol Ether	No change	Brilliant green → olive green	No change	Green	Test 7—Deep green
Glycin	Water	—	—	—	—	—

0·04%. Must give sulphate reaction. Ash ⩽0·1%. Volatile matter ⩽0·3%. Iron ⩽2·5%. Amount of p-aminophenol ⩽2.5%.

Characteristic reactions: purple colour in less than 5 minutes by adding 0·2% mercuric acetate to 0·1% metol. Immediate colour when 1 cc of 2% caustic soda is added to 50 cc 2% metol.

Absence of dimethyl-p-phenylene diamine (toxic to the skin): Dissolve 2 g metol in 10 cc water. Filter into a 100-cc separating funnel. Add 10 cc 40% caustic soda and 10 cc ether. Shake. Separate the aqueous layer. Rinse with 10 cc water without shaking. Run off the water. Add 10 cc 10% (by volume) H_2SO_4, shake and run off the acid. Divide the ether solution equally between two tubes with ground stoppers. Shake one of the tubes for one minute—no pink colour must form. Add 2 cc 10% nitrite to the second and shake. There must be no brown colour or precipitate.

Hydroquinone: M.Pt. 170–174°C. 5 g must dissolve cold in 100 cc distilled water, 95% alcohol or ether. Ash ⩽0·075%. Iron ⩽0·001%. Negative result with lead acetate test for resorcinol.

Chlorhydroquinone: M.Pt. 103–106°C with softening at 90–95°C. Ash ⩽0·1°. Iron ⩽0·005%. Chlorine 24·1–25·1%.

Pyrocatechin: colour—white to pink. M.Pt. 101–104°C. Ash ⩽0·1%. Iron ⩽0·001%. Intense green colour on adding $FeCl_3$ to the hydrochloric acid solution.

Pyrogallol: white to blue-grey crystalline powder. M.Pt. 130–133°C. Ash ⩽0·02%. Iron ⩽0·001%.

p-aminophenol hydrochloride: the free base, precipitated by sulphite, washed and dried for one hour at 70°C must melt between 185 and 190°C. 5 g of p-aminophenol hydrochloride must dissolve completely in 100 cc cold water. Ether-soluble fraction maximum 0·04%. Cl 24–25%. Ash ⩽0·5%. Volatile matter ⩽0·5%. Iron ⩽0·005%.

Glycin. M.Pt. (with decomposition) 220°C. 1 g must dissolve completely in 10 cc of hydrochloric acid diluted with 10 cc water, or in 10 cc 10% caustic (slight opalescence). The fraction soluble in cold water or in acetic acid must not exceed 0·04%. Ash ⩽1%. Volatile fraction ⩽0·5%. Iron ⩽0·005%. By adding $FeCl_3$ to hydrochloric acid solution: red-brown colour turning grey-green and violet.

Diaminophenol (*hydrochloride*). White or blue-grey cryst. powder. 5 g must dissolve in 100 cc cold water with no residue, in 30 minutes. When 5 cc of 10% sodium carbonate is added to this solution there must be no smell of ammonia. Cl 35·5–36·5%. Ash ⩽1%. Volatile matter at 85–95°C ⩽0·5%. Iron ⩽0·001%. By adding 4 cc of 10% nitrite in 100 cc of 1% solution of the product a deep red colour is produced. By adding one drop of a solution containing 1% of the compound and 10% sulphite to potassium carbonate, a bluish colour is produced.

p-phenylenediamine (base). 1 g must dissolve completely in 100 cc cold water or 20 cc absolute alcohol. Ash ⩽0·1%. Iron ⩽0·005%. Add 5 cc of 3% acetic acid to 1 cc of 1% solution; heat to 45°C and add 1 drop of a saturated aqueous solution of aniline and a few crystals of ammonium persulphate: blue-green colour in 5 seconds.

p-phenylenediamine (*hydrochloride*). 5g must dissolve completely in 100 cc cold water. Fraction soluble in absolute alcohol ⩽0·08%; in ether ⩽0·04%; Cl 39·5–41%. Ash ⩽0·1%. Volatile matter ⩽0·5%. Iron ⩽0·005%. $FeCl_3$ added to hydrochloric solution → green colour turning brown.

137. A.S.A. standards of purity for photographic chemicals(35)

Sodium sulphite anhydrous: sulphite content ⩾96%. Carbonate ⩽0·15%. Hypo cryst. ⩽0·1%. Precipitation by ammonia ⩽0·5%. Heavy metals (Pb) ⩽0·002%. Iron ⩽0·005%. Reducing agents—see carbonate.

Potassium metabisulphite: $K_2S_2O_5$ ⩾90%. Hypo ⩽0·1%. Insoluble in ammonia ⩽0·5%. Heavy metals 0·005%. Iron ⩽0·005%.

Sodium carbonate: Na_2CO_3 ⩾98%. Caustic soda ⩽0·5%. Bicarbonate ⩽0·17%. Lead ⩽0·001%. Iron ⩽0·001%. Presence of reducing agents: one gramme of carbonate is dissolved in 20 cc distilled water, and 10 cc of ammoniacal silver nitrate (prepared from 10% $AgNO_3$ and ammonia) is added. After 2 minutes, the solution must be neither turbid nor more coloured than a blank test. This test is also used for sulphite and metasulphite.

Borax: content 99–103% (efflorescence). No effervescence with HCl. Pb ⩽0·001%. Fe ⩽0·03. Presence of reducing agents—see carbonate.

Metaborate: $Na_2B_2O_48H_2O$ ⩾98·5%. Acidity HBO_3 ⩽1%. Free NaOH ⩽0·2%. Ca ⩽0·01%. Pb ⩽0·001%. Fe ⩽0·003%.

Caustic soda: Na_2CO_3 ⩽2·5%. NaCl ⩽0·5%. Heavy metals 0·001%. Fe ⩽0·003%.

Potassium bromide: KBr ⩾99%. NaCl ⩽0·3%. H_2O ⩽0·3%. Neutrality: a solution of 1 g in 50 cc water must not colour phenolphthalein, but the addition of one drop of N/10 caustic soda must give a pink colour. Presence of iodide: dissolve 1 g KBr in 10 cc water and add 1 cc 10% H_2So_4, 0·5 cc $FeCl_3$, then 1 cc chloroform or carbon tetrachloride: the solvent layer must not be coloured. Absence of oxidizing agents: 1 g in 10 cc water + 0·5 g KI + 1 cc chloroform: no colour in chloroform. Na_2S ⩽0·0005. Ammonia precipitate ⩽0·75%. Heavy metals 0·0005%. Iron 0·0005%.

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Chapter XI

FIXING, WASHING AND DRYING

138. Stop baths

The stop bath, which follows development, quickly checks the action of the developer on the sensitive layer by neutralizing the alkali. The rapid lowering of the pH which results, increases the redox potential, and consequently reduces the energy of the developer.

The *acid* retarders which are added to a developer to slow down development, are not more than diluted stop bath constituents which lower the pH.

The developed image is immersed for 10–20 seconds in the following solution, then rinsed and fixed:

Water	1000 cc
Acetic acid	40 cc

For papers, the acetic acid can be reduced to 15 cc.

In the absence of acetic acid, sodium *bisulphite lye* can be used at a concentration of 50–100 cc per litre, or the equivalent of sodium or potassium *metabisulphite* (25–50 g). Monosodium citrate can also be used at a concentration of 5–10%.

To prevent the gelatin from swelling, sodium *sulphate* can be added to the acetic acid solution, for example:

SB.5a	Sodium aulphate anh.	45 g
	Acetic acid	20 cc
	Water to	1 litre

Treatment time: 3 mins. Temperature up to 26°C. Sufficient for twenty-five films.

139. Hardening stop baths

Hardening stop baths for negative emulsions are generally *chrome alum* solutions:

SB.3	Chrome alum	30 g
	Water to	1 litre

Treatment time: 3–5 mins.

SB.4	Sodium sulphate anh.	60 g (or cryst. 140 g)
	Chrome alum	30 g
	Water to	1 litre

The activity of this bath falls rapidly. It must be renewed when it becomes yellow-green in colour or if it becomes covered with scum.

Chrome alum is the double sulphate of chromium and potassium $Cr_2(SO_4)_3 . K_2SO_4 . 24H_2O$. It crystallizes in regular violet octahedral crystals. It is isomorphous with *ordinary alum* $Al_2(SO_4)_3 . K_2SO_4 . 24H_2O$ which is also a gelatin hardener.

Chrome alum gives the violet $Cr(H_2O)_6^{+++}$ ions, which, when acidified slowly, become the green $Cr(H_2O)_5(OH)^{++}$ and ordinary alum gives complex hydrated ions such as $Al(H_2O)_6^{+++}$, $Al(H_2O)_5OH^+$, $Al(H_2O)_4(OH)_2^+$, $Al(H_2O)_3(OH)_3^+$, which are the gelatin hardening functions.

With the carboxyl groups of the gelatin molecule, these ions form co-ordination compounds. These compounds are broken down in the presence of citrate or tartrate ions, with a greater tendency to form co-ordination compounds which destroy the hardening properties of the bath. Baumbach and Gausman put forward the hypothesis that water molecules, being polar, attach themselves to groups which are also polar; now the number of ionic groups is reduced by co-ordination with the aluminium complex ions. The swelling of the gelatin is therefore reduced. The necessity of having a large number of positively charged Cr ions and a large number of negatively charged gelatin carboxyl groups impose two opposing conditions which reduce the pH range in which hardening is possible. In fact, the chromium ions lose their positive charge when the pH exceeds 4·7.

In 1934, Spiers showed that the chromium atoms are linked to the polypeptide chains by a carboxyl and an amino group. At moderate acidity the polypeptide chain is coiled up, and this favours the formation of intermediate bridging, therefore hardening.(1)

140. Control of stop baths

Stop baths will keep indefinitely in corked bottles. In a tank the average life is a month. In dishes the life is much shorter—three days for acetic acid baths, and one day for chrome alum ones. They have the following exhaustion properties: Acetic acid baths—55 dm^2, weak acetic acid—100 dm^2 of paper, SB.5a—150 dm^2, SB.3—32 dm^2, SB.4—32 dm^2.

The SB.5a is generally better for amateur work.

The condition of a stop bath can be calculated with reference to the volume of carry-over and the amount of acid added, using Hentzberger and Henn's equation,(2) but in practice an empirical method is used. Henn and Crabtree(3) recommend the addition of 11 cc of 10% acetic acid for each spool removed. For a 120-l. tank, 5 l. glacial acetic acid must be added after treating 5,000 spools. The bath is discarded after treatment of 35,000 spools.

Measurement of pH is a simple way of controlling the activity of stop baths. Without a meter, *indicator dyes* can be used. The pH should be about 4 for a fresh bath, always below 4·7 when it contains chrome alum, and can go up to 5 during use (5·5 for prints). The following indicators are recommended:(4)

Bromocresol green (for acetic acid negative baths). Yellow when the bath is fresh, green when in good condition during use, and blue when it is not acid enough.

Bromocresol purple (for prints). Yellow when the bath is new, orange when the bath is still in good condition and purple when there is too little acid present.

Risso-Dominguez(5) suggested Congo red and alizarin red S.

Congo red: blue at pH 3, red at pH 5.

Arlizarin red S: yellow at pH 3·7 and pink at pH 5·2.

A paper impregnated with Congo red appears black or colourless in red light depending on whether or not the bath is sufficiently acid.

141. Formalin hardeners

Formalin(6) is a very active gelatin hardener. It can be used either as a hardening fore-bath before development to harden the gelatin thoroughly, or after development, or after washing.

Hardening forebath (before development):

SH.5	—Sodium carbonate anh.	10 g
	Sodium sulphate anh.	50 g
	Benzotriazole (0·5% alcoholic soln.)	40 cc
	Water to	1 litre

Add 5 cc formalin just before use.

The benzotriazole is an antifoggant and can be replaced by 6-nitrobenziminazole nitrate.(7) The quantity must be doubled for development at 42°C.

The films are left in this bath for 10 mins. and are then rinsed for 30 secs. The development times then become:

at 24°C (75·2°F)—same time as for 18°C. (64·4°F).
29°C (84·2°F)—time reduced to 70%
32°C (89·6°F)—time reduced to 60%
35°C (95°F)—time reduced to 50%
43°C (109°F)—time reduced to 25%.

Bath for hardening after development: 5% formalin solution, preferably containing 40 cc 0·5% benzotriazole—treatment time 1 min. This method is not widely used but has sometimes been recommended for photomechanical emulsions.

Bath for hardening after washing. For papers which are insufficiently hard because they are too new, dip in a 5% formalin solution for 2 mins. then wash for 3 mins.

Films which are to be intensified or reduced are hardened for 3 mins. in:

SH.1	Sodium carbonate anh.	5 g
	Formalin	10 cc
	Water to	1 litre

Wash for 5 mins. It is sometimes advisable to fix again in a fresh acid bath and wash thoroughly.

142. Silver halide solvents

The removal of the unaffected silver bromide remaining after development is called *fixation*. This operation makes the photographic layer transparent and permanent and prevents subsequent darkening.

The silver halide is made soluble by converting it to a *complex double salt of silver and alkali metal* which can be eliminated by washing with water.

The silver halides (chloride, bromide and iodide) are soluble in solutions of several substances, mostly inorganic, amongst which are the following:

Sodium thiosulphate (see next paragraph).

Ammonia NH_4OH, is a solvent for silver chloride. The soluble chloride of a complex silver-ammonium ion is formed. By evaporating, the solution slowly loses ammonia, and octahedral crystals of silver chloride are deposited. A 4% ammonia solution dissolves silver chloride in 2–5 mins.; it has less effect on solver bromide, and none on silver iodide. Ammonia can be replaced by neutral ammonium carbonate.

Potassium Bromide KBr. In a concentrated solution it dissolves silver chloride and bromide, but works slowly with iodide. As it attacks gelatin strongly, it can only be used in the presence of a hardening agent:

Water	1000 cc
Potassium bromide	350 g
Potash alum	10 g

Fixing time: 12 mins.

With silver bromide, a soluble double bromide of silver and potassium AgBr . KBr is formed.

Potassium iodide KI. In a concentrated solution it dissolves silver chloride, bromide and iodide: chloride and iodide rapidly—four times more quickly than bromide. The gelatin swells and breaks up without a hardener; in all these cases the image when wet appears in relief. The following formula can be used:

A	Water	1000 cc
	Potassium iodide	200 g
B	Water	1000 cc
	Potash alum	100 g
	Acetic acid	3 cc

Take 5 parts of A to 1 part of B. Fixing time: 5–10 minutes for silver iodide. After several days the bath becomes brown due to the liberation of iodine; it then stains the gelatin.

Potassium thiocyanate KCNS. It only dissolves silver bromide and chloride well, with the formation of a double silver and potassium thiocyanate:

$$\underset{\substack{\text{Silver}\\\text{bromide}}}{AgBr} + \underset{\substack{\text{Potassium}\\\text{thiocyanate}}}{2KCNS} = \underset{\substack{\text{Silver potassium}\\\text{thiocyanate}}}{AgCNS \,.\, KCNS} + \underset{\substack{\text{Potassium}\\\text{bromide}}}{KBr}$$

Thiocyanate can only be used in relatively weak solutions:

Water	1000 cc
Potassium thiocyanate	50 g
Potash alum	10 g

Fixing time 2–5 mins., followed by a rinse in a fresh bath before washing, to avoid precipitation of the double salt in the gelatin.

Potassium cyanide and potassium ferrocyanide are also solvents for silver halides. The former is very effective but it is too poisonous for practical use. It forms double cyanides $AgCN . KCN$, and reticulates and disaggregates the gelatin.

Magnesium chloride $MgCl_2$, *sodium sulphite* Na_2SO_3, *thiourea* $CS(NH_2)_2$, and *thiosinamine* (or allyl thiourea) $NH_2—CS—NH . CH_2—CH = CH_2$, are only effective with silver chloride.

Magnesium chloride and thiourea attack the gelatin. In the presence of silver nitrate, thiourea gives an insoluble precipitate which remains in the gelatin layer.

Thiosinamine is easier to use. A slightly acidified 1 % solution dissolves silver chloride in 5 mins.

143. Fixing with thiosulphate

The fixing agent which is almost always used in current practice is sodium *thiosulphate* or 'hypo' $Na_2S_2O_3 . 5H_2O$. It is effective with all the silver halides, and attacks neither the gelatin nor the silver image.

Silver bromide reacts with hypo to give the *argentothiosulphates* following the reaction:

$$x\,Na_2S_2O_3 + y\,AgBr \rightarrow Ag\,y\,(S_2O_3)x^{(2x-y)(-)} + y\,Br^- + 2x\,Na^+$$

The thiosulphate *ions*, adsorbed by the surface of the grains, form the complex salt $Na[Ag(S_2O_3)]$ which, with an excess of thiosulphate, becomes water-soluble $Na_3[Ag(S_2O_3)_2]$. The existence of numerous other compounds has been proved (see para. 149). What is certain, is the formation of insoluble argentothiosulphates when silver ions are in excess.

The fixing of a sensitive layer takes place by *double diffusion*: the hypo towards the silver bromide grains and, in the opposite direction, the argentothiosulphate towards the liquid. Agitation speeds up this process. If the material is placed in stagnant fixer, sensitive surface down, diffusion is assisted by the tendency of the heavy complex salts to fall. If the gelatin is swollen, the increased thickness counteracts in practice the speeding up of diffusion.(8)

Sodium thiosulphate crystallizes in transparent clinorhombic prisms which have a bitter taste and are very soluble in water. Dissolving the crystals lowers the temperature. The crystalline salt melts at 48°C (118·4°F) and is dehydrated to the anhydrous salt $Na_2S_2O_3$ of which 0·64 g is equivalent to 1 g of crystals.

Hypo is prepared by boiling a solution of sodium sulphite with sulphur following the reaction:

$$\underset{\text{Sodium sulphite}}{Na_2SO_3} + \underset{\text{Sulphur}}{1/2S_2} = \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

The raction mixture is filtered, evaporated and crystallized.

It is also prepared by the action of sulphur dioxide, SO_2, on calcium sulphide CaS; this gives calcium thiosulphate which is treated with sodium carbonate to give the sodium salt.

Hypo is formed when an excess of flowers of sulphur is boiled in a solution of caustic soda. After filtering it is treated with sulphur dioxide until colourless, and crystallized after evaporation.

It is also obtained by fusing 100 parts of crystalline carbonate with 30 parts of powdered sulphur. The sulphite formed is extracted with water and boiled with a further quantity of sulphur, filtered and crystallized.

Finally a 20% hypo solution can be obtained by the action of sodium amalgam on bisulphite (F.P. 825,226, 1937).

Density of solutions of hypo crystals at 19°C

2%	1·010	12%	1·063	22%	1·120	32%	1·180
4%	1·021	14%	1·075	24%	1·132	34%	1·192
6%	1·031	16%	1·086	26%	1·144	36%	1·204
8%	1·042	18%	1·097	28%	1·155	38%	1·217
10%	1·052	20%	1·108	30%	1·167	40%	1·229

144. Acid fixers

The alkali of the developer, carried over in the photographic layers, can decompose the soluble argentothiosulphate, giving rise to stains. Furthermore, the developing agents from the developer will be oxidized in the fixing bath to coloured compounds.

Acids on the other hand decompose hypo to *sulphur* and *sulphur dioxide. Hydrogen sulphide* and *sodium trithionate* $Na_2S_3O_6$ are then formed. The action of S on SO_2 in addition produces pentathionic acids

$$5\,S + 5\,SO_2 + 2\,H_2O = 2\,H_2S_5O_6$$

The decomposition of fixing baths can be prevented by adding sodium *bisulphite* or *metabisulphite* and a little *sulphite.* In this way the hypo is buffered against both acids and alkalis. The bisulphite neutralizes the developer alkali, giving sulphite, whilst the sulphite is converted to bisulphite by acids, before the hypo is decomposed.

If the hypo is oxidized to tetrathionate and the sulphite to sulphate with iodine, the trithionate remains, which by boiling with barium chloride is decomposed to sulphuric acid (as $BaSO_4$), sulphur and SO_2; this is a method of estimating the trithionate.(9)

$$H_2S_3O_6 \rightarrow H_2SO_4 + S + SO_2$$

In a neutralized solution, the sulphite splits the pentathionate, contained in a hypo solution, into trithionate and hypo:

$$\underset{\text{pentathionate}}{Na_2S_5O_6} + \underset{\text{sulphite}}{2\,Na_2SO_3} \rightarrow \underset{\text{trithionate}}{Na_2S_3O_6} + \underset{\text{hypo}}{2\,Na_2S_2O_3}$$

By estimating the trithionate formed, the amount of pentathionate can be found.

An *acid fixing bath* is made up as follows:

Water to	1000 cc
Hypo cryst.	250 to 300 g
Bisulphite lye (S.G. 1·35)	50 cc
Sodium sulphite	10 g

Fixing time: 5–10 mins.

The neutral sulphite is frequently wrongly omitted. With 350 g per litre hypo, the bisulphite must be increased to 70 cc. In addition the latter can be replaced by 25–30 g metabisulphite.

250 g of crystalline hypo can be replaced by 159 g of *anhydrous hypo.*

The above bath can fix 60 dm^2 per litre without a stop bath, and 90 dm^2 with an intermediate stop bath. It will keep for 3 months in a stoppered bottle, one month in a tank, and a week in a dish.

Fixing rate. The speed of fixing is greatest at a concentration of 30%. It increases with the temperature—2·3 times for 10°C (18°F).

145. Hardening fixers

The fixing bath can also be made to harden, by incorporating *potash alum* or *chrome alum.*

For the alum to retain its hardening properties, the pH of the bath must not exceed 6·3 for potash alum or 4·7 for chrome alum. On the other hand, the pH must not be less than 3·7 for below this the hypo will decompose. Also, to stabilize the pH of the bath by a buffer effect *neutral sulphite* is used at a maximum concentration of 20 g per litre. The acidity is provided by sodium *bisulphite* $NaHSO_3$ or *bisulphate* $NaHSO_4$ in the case of chrome alum, and by *acetic* or *boric* acid or sodium *bisulphate* in the case of potash alum.

Potash alum hardening fixers. The quantity of alum used is 10–50 g per litre. Above this, the emulsion becomes opalescent. As a buffer, sodium acetate CH_3COONa is used. The latter, furthermore, together with boric acid retards the formation of sludge in the bath. In the presence of an acetate buffer, the amount of sodium bisulphate can be much higher without risk of decomposing the hypo.

The following formula studied by Woolsey and Pankhurst give good results(10) and will keep for 3 months.

	Negatives	Negatives	Positives	Cine Positives	X-ray
Water to	1000 cc	1000 cc	1000 cc	1000 cc	1000 cc
Hypo cryst.	240 g	350 g	240 g	350 g	250 g
Sodium sulphite anh.	15 g	8 g	15 g	15 g	15 g
Sodium acetate	—	15 g	—	15 g	15 g
Boric acid	7·5 g	10 g	—	10 g	10 g
Sodium bisulphate	—	15 g	—	15 g	15 g
Potash alum	15 g	10 g	15 g	30 g	30 g
Acetic acid	18 cc	—	18 cc	—	—

The hypo is dissolved first at 50°C (122°F), then in succession the sulphite, the acetate and the boric acid. The bisulphate and alum are dissolved separately at 50°C and this solution is poured into the former with stirring. The total volume is then made to 1 litre. In the formulas containing acetic acid, this is added after the sulphite; the boric acid and alum and then dissolved.

For the preparation of *dry powders* to be dissolved as required, anhydrous hypo is used with sulphite, sodium acetate and boric acid. The alum and sodium bisulphate are contained in a separate packet.

During use, the pH of the hardening bath is increased, and its hardening power decreases: when the pH increases from about 4·5 to 7, the fixing time is trebled.

Chrome alum hardening fixers. These baths harden gelatin very well, the melting point being much higher than with potash alum. The hardening power, however, is much more sensitive to pH variations. Sodium acetate reduces this power. Furthermore, as there is no tendency for a sludge to form, the boric acid is unnecessary. Chrome alum baths do not keep as well as those with ordinary alum (one week).

Chrome alum formulas:

	A	B	C
Water to	1000 cc	1000 cc	1000 cc
Hypo cryst.	250 g	340 g	250 g
Sulphite anh.	15 g	17 g	15 g
Sod. bisulphate	—	—	15 g
Bisulphite lye	—	100 cc	—
Chrome alum	15 g	30 g	10 g
Sulphuric acid	2 cc	—	—

The chrome alum is dissolved separately in 250 cc water and added to the solution of the other items with stirring. The bath B is suitable for machine development. After treatment 500 ft. of film, 10 litres of new solution are added to 140 litres of old bath and so on. The formula C can be prepared in a powder form; the chrome alum is kept separate and the crystalline hypo is replaced by anhydrous.

The temperature of hardening fixers must not exceed 21°C (70°F).

146. The fixing operation

1. When a photographic emulsion is immersed in a fixing bath, it becomes transparent in a few mins. and all milkiness disappears. At this point about 5% of the silver bromide still remains in the gelatin. To reduce this to less than 0·25% treatment must be continued for at least as long again as the time taken to clear. In practice the fixing time is rather more than double this (clearing time × 2).

The *speed of solution* of the silver bromide is dependent on many factors: thickness and grain size; amount of halide in the layer; *concentration of silver iodide*, which slows down fixing; temperature,(12) agitation, exhaustion of the bath, to say nothing of the initial hypo content of the bath which has been shown to vary from 20–35%, with an optimum at 30%.

In cold weather, fixing can be accelerated by adding *ammonium chloride* NH_4Cl; by double decomposition this gives ammonium thiosulphate which is more active but much less stable than the sodium salt.

2. *Exhaustion of the bath.* When the clearing time becomes more than twice that of the new bath the solution is considered to be exhausted. A drop of the bath applied to paper and exposed to light becomes brown when the fixer is exhausted. A fixed print, washed for one hour and treated in 0·2% monosulphide, must be free from fog.

A litre of solution can fix about 10 sq. ft. of negative and 20 sq. ft. of paper. Chrome alum solutions are exhausted before potash alum, especially when no stop-bath is used.

Acidity control. The acidity limits differ for each type of fixing bath. The upper pH limit is 6·3 in the case of potash alum and 4·7 for chrome alum.

A turbid potash alum fixer must be discarded. Neutralization can be retarded by adding one-third of the normal amount of acetic acid (diluted). This can only be repeated three times.

Chrome alum fixers cannot be re-acidified.

The pH of the solutions can be controlled electrometrically, or failing that, with dye indicators. Rzymkowski(13) proposed using *fluorescent indicators* such as pyranine, which becomes yellow with green fluorescence above pH 7. Concentration: 20 cc of 0·1% dye per litre of the bath. The fluorescence can be brought about using an immersed blue phosphorescent tube (Permaphan of Auergesellschaft, Berlin). In the dark, an intense fluorescence can be seen around the tube when the bath becomes alkaline.

147. Rapid fixing

Fixing can be accelerated, especially in cold weather, by adding 50 g per litre *ammonium chloride* to the bath. However, better results are obtained by replacing the hypo with *ammonium thiosulphate* (Hoechst rapid fixing salts).

The fixing time with ammonium thiosulphate is reduced by 75%. With alum, the hardening is retained over a wider pH range. The only disadvantage is a possible *reduction* of the image if the grain is fine. At 15%, however, this attack is negligible.

Allnut's formula(14) (Hardening bath):

Water to	1000 cc
Ammonium thiosulphate cryst.	200 g
Sulphite anh.	15 g
Acetic acid	15 cc
Boric acid	7·5 g
Alum (potash)	2·5 g

One way of manufacturing anhydrous ammonium thiosulphate(15) is to react ammonium sulphite with sulphur in ammonia at 50°C in the presence of a trace of ammonium sulphide. The filtered liquid is then evaporated in a current of ammonia gas.

A *sodium and ammonium double thiosulphate* has been described(16) as being more soluble and more active than ordinary hypo.

Finally, Barnes has proposed amidine and guanidine thiosulphates.

Acceleration with active cations. The negative potential barrier surrounding each silver bromide grain can be reduced with a substance capable of providing positively charged ions: *ammonium chloride* works in this way, but good results are also obtained with *ethylenediamine* and quaternary ammonium compounds such as those of *pyridine* and *piperidine* (para. 41)(17) at a concentration of 40 g per litre. The fixing time is reduced by 50%.

Extra rapid fixing. Fixing can be accelerated by making the fixer alkaline or by raising the temperature of a hypo, or better still, ammonium thiosulphate (15–30%) bath, to 50–60°C (122–140°F). An increase of 10°C (18°F) increases the speed 2·3 times. The addition of thiocyanate can treble it. The maximum rate of fixing is, however, obtained using potassium cyanide which can fix a photograph in 1 second. Because cyanide is so poisonous, it is preferable to use 50% ammonium thiocyanate at a temperature below 54°C (129°F). The fixing time then varies from 2–15 seconds. To avoid disintegration of the gelatin, 35 cc per litre of formalin is added. The plate can also be printed immediately after clearing, preferably by projection. Emulsions which are to be fixed rapidly must, of course, be hardened beforehand.

148. Simultaneous development and fixation

The baths used for this purpose can be criticized for their irregular action and instability as well as for the loss of sensitivity which they cause. For the most part, these disadvantages can be overcome by adding a buffer whose purpose is to keep the pH constant. Alburger used sodium aluminate; Keller Maetzig and Möglich,(18) sodium zincate or plumbite. For example, with the solution: water 1000, caustic soda 25, alum 40, sulphite 50, glycin 10, metol 10, bromide 7, hypo 100, development and fixation take place simultaneously at 30°C (86°F), a negative in 2½ minutes ($\gamma = 0{\cdot}6$) and a positive in 1 minute (pH 11·8).

The equilibrium between development and fixing depends on the emulsion, and is valid only for one type. *The amount of fixer added must be adjusted in each case.* The figures given can be used as a basis for experiments.

Keelan(19) has given the following formulas derived from those of Alburger:

	No. 212	No. 365	No. 315	No. 348
Water to	1000 cc	1000 cc	1000 cc	1000 cc
Metol	1·5 g	1·9 g	10 g	33·5 g
Sulphite anh.	25 g	33 g	50 g	50 g
Hydroquinone	13·5 g	17·1 g	40 g	15 g
Alum (potash)	5 g	20 g	20 g	20 g
Caustic soda	9 g	16 g	35 g	30 g
Hypo	30 g	60 g	110 g	50 g
Benzotriazole	1 g	1 g	—	—
6-Nitrobenziminazole (0·5%)	—	—	20 cc	20 cc
Potassium bromide	3·35 g	—	—	—
Gluconic acid	0·1 g	—	—	—
pH	*11·2*	*11·3*	*11·55*	*11·35*

Formula 212 for slow contact papers: 2–3 mins. (20 sq. ft.).

Formula 365 for fast bromide papers: 3 mins. + 40 secs. in hypo.

Formula 315 for negative emulsions of the Aero XX type: 3 mins. at 24°C (75°F). Fog $= 0{\cdot}3$, $\gamma = 1{\cdot}3$.

Formula 348 for emulsions of the Super XX type: 10 mins. at 20°C (68°F) in a machine. Fog $= 0{\cdot}3$, $\gamma = 1{\cdot}7$.

Another simpler formula has been published for giving satisfactory results:(20)

Water to	1000 cc
Sulphite anh.	30 g
Hydroquinone	15 g
Caustic soda	12·5 g
Hypo	50 g

Development-fixing time, 2 mins. at 20°C (68°F) for Aero-XX with supplementary fixing, or 6 mins. in the single bath. The low densities have finer grain.

With all of these solutions, if the γ drops, the fixer must be reduced, or the developer and alkali increased. As they usually contain caustic soda their life is short. Colloidal silver rapidly forms a mud from which the solution must be decanted.

149. Stabilizing images by fixing

Stabilization of images by simple fixing, not followed by washing is due to the conversion of the residual halides to colourless silver complexes which are not light sensitive. Stabilization enables photographic negatives and prints to be obtained very quickly in all cases where a saving of time is essential.

Even in 1893 Bögish stabilized images with thiourea, but thiocyanates, thiosulphates and organic compounds R–SH such as thiosalicylic acid can also be used.

Stabilization with thiosulphates of sodium or magnesium. Those of ammonium or the amines give less stable results.

The thiosulphates have the advantage over the other stabilizers that they can be eliminated by washing. Basset and Lemon(21) have isolated four stable complex salts:

$$\begin{array}{ll} \left.\begin{array}{r} 5Na_2S_2O_3 \,.\, Ag_2S_2O_3 \,.\, 4H_2O \\ 3Na_2S_2O_3 \,.\, Ag_2S_2O_3 \,.\, 4H_2O \end{array}\right\} & \text{very soluble} \\ \quad\;\; Na_2S_2O_3 \,.\, Ag_2S_2O_3 \,.\, 2H_2O & \text{slightly soluble} \\ \quad\;\; Na_2S_2O_3 \,.\, 3Ag_2S_2O_3 \,.\, 2H_2O & \text{insoluble} \end{array}$$

For films(22) the best stabilizer is 30% hypo containing 5% bisulphite. After treatment, rinse for 10 seconds in pure water, or better, in a solution of sodium metaborate to avoid superficial crystallization. To stabilize quickly, work at a high temperature, 38°C (100°F) for example. Wipe off surplus water and dry.

For papers, develop 4–10 secs. in dilute D72 at 38°C (100°F), stop development by immersing for 4–10 secs. in 5% acetic acid and stabilize 4–10 secs. at 38°C in 30% (or less) hypo, containing 4·5% bisulphite and 1·5% anhydrous sulphite. Press between blotting paper.(23)

An excess of stabilizer eventually results in subsequent fading, whereas insufficient amount results in darkening. A short rinse improves keeping.

Prints always become discoloured, although they remain legible for several years.

Stabilizing with thiourea. Thiourea stabilizers are neutral, for in alkaline solution silver sulphide is produced. According to Levinos and Burners' method(24) the exposed layer is developed in amidol at pH 7 (stabilized against oxidation with 0·1% carboxymethylcellulose), and films are stopped in 3% chrome alum, papers in 3% bisulphite, for 3 mins. Stabilize films in 3% thiourea and 2% glycerin. For papers, halve the amount of thiourea and omit glycerin. Blot well but do not wash (unless followed by fixing and a thorough wash).

Thiourea stabilized images kept in a hot damp atmosphere become stained in the highlights due to decomposition of the complex. They fade if the bath is too concentrated. Separate stored sheets with sheets of cellophane. A litre of solution is sufficient for 13 sq. ft. of sensitive material.

Other stabilizers have been used more or less successfully: ammonium thiocyanate, allylthiourea, thiosemicarbazide, sulphonates, RSH derivatives such as thioglycolic or thiosalicylic acid, monothiohydroquinone, etc.

150. Washing

Unless the image is stabilized as in the preceding paragraph, or is only kept for a short time, the silver complexes remaining in the gelatin are likely to decompose into yellow-brown silver sulphide and sulphuric acid. The free thiosulphate decomposes to hydrogen sulphide, sulphur and sulphur dioxide which attack the silver image and sulphide it at the same time. This is why all traces of fixer must be carefully eliminated by *washing* for a long period.

Perfect keeping is only achieved by *complete washing*. In this operation, the soluble salts are eliminated from the gelatin by *osmosis*, the osmotic pressure being in the order of 15 kg/cm². Washing is much more efficient and rapid if fresh water is constantly brought to the surface so that the concentration difference is always the maximum (mechanical or air agitation).(24b)

The washing time depends on the thickness of the layer and the method of washing; usually it is 15–30 mins. for ciné films and 30 mins. to 2 hours for still materials. For washing by changing the water at intervals, at least 2 litres per sq. foot must be used (for 5 mins.) changing the water six times. This method is economical.

Washing becomes faster as the temperature is raised (2·3 times for a 10°C (18°F) rise). It is more difficult when the fixer is exhausted, that is, containing a high concentration of silver complexes.

Crabtree, Eaton and Muehler have shown that washing in *ammonia water* (pH alkaline) is a better eliminator for the thiosulphates and argentothiosulphates retained by the gelatin than plain water. Perhaps the co-ordination compound formed between the gelatin and the argentothiosulphate ion $(AgS_2O_3)^-$ is ruptured. Concentration of ammonia 70 cc/l.

The ease of washing also depends on the composition of the fixer and its pH. Thus with an alum fixer, elimination is not complete until the pH of the fixer is equal to or greater than 4·9. Washing is more efficient if the layer is first hardened in alum, then fixed.

Crabtree and Eaton have investigated washing with *sea water*.(25) The hypo is expelled from the gelatin more easily as the sea water tends to shrink rather than swell the gelatin. Five minutes wash in sea water is adequate but a final wash in soft water is necessary.

Washing in a closed circuit with ion exchangers. Gregor and Sherman have perfected a method of washing with a small amount of water, which is purified in a closed circuit, using ion exchangers. For the cation they used a phenol-formaldehyde resin, and for the anion, an aniline-formaldehyde resin, or guanidine or quaternary base-formaldehyde.

Dowex 50 (Dow Chem. Co.) is useful for the cations and Ionac A 300 (Amer. Cyanamide Co.) for the anion. A column 45 cm high and 2·5 cm in diameter passes 5–10 cc per minute. The cation exchanger is acidified with HCl. The liberated thiosulphuric acid is split to SO_2 and S, which produces AgS; the excess is taken up by the anion exchanger. The production of pure water is avoided by adding urea which is not absorbed by the resins.

Wetting agents. The inclusion of a wetting agent in the final wash avoids the formation of large drops on drying, and helps glazing. On the other hand, they encourage the formation of froth especially with hard water. Commercial wetting agents (see para. 356) are sold in concentrated solutions. For use, first prepare a 10% solution, 5 cc of which is used per litre of wash water. The immersion time should be about 2 mins.

Wetting agents facilitate the removal of excess water and prevent the formation of air bubbles when prints are squeegeed onto glazing plates.

Organic deposits in washing tanks. Running water brings about the formation of organic deposits which accumulate on the washing tank walls. They are removed by periodic brushing and rinsing. If this is not done, particles may be detached and stick to the emulsion surface. Deep tanks can be washed with hypochlorite solution diluted with six volumes of water.

Calcium and silica mud is formed in addition to the organic deposit, and this frequently marks the gelatin surface. It must be removed with damp cotton wool.

151. Control of the wash water

This generally consists of checking for the presence of hypo in either the water in the wash tanks, or in the drops collected from the emulsion.

Electrometric control

This is based upon the conductivity difference between the fresh water and the water containing salts.(27) To avoid electrode polarization, alternating current is preferably used. A neon lamp serves as an indicator.

Chemical control of hypo elimination

(*a*) *Permanganate test.* A few drops of water from the washed material are added to a drop of the following reagent:

Water	1000 cc
Sodium carbonate	10 g
Potassium permanganate	1 g

The pink colour must remain. If the liquid becomes greenish there is hypo in the wash water. The permanganate is reduced to manganage and the hypo is oxidized to tetrathionate.

(*b*) *Iodine test.* Starch paper, made blue with a weak iodine + KI solution is decolorized by a few drops of water containing hypo; the iodine is reduced to sodium iodide whilst the hypo is oxidized to tetrathionate.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

By using known solutions, the hypo content of the wash water can be found; comparison is made with standard hypo solutions.

The following methods are more sensitive:

(*c*) Decolorization of starch-iodine blue in the presence of *sodium nitride* following Jelley and Clark.(28)

(*d*) *Colorimetric estimation with silver nitrate* used by Lumiere and Seyewetz, then by Hackl (see following paragraph).

(*e*) *Mercuric chloride test* disclosed by Crabtree and Ross;(29) a mercury chlorosulphide $HgCl_2 . 2HgS$ is formed and 0·5 mg per litre hypo can be detected, which is one-twentieth of the limit with permanganate.

The silver nitrate method is sensitive to 1 mg per litre and the nitride test to 6 mg per litre.

152. Control of the washed image

The fact that the wash water contains only a trace of hypo does not necessarily mean that the image will be stable, but only as Crabtree said, that there is no point in prolonging the washing. It is therefore necessary to check if any fixer remains in the washed photographic layer. In this case it is the material itself which is treated with the reagent, using one of the following methods:

(*a*) *Iodine test.*(30) An N/10 iodine solution is prepared by dissolving 12·7 g iodine and 30 g potassium iodide in water to make one litre. Twenty-five cc of this solution is then diluted to 1000 cc. Five drops of the dilute solution are put on the four corners and the back of a 6 in. print. Washing is insufficient if the stain disappears quickly. The discoloration indicates at least 4 mg hypo per sq. ft.

(*b*) *Mercuric chloride test*:(31) The reagent is a solution of 2·5% potassium bromide and 2·5% mercuric chloride (poison). A piece of film 1 in. square is folded and placed in a test tube ¾ in. diameter. Increasing amounts of hypo (1 : 20,000 to 1 : 1000 solns.) are introduced into seven other similar tubes: 0, 0·005, 0·01, 0·02, 0·04, 0·1 and 0·2 mg hypo (calculated anhydrous), and 10 cc of reagent is added to the tube containing the film and to each of the control tubes. After leaving for 15 mins., the turbidity is observed which is due to a precipitate of mercuric chlorosulphide, showing the presence of hypo.

(*c*) *Silver nitrate test* applicable to papers:(32) The test piece is first treated for 3 mins. in 1% silver nitrate containing 0·5% sulphuric acid (by volume) and 2% acetic acid, then for 3 mins. in 5% sodium chloride, and finally in a fixing solution of 5% hypo and 2% sulphite. It is then washed and dried. The density of the silver sulphide stain is measured, showing the amount of residual hypo.

For films, the method has been modified as follows:(33) a drop of a solution containing 0·75% silver nitrate and 3% acetic acid is placed on the image face of the film. After two minutes the excess is removed and the resulting stain is compared with a colour scale printed on acetate sheet. The palest stain corresponds to the washing necessary for films which are to be stored for reference.

(*d*) *Selenium test*, recommended by Henn and Crabtree,(33b) already known in fixing-bath analysis (para. 154). It has the advantage not to react with the baryta coating and to produce well-defined spots. Make a paste with 10 g black selenium and 100 g sulphite in a little water at 90°C. Add 125 cc water, then dilute to 1/20. A selenosulphate solution is obtained which contains 0·2% Se. A mixture of selenium toner and hypo can also be used.

153. Elimination of hypo by oxidation

The best way of eliminating the residual hypo in a photographic layer is by treating with alkaline *hydrogen peroxide.* After washing, treat for 6 mins. at 18°C (65°F) in the following bath, mixed just before use:

HE.1	Water	500 cc
	Hydrogen peroxide 10 vol.	125 cc
	Ammonia S.G. ·920	14·5 cc
	Water	85·5 cc
	Water to	1000 cc

This solution does not keep and must not be placed in stoppered bottles as gas is evolved which may cause breakage.

Wash 10 mins. after treatment.

Area treated: 5 sq. ft. per litre.

With 300 cc 10 vol. peroxide 8·5 sq. ft. can be treated (HE. 2 bath).

Use of these baths may cause either a slight change in the image colour, a slight yellowing of the whites or softening of the gelatin causing prints to stick when glazed hot. The colour change can be avoided by adding 1 g bromide, and the yellowing is destroyed by 2 mins. treatment in 1% acetic acid or 2% sulphite followed by washing. The same treatment will harden the softened gelatin, but where sticking occurs, bathe in 50% alcohol.

The hypo can also be destroyed by oxidation with 1% potassium or ammonium persulphate in the presence of a trisodium citrate buffer. Unfortunately thionates are produced which can quickly sulphide a silver image.

154. Fixing bath analysis

Silver. To estimate the silver content of the fixing bath, it is precipitated as sulphide. A 50 cc sample is diluted to 100 cc and heated to 50°C. Thirty cc of 20% sodium sulphide are added and after half an hour at 70–80°C (158°–176°F) the precipitate coagulates. It is filtered off and dissolved in 25 cc boiling concentrated nitric acid. The solution is diluted and treated with hydrochloric acid, the precipitated silver chloride is filtered, washed, dried and weighed.

The nitric acid solution of the silver can also be titrated with ammonium thiocyanate in the presence of ferric sulphate.

Another method of estimating the silver content, due to M. Abribat(34) is to treat the exhausted fixer with sodium selenosulphate or selenotrithionate in the presence of gelatin. A colloidal suspension of the corresponding silver salt is produced and the amount can be determined colorimetrically, the density being proportional to the amount of silver present. Ten cc of 0·15% reagent containing 0·4% gelatin are added to 0·5 cc of fixer and two drops of soda lye; the colour is then compared with a standard.

Hypo. The sulphite must first be converted to a compound which does not react with iodide. To do this, 2 cc of fixer is treated with 2 cc of formalin in 200 cc of iced water. The solution is then acidified with a little acetic acid and titrated with decinormal iodine using a starch indicator. The process is repeated without the formalin treatment which gives the total hypo + sulphite content. The *sulphite concentration* is obtained by subtraction of the hypo figure (Atkinson and Shaner).

The *alum* (chrome or potassium) is estimated gravimetrically by precipitation with ammonia, and after washing the precipitate with a warm solution of ammonium nitrate, it is ignited to Al_2O_3 or Cr_2O_3.

The *total acidity* is obtained by titrating with soda using a bromocresol green or bromothymol blue indicator.

Boric acid is estimated after precipitation of the alum with ammonia, and the hypo and sulphite with mercuric chloride. The solution is filtered and boiled to remove the acetic acid. Excess sulphuric acid is added to neutralize to bromocresol green, and finally the titration is made with sodium carbonate in the presence of glycerin.

Sodium acetate. Fifty cc of fixer is precipitated with mercuric chloride, and the absence of sulphite is confirmed by testing with iodine and starch. Fifteen cc phosphoric acid is then added and the solution is distilled. The acetic acid is distilled over and is titrated in the usual way with a phenolphthalein indicator. (Atkinson and Shaner, *loc. cit.*)

Bromide. The fixer, treated with ammonia to eliminate the alum, is boiled, filtered and precipitated with mercuric or lead chloride. After further boiling and filtering, the solution is acidified with nitric acid and excess silver nitrate is added and back-titrated with ammonium thiocyanate in the presence of a ferric salt.

Ammonium salts. The fixer is made alkaline with soda and distilled and the ammonia vapour is absorbed in boric acid. The resulting borate is then titrated with HCl using a methyl orange indicator.

Sulphates. After precipitating the alum with ammonia and neutralizing, the sulphate, thiosulphate and sulphite are precipitated with a lead salt. Knowing the hypo and sulphite content, the sulphate concentration can be calculated.

Polarographic method. Shaner and Sparks have worked out a method of estimating alums, sulphite and silver polarographically.(35) The alum must first be separated from the fixer by precipitating with ammonia.

155. Recovery of silver from hypo baths

There are several methods of recovering the silver from spent fixing baths (containing about 5 g per litre). However, a fixing bath, evaporated to one quarter of its volume will deposit almost pure hypo on cooling. All the argentothiosulphate remains in the mother liquor. This can then be treated to recover the metal.

1. *Precipitation with zinc.* Zinc displaces silver from its salts forming the corresponding zinc salt and precipitating the metallic silver slowly. The fixing bath is left to evaporate in a shallow vat, and is then treated with zinc foil (0·2 sq. ft. per litre). A considerable black deposit forms on the zinc and some sulphur is precipitated. The metallic deposit is brushed off every day. After

about two weeks the operation is complete.(36) It is also possible to neutralize the old bath, re-acidify it with 2·5 cc H_2SO_4 per litre, and precipitate the silver with 200 g granulated zinc (per litre) contained in a cloth bag.

The precipitate, composed of silver and sulphur is collected, washed and dried. It can be fused in the presence of sodium carbonate, or the silver can be dissolved in nitric acid.

2. *Precipitation with guanidine compounds.*(37) The silver from the fixing bath can be precipitated by guanidine anthranilate or ethyl-xanthate. The bath treated in this way can be mixed with a fresh bath after addition of alkali to raise the pH to 10. One g of the guanidine salt is used for each litre of fixer.

Guanidine is a strong base related to urea $CO : (NH_2)_2$ in which the oxygen is replaced by an NH group giving $C(NH) : (NH_2)_2$. It is formed when ammonium thiocyanate NH_4CNS is heated to 180°C.

Hydroxylamine hydrochloride also precipitates silver in caustic soda solution.

3. *Precipitation with sodium sulphide.* This is the most commonly used method. The bath is first neutralized with sodium carbonate when the alum, if present, is precipitated.

A 20% solution of sodium sulphide Na_2S is then added until no further precipitate forms. As an excess of the reagent must be avoided, small additions are made to test quantities of the supernatent liquid. The precipitate is silver *sulphide.*

After decanting and filtering, the precipitate is dried. It contains 750–800 g silver per kg.

To recover the metal(38) the silver sulphide is mixed with the same weight of potassium nitrate KNO_3. The mixture is placed in a crucible and heated to 200°C then ignited. The mass becomes incandescent. The sulphide is reduced to silver and potassium sulphate and nitric oxide is liberated.

$$Ag_2S + 2KNO_3 = Ag_2 + K_2SO_4 + 2NO$$

Before it solidifies, the mass is poured into water where it dissolves. The precipitate, of crude silver, is washed by decantation.

By fusing the crude metal with a small quantity of borax, silver of 97–99% assay is obtained.

Another method is to roast the sulphide in air and then to heat this product to white heat with sodium and potassium carbonates.

4. *Precipitation with hydrosulphite.* The pH of the fixer is adjusted to 8 with carbonate, and hydrosulphite is added. A yellowish deposit is produced which is complete after 24 hours. A copper wire dipped in the solution should not be silvered (lack of reagent) nor should it be blackened (excess of reagent).

5. *Electrolytic recovery* of the silver from fixing baths enables the solutions to be re-used. It has the disadvantage, however, that elaborate equipment is required and there must be close control of the operation.

The recovered bath must be made up and re-acidified before re-use. It must not be used for fixing papers as yellow staining may result.

One system is to pass an electric current through a vat filled with the old filtered fixer. A series of stainless steel cathodes and graphite anodes are immersed in the bath which must be vigorously agitated. The silver is, of course, deposited on the cathodes. A voltage of 0·3–0·5 is used. Agitation is necessary to avoid low Ag^+ ion concentration near the cathode.

A high current density is generally used in large installations.(39) On the contrary, small units give the best results when working at 1–2 mA per dm^2 only. They present the great advantage not to need any agitation. In the Doffin 'Purhypo' process,(40) the cathode is a stainless steel grid and the anode is a carbon rod (F.P. 813,483).

The fixer may become coloured during regeneration. This coloration occurs at the anode and is due to the presence of developing agents. It is slight when low current densities are used and when the solution contains bisulphite.(41)

Rasch and Crabtree(41b) recommend moderate current densities without agitation: with an acid sodium thiosulphite solution containing 8 g sulphite and 0·5 g silver per litre, the current density must be 0·01 to 0·02 A/dm^2; with ammonium thiosulphate c.d. = 0·02 to 0·04 A/dm^2. Sulphite prevents chain reactions and sulphide formation. The latter is also prevented by the small quantity of gelatin deposited on the cathode.

In all cases of electrolytic recovery rigorous control must be exercised over the solution concentration, the pH, the agitation and the temperature.

6. *Electrolysis with no external electric source.* The external electrical source can be dispensed with by using a stainless-steel electrode and a zinc electrode, joined externally via a rheostat and a milliammeter.(42) The zinc electrode is wrapped in cloth or in cellulose paste. With an immersed area 16×22 cm, 0·5 A can be delivered over 48 hours, but 12 mA per dm^2 is enough. Twenty-two g of zinc are used for 10 g silver. Most of the silver is deposited on the stainless-steel cathode from which it is separated by slight flexing.

Recovery of the iodide: precipitation with thallous sulphate(43) gives thallous iodide. The bromide precipitates after the iodide. This operation has no practical importance.

156. Drying

After removing the surface water by mechanical or pneumatic means, the developed, fixed and washed photographic element is dried in a current of filtered air. The quantity of water retained by the gelatin is between 5 and 20 g per sq. foot, depending on the thickness of the layer and the nature of the gelatin. Generally 1000 feet of negative film absorb 1000 g of water; positive film, with its thinner coating, only one half of this.

With photographic papers the water absorbed by the base must be taken into account as it greatly retards drying.

The temperature used for drying is between 24° and 28°C (75° and 82·5°F). Drying is stopped when the water content is again about 15 %, otherwise the gelatin becomes brittle.

With a relative humidity of 60–75 %, film drying takes 15–40 mins. for negatives and 8–20 mins. for positive. Drying must be preceded by either air-squeegeeing (sucking or blowing) or by mechanical wiping with cotton wool. A cine negative film still contains over a litre of water per 1000 feet after the surface water has been removed; a positive film contains about 450 cc per 1000 feet. The speed of drying depends on the thickness of the layer (therefore on hardening) and the rate of air circulation and the relative humidity. Drying which is too rapid can result in curled edges and water-drop marks.

Where necessary, a rapid drying process can be used for a plate by immersing it in 80 % *alcohol* for three minutes, draining and drying in a stream of warm air.

Another expedient is to treat the plate in a concentrated solution of *potassium carbonate*—1000 g per litre—and after draining, to wipe and polish the surface of the gelatin. A negative treated in this way will not be permanent. At the first opportunity it should be washed and dried normally.

Deformations. The dry photographic image can suffer from two sorts of deformation: those due to the contraction or expansion of a flexible support, and those due to *internal stressing of the gelatin* during the drying of the unexposed or processed emulsion. The stresses become greater as the thickness of the layer increases.

If drying is too rapid, the presence of drops of water results in areas of lower density. Hardening reduces these deformations, for the gelatin swells less; on the other hand, where the marks are present, they cannot be removed whereas with an unhardened emulsion there is always the possibility of restoring the gelatin to its original condition by immersing in water, then in alcohol.

These marks are inconvenient in *photogrammetry.* To avoid them to some degree, the unexposed emulsion is soaked in water for half an hour, washed with alcohol and dried. The drying must be slow and in damp air.

The errors due to deformation of the gelatin are of the order of 1–4μ .

Shrinkage of motion-picture base amounts 0·06–0·2 %.(44)

Effect of drying on density. R. Pinoir has shown(44) that the temperature and relative humidity of the drying air have a considerable effect on density by altering the physical state of the gelatin.

Raising the temperature and the relative humidity increase the density, although these two factors work in different directions, the one opposing the other, and this affects the drying rate. For example a density of 3·08 obtained at 30°C 75 % R.H. falls to 2·35 at 22°C and 35 % R.H.—a difference of 0·73.

The effect is greatest with the large grains. It is less pronounced with hardened layers. It necessitates rigorous control of all factors when drying sensitometric strips, and even films.

The effect of drying upon density is explained by Silberstein's theory of the rotation of the grains, and also by the theory of compression of the grains which have a filamentary rather than a solid structure.

Rapid drying. Great progress has been made in this operation in the last few years and it is due to the necessity for projection immediately after taking of radar and television film images, to say nothing of the many other applications. Extra rapid treatment is mainly given to special films which have thin, hardened emulsions.

We have already seen that by raising the temperature to 50 or 60°C (122 or 140°F), developing and fixing can be carried out in a few seconds.(45) Thus Tuttle and Brown(46) carried out the complete cycle in 4 secs. (development 0·8 sec., fixing 1·7 sec., washing 0·3 sec. and drying 1·2 sec.). At a temperature of 60°C (140°F) with a liquid flow of 50 cc per sec. and avoiding fixing, they even cut the time down to 0·34 sec. A film treated in this way can be kept for a week if tightly wound. After this time, it must be well washed.

When using 70 mm radiographic film, the total time can be one minute without inconvenience, giving 15 sec. for each stage; temperature 50°C (122°F).

Rapid drying can be achieved in four different ways:

(*a*) On a *heated drum*: 2 sec. for a film moving at 5 ft./min. (Ives and Kunz). Disadvantage: poor conductivity of the cellulose support.

(*b*) Hot-air blast at 60 ft./sec. and a temperature between 50 and 90°C (122 and 194°F). Miller(47) made a device for this, having 256 jets on the front and 128 on the rear of the film, with a total air flow of 2·3 m^3/min. At 60 ft./sec. it takes 8 secs. to dry Plus-X film to 10% humidity at 93°C (200°F), 12 secs. at 65°C (150°F) and 18 secs. at 52°C (125°F). There is an optimum air flow at each speed.

The physical properties of a film dried in this way are excellent.

The slowness of normal drying is due to the presence of a stagnant layer of saturated air between the gelatin and the atmosphere. This can only be disturbed by violent *turbulation*—not to be confused with simple agitation—using an apparatus similar to Miller's.

Katz(48) has thought of another method of turbulent drying in which the film is wound on a 35 cm diameter drum, heated internally with a 3 kW heater to compensate for the cooling produced by rapid evaporation. A 3 h.p. fan blows air onto the moving film at a rate of 0·425 m^3/min. and a pressure of 0·35 kg/cm^2. Five kg of water per hour is evaporated in this way at 48°C (118°F).

(*c*) *Drying with organic solvents.* This interesting method, due to Davies and Soper(49) enables films of a limited area—radiographs for example—to be dried rapidly, taking a minute at the most.

The blotted film is immersed in a solution of 25% *diacetone alcohol* in petroleum ether (inflammable), and is gently agitated. The diacetone removes the water from the swollen gelatin and falls to the bottom of the vessel, as a layer which is not miscible with petroleum ether.

157. Reticulation

Reticulation is an irregularity of the surface of a gelatin layer, produced by a rapid change of temperature when the material is passed from one solution to another, for example, warm fixer after a cold wash. It is due to the gelatin being distended parallel to the support, only the surface being able to move.(50)

Reticulation can be produced artificially by treatment in dilute acid or in a concentrated solution of potassium bromide or iodide. Smethurst(51) obtained the same result by tanning superficially in a 5% acetone solution of chromic acid or an alcoholic solution of formaldehyde, or swelling in phosphoric acid, or, best, in an alcohol solution of gaseous formaldehyde.

The internal tension does not occur if drying is carried out at a temperature above the melting point of the gelatin, that is, without turning the layer to a jelly.

158. Glazing and drying prints

Positive paper prints can be given a high gloss by being in intimate contact with a polished surface during drying. This surface can be a sheet of glass, a chromed cylinder or a chromed sheet. The gloss of the print surface depends on the gloss of the glazing surface.

Cold glazing. The washed print is applied wet to a very clean sheet of glass previously damped with a *wetting agent* (sulphonated lauryl alcohol, ox-gall, etc.) or a sulphoricinate. The dry paper comes away by itself. This process gives the best results, but it is slow.

Hot wet glazing. This is carried out with special glazing apparatus—convex sheets or rotating cylinders heated to 75°C (167°F). The prints are kept in perfect contact with a stretched cloth which must be removed and washed periodically. The gelatin must be well hardened or it will melt and stick to the metal. Excess hardness due to old material or too much hardener during emulsion preparation produces unglazed spots. If the paper is freshly coated (less than two weeks) the gelatin may melt. It is advisable to damp the washed prints with a wetting agent before putting them on the hot plate to ensure uniform application. Faults in the baryta coating can result in unglazed areas.

Dry glazing. Hot dry glazing of photographic prints is much more rapid than wet glazing. Although the gloss is not as good, it is used for commercial work such as the production of postcards.

Dry glazing is only possible if the gelatin contains 10–15% moisture and if the temperature is above 80°C (176°F). The best results are obtained between 110 and 120°C (230 and 248°F). The critical optimum temperature depends on the gelatin and its moisture content. If it is too wet, the gelatin sticks, and if too dry, no gloss results. If the cylinder is too hot, yellowing results. Undoubtedly, there are many other unknown factors involved, for dry glazing is generally a source of 'inexplicable' troubles. Calcium deposits can also reduce the brilliance. Also, contrary to the general belief, a cylinder which is too clean can cause prints to stick. Any use of wetting agents, soaps, or organic solvents on the gelatin, before glazing, is undesirable.

Drying on the glazer. A print placed in the glazer, gelatin to the blanket, will be dried without glazing. Matt surface papers and document papers can be treated in this way. Gelatin which is too soft or freshly coated, will stick to the cloth making it necessary to pull the print off. If the paper paste has not an even structure the dry print will roll up or be deformed irregularly.

159. Analytical examination of image marks

Henn(52) has worked out a method of determining the nature of stains and spots accidentally present on photographic images. The test is carried out on a piece of scrap. Two drops of solvent are placed on the stain. After dissolving, a drop of the solution is transferred to a glass or porcelain plate to be treated with the identifying reagent.

Calcium. Solvent: 40% acetic acid. Neutralize with AmOH. Precipitate with 4% sodium oxalate. Or dissolve the mark in warm HCl. Add 2 drops 10% AmOH then 1 drop of 0·1% Alizarin S. A blue colour is produced with Ca, with crystals visible under the microscope.

Aluminium. Solvent: 40% acetic acid or 10% (soda + sodium sulphate). Add 1 drop of alcoholic solution of morin (then 1 drop of acetic acid if the soda solvent was used): coloration—brown to yellow-green. The lake obtained fluoresces in U.V. radiation or in sunlight filtered with a Wratten 35 filter.

Chromium. Solvent: dilute HCl. Add 1 drop of bromine water. The chromic ion produced is neutralized with soda and the excess bromine with phenol, and 1% alcoholic diphenylcarbazide is added with 2N H_2SO_4: a blue-violet colour is produced.

Iron. Yellow stains soluble in 5% potassium oxalate containing 5% HCl.

Blue stains—decolorized with soda.

The hydrochloric acid solution gives a blue precipitate with potassium ferrocyanide.

Silver. Yellow or brownish stains, frequently dichroic, soluble in ferricyanide + hypo. A nitric acid solution of the stain gives a precipitate with hydrochloric acid. Also reacts with p-dimethylamino-benzilidene-rhodanine.

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Chapter XII

REVERSAL

160. Reversal, reduction and intensification

The name *reversal* is given to the sequence of operations which enables a *positive image* to be obtained in the same layer which has recorded the negative image. The principle is quite simple:

After developing the negative image, the silver of which it is composed is dissolved in a *reducer* (or reversal bath). The residual silver bromide is exposed and developed to give the corresponding positive. In the areas where the negative was dense (subject highlights) there is no residual silver salt to be blackened and the final image is transparent; on the contrary, in the areas where the negative was clear (subject shadows), the whole of the silver salt is left to be blackened and the image is dense.

To reverse a negative to a positive, two conditions must be complied with:

(*a*) *The thickness of the sensitive layer* must be reduced so that the maximum density of the negative corresponding to the subject highlights is equal to the total density which can be given by this layer: the light parts of the subject are in this way reproduced in the positive by transparent areas and the whites are pure. On the other hand, the maximum black must be high enough to enable the subject shadows to be reproduced by sufficiently high densities. In practice, the absolute maximum black is slightly greater than the useful maximum density; we shall see why later.

(*b*) The negative image must be developed to a higher contrast than that of a normal photograph, in fact to a contrast at least equal to that which is required in the positive image.

161. First development

The negative image can be developed in any type of developer.

It is, however, preferable to use a developer containing a silver bromide *solvent*: ammonia, hypo, thiocyanate, or p-phenylenediamine.

The object of this addition is to dissolve a certain amount of the silver bromide of the sensitive layer slowly and progressively as development proceeds. The layer contains more silver salt than is necessary to give the maximum useful density: the solvent reduces this concentration of sensitive salt by the required amount, for once the maximum contrast is reached any continuation of development merely dissolves the excess silver bromide. In this way the maximum black can be increased or reduced to a certain extent to correct exposure errors.

The most widely used developers contain metol and hydroquinone together with potassium thiocyanate: 2 g of metol, 8 g of hydroquinone and 5 g of potassium thiocyanate are the optimum concentrations.

The effect of thiocyanate and bromide are shown in the following tables based on the work of Verkinderen:⁽¹⁾

	γ	D max.	D min.
Thiocyanate			
0	1·6	3·15	0·3
0·2%	1·6	3·0	0·1
0·5%	1·6	2·5	0·0
0·7%	1·4	1·9	0·0
Bromide			
0·2%	1·3	1·9	0·0
0·5%	1·6	2·5	0·0
1%	1·6	2·6	0·0

A development time should be chosen so that a D max. of about 2·4 is obtained. When a coarse-grain emulsion is used it develops slowly. A caustic developer such as D 8 containing a solvent is therefore used.⁽²⁾ A formalin+benzotriazole pre-hardener is recommended.

The following thiocyanate formula⁽³⁾ also gives good results:

Water to	1000 cc
Metol	1 g
Hydroquinone	8 g
Sodium sulphite anh.	50 g
Sodium carbonate anh.	35 g
Potassium bromide	5 g
Potassium thiocyanate	9 g

Development time: 4–5 mins.

Hydroquinone-hypo developer:

Water to	1000 cc
Sodium sulphite anh.	70 g
Hydroquinone	10 g
Sodium carbonate anh.	35 g
Caustic potash	5 g
Potassium bromide	8 g
Hypo crystals	2 g

Metol-hydroquinone-ammonia developer:

Water to	1000 cc
Metol	4 g
Sodium sulphite anh.	25 g
Hydroquinone	2 g
Ammonia S.G. 0·920	8 cc
Potassium bromide	1 g

p-Phenylenediamine caustic developer:

Water to	1000 cc
p-Phenylenediamine hydrochloride	10 g
Sodium sulphite anh.	25 g
Caustic soda	10 g
Potassium bromide	4 g

After development the negative image is *rinsed* for 1 or 2 minutes, or is treated in a *stop-bath* for 30–60 seconds then washed for 2 minutes.

Hardening the gelatin in a bath such as the following is sometimes recommended:

Water to	1000 cc
40% Formalin	25 cc
Caustic soda	1·5 g
Sodium sulphate anh.	150 g

Harden for 2 minutes then wash 2–3 minutes.

162. Reversal baths

The reversal operation consists of dissolving the silver which makes up the negative image. To do this a reducing solution(4) of the permanganate, dichromate, or cerium sulphate type is used.

(*a*) *Permanganate reversing bath.* Potassium permanganate, $KMnO_4$, in a sulphuric acid solution oxidizes the silver, converting it to silver sulphate Ag_2SO_4, whilst the permanganate itself is reduced to manganese sulphate $MnSO_4$

$$2\,KMnO_4 + 8H_2SO_4 + 5Ag_2 = 5Ag_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Furthermore, a small amount of permanganate is reduced by the gelatin to manganese dioxide which gives the image a brown colour.

$$2KMnO_4 + H_2SO_4 = 2MnO_2 + K_2SO_4 + 3O + H_2O$$

In practice, the bath has the following composition:

Water to	1000 cc
Potassium permanganate	3 g
Sulphuric acid S.G. 1·87	10 cc

Treatment time: 4 minutes. Wash: 2–5 minutes.

The permanganate bath reduces the dense parts of the image more rapidly than the light areas; the rate of reaction is higher at the bottom of the layer than at the surface.

Potassium permanganate(5) is in the well-known form of violet crystals. Dilute solutions are bluish pink. The crystals must not be allowed to come in contact with sulphuric acid which decomposes them violently. Permanganate is readily reduced by sulphurous acid, hypo, ferrous sulphate, organic substances, etc.

(*b*) *Dichromate reversing bath.* Potassium dichromate $K_2Cr_2O_7$ is a vigorous oxidizing agent. In sulphuric solutions it converts silver to the soluble silver sulphate. At the same time the dichromate is reduced to chromium sulphate $Cr_2(SO_4)_3$ and potassium sulphate K_2SO_4:

$$K_2Cr_2O_7 + 5H_2SO_4 + 2Ag = Ag_2SO_4 + Cr_2(SO_4)_3 + K_2SO_4 + O_2 + 5H_2O$$

The gelatin reduces a very small amount of dichromate forming the greenish chromium oxide Cr_2O_3 which must be removed

$$K_2Cr_2O_7 + H_2SO_4 = Cr_2O_3 + K_2SO_4 + H_2O + 3O$$

The dichromate solution is composed of:

Water to	1000 cc
Potassium dichromate	5–8 g
Sulphuric acid S.G. 1·87	10 cc

Reversal time: 2–3 minutes. Wash: 2–5 minutes.

Like permanganate, dichromate reacts mainly deep in the layer on the dense parts of the image.

Potassium dichromate is in the form of orange-red triclinic crystals.

(*c*) *Cerium sulphate reversing solution.* Yellow cerium sulphate $Ce_2(SO_4)_3$ in weak sulphuric acid oxidizes the image to silver sulphate and is itself reduced to colourless cerous sulphate, $CeSO_4$.

$$\begin{aligned} Ce^{+++} + e &= Ce^{++} \\ Ag \quad - e &= Ag^{+} \end{aligned}$$

The ceric ion takes an electron from the atom of silver metal and is converted to the cerous ion whilst the Ag loses this electron to become the ion Ag^+.

The bath is made up of:

Water to	1000 cc
Ceric sulphate	10 g
Sulphuric acid	4 cc

which can be diluted if desired.

Ceric sulphate dissolves very readily in water. An excess of water without sulphuric acid precipitates a basic sulphate.

The ceric bath acts uniformly on the silver image. It has the disadvantage of being more costly than the previous solutions.

163. Clearing the reversed image

When the gelatin layer is removed from the reversal bath, it is stained with a precipitate of brown manganese dioxide or greenish chromium oxide.

A solution containing 25–50 cc per litre of *sodium bishulphite lye* is used to decolorize the layer.(6) The image is treated in this solution for two minutes, then washed for three minutes. The oxides are converted to the soluble manganese or chromium sulphates.

The bisulphite (or sulphite) has the property of partially restoring the sensitivity of the emulsion which is destroyed by the oxidizing agent.

164. Second exposure

After the negative image has been dissolved in the reversal bath, the residual silver bromide is *re-exposed to light* so that it, in turn, can be developed.

An exposure of one to three minutes at 18 in. from a 100-W lamp is usually enough for ciné films.

Second exposure method. Instead of fogging the reversed film completely, the amount of light is regulated according to the density of the residual sensitive salt. If the film is overexposed, the amount of residual bromide is small, and it is therefore strongly exposed; if the film is underexposed, there is a much greater amount of residual bromide and, in this case, the intensity of the light is reduced so that the positive image will not be too dense. The intensity of the lamp is varied automatically: an infra-red beam passes through the reversed film and is modulated according to the latter's density; it is received by a thermocouple which adjusts the exposure *via* a relay. The infra-red radiation has no effect on the silver bromide. Each scene on a roll therefore receives a suitable exposure so that exposure errors are corrected.

This second exposure control, originated by Capstaff, is based on the following observation: in the strongly exposed negative areas the *large grains* of silver bromide—the most sensitive—are exposed and developed. None remain in the residual bromide. In the underexposed negative images, on the contrary, the large fast grains are only slightly affected, and a large proportion remain in the residual halide. If the intensity of the second exposure is adjusted so that only grains of a certain sensitivity (or size) are affected, it is obvious that low negative exposure areas will be affected more than high negative exposures.

A variation of the second exposure technique (Fred-Jeannot) is to re-expose the film with a weak *even* light, equal to that necessary for an underexposed image. After development, the film receives a *third exposure* controlled by the density of the image, so that an underexposed image receives no appreciable further exposure, whilst an overexposed image receives a strong supplementary exposure.

165. Reversal without re-exposure

Second exposure can be avoided by treating in a solution of a *fogging agent*(7) such as a hydrazine or a semicarbazide, for example, 10 g per litre of semicarbazide hydrochloride.

The fogging agent can be added directly to the second developer.

166. Second development

Second development can be carried out in any developing solution which will result in complete or controlled reduction of the residual halide in 4 or 5 minutes. Metol-hydroquinone developers are suitable, for example:

	A	B
Water to	1000	1000 cc
Metol	1	3 g
Hydroquinone	5	3 g
Sodium sulphite anh.	55	25 g
Sodium carbonate anh.	25	25 g
Potassium bromide	1	2 g

The contrast of the positive image can be reduced by shortening the developing time or by using a less active solution.

After this operation the film is rinsed, fixed—preferably in a hardening bath—and then washed and dried.

167. Single bath reversal

The exposed film is developed in a developer-fixer (see para. 148). It is then re-exposed on both sides and development is finished in the same solution. It is then washed and dried.

For example, Miller(8) used the following procedure with Super Panchro Press: Developer D 19+5 g caustic soda and 25 g hypo. Develop 15 minutes at 20°C, expose for 10 seconds, redevelop and wash.

A reversed image is superimposed on the normal one; it is more contrasty but this is therefore partly counteracted. This method demands exact exposure.

168. Reversal identity photographs

A widespread method of producing identity photographs rapidly, uses reversal of waterproof card material, coated with a reversal type negative emulsion. The sequence of operations is as follows: exposure 1/10th second—1st development in M.Q. developer 90 seconds at 18°C—rinse 17 seconds—reversal 45 seconds—wash 17 seconds—second exposure 45 seconds—wash 17 seconds—dry 45 seconds.

169. Reduction

Reduction is the name given to the process of *lowering the density* of a photograph. If reduction is carried out to finality, the image is dissolved away and disappears completely; this is exactly what happens with *reversal baths.*

The reduction of the density of overexposed or overdeveloped images is not widely used in current practice except in photomechanical processes, as it often leads to uneven results.(9) On the other hand, the complete removal of silver images by means of reducers is essential for colour photography as we shall see in the part III: reduction is then called *bleaching.*

Reducers are normally divided into three classes according to their action on the image: cutting, proportional and superproportional.

Cutting and proportional reducers lower the resolving power as this is highest in the upper part of the image—the part which is affected. Superproportional reducers improve resolving power in the low densities and lower it in the mid-densities.(10)

Reduction can be carried out by local application, or after applying a protective layer. To do this, natural *latex* in ammoniacal solution can be applied with a brush; this coagulates in air. The protective layer is finally removed by rubbing with carbon tetrachloride.

Harmonizing. This is the reduction of only the high densities of a negative, to make them more transparent. Instead of direct partial reduction of the image, it is preferable to first bleach it completely, for example in cupric chloride, then, after fully exposing the bleached negative, re-develop it in a slow-acting developer so that development is stopped before the high densities are completely blackened. Slow developers such as diluted glycin, D.76, and p-phenylenediamine, are suitable for this sort of work although any other developer either diluted or acidified could also be used.

170. Cutting reducers

The effect on the image takes place at the surface of the layer. As the reduction of density is uniform without changing the contrast, they can be used for overexposed or fogged images.

The image silver is always dissolved by means of an *oxidizing agent*; this removes an electron from the silver metal and converts it to a silver ion:

$$\mathrm{Ag} - e \rightarrow \mathrm{Ag}^+$$

As we have already pointed out in the chapter on oxidation and reduction, an oxidizing agent is a substance which acquires electrons as it tends to pass to a lower valency. The electron removed from the silver therefore converts it to a more electronegative reduced form.

The silver ion readily reacts with a negative ion present in the solution to give either a silver halide or a soluble silver salt.

(*a*) *Bromine water*, *chlorine water* and *iodine water* can all be used to oxidize the image, converting it respectively to silver bromide, chloride or iodide which can then be dissolved in hypo. With iodine water the following bath can be used:

Water to	1000 cc
Potassium iodide	15 g
Iodine	5 g

in which the potassium iodide behaves as a solvent for the iodine whose solubility in pure water is low.

(*b*) Cupric chloride reducers:

Most salts in which the metal ion can reduce its valency can be used as oxidizing agents, the most common being the *cupric* and *ferric* salts. Thus with cupric salts the valency changes from 2 to 1: $\mathrm{Cu}^{++} + \mathrm{e} = \mathrm{Cu}^+$ and the cupric salt is converted to the insoluble cuprous salt.

Water to	1000 cc
Cupric chloride	30 g
Hydrochloric acid	3 cc

The image is bleached and, if carried out completely, gives silver chloride which can be dissolved in hypo.

If the cupric chloride is replaced by cupric bromide $CuBr_2$, the silver image is converted to silver bromide and insoluble cuprous bromide which is treated in the same way.

Copper sulphate formula. The cupric bromide can be replaced by a mixture of cupric sulphate ($CuSO_4 . 5H_2O$) and potassium bromide which acts in the same way. The oxidized silver is converted to silver sulphate which is precipitated by the alkali bromide as insoluble silver bromide.

Water	1000 cc
Copper sulphate cryst.	40 g
Potassium bromide	40 g
Acetic acid	0·5 cc

The silver bromide is then dissolved in hypo. With copper sulphate and sodium or potassium chloride a silver chloride image will be obtained.

Single-bath sopper reducer. The cupric salt and the hypo can be used in the same bath in the following way: the cupric salt is converted to a *cuprammonium complex salt* which is not precipitated by hypo, as the copper ion is in the form of a complex ion. To prepare it, it is only necessary to add ammonia to a 5% cupric chloride solution until the precipitate of copper hydroxide is just redissolved (with no excess). A 20% hypo solution is also prepared. Just before use, take cuprammonium solution 50 cc, hypo solution 500 cc, water 450 cc. If the cupric solution is used alone, a silver chloride image will be obtained which can be redeveloped.

171. Potassium ferricyanide cutting reducers

Potassium ferricyanide $K_3[Fe(CN)_6]$ is a complex salt in which the iron atom is in the complex ion $[Fe(CN)_6]^{---}$ and consequently can be mixed with hypo without mutual action.

The iron in the ferricyanide ion is trivalent: six negative valencies of the $6(CN)^-$ ions are partially neutralized by three positive valencies of the Fe^{+++} ion; three negative valencies of the total complex ion therefore remain.

If the Fe^{+++} ion is provided with an electron, it is naturally reduced to the ferrous Fe^{++} ion: $Fe^{+++} + e \rightarrow Fe^{++}$.

As the Fe^{++} ion has only two positive valencies against the $6(CN)^-$ of the iron cyanide ion, the resulting valence of this ion becomes $6(-) - 2(+) = 4(-)$, giving $[Fe(CN)_6]^{----}$ which is the ferrocyanide ion.

Thus *potassium ferricyanide is an oxidizing agent* which is itself reduced to potassium ferrocyanide by a reduction in the valency of the iron ion. The electron is provided by the oxidized compound which, in this case, is silver which passes, as we have already seen, from the metallic state to the ionic: $Ag = Ag^+ + e$. The change from the ferricyanide to the ferrocyanide is summed up as follows:

$$[Fe^{+++}(CN)^-{}_6]^{---} + e = [Fe^{++}(CN)^-{}_6]^{----}$$

The silver image oxidized by ferricyanide is converted to silver ferrocyanide which is insoluble in water but soluble in the usual silver halide solvents.⁽¹²⁾

Ferricyanide solutions are decomposed by light, giving $K_2[Fe(CN)_5]$. H_2O.(13) For this reason they should not only be kept in darkness but should only be used in dim light.

Bleaching is accelerated by having the solution slightly alkaline. It is dependent also on the size of the silver grains and the thickness of the gelatin layer.

Farmer's reducer is made up of a mixture of *ferricyanide* and *hypo*. It is unstable and must be prepared just before use. The presence of an alkali increases its stability.

A.	Water	1000 cc
	Hypo	100 g
B.	Water	200 cc
	Ferricyanide	20 g

Take A 100 cc, B 20 cc, water 200 cc.

This mixture produces a density reduction which in 5 minutes is equivalent to a speed reduction of 2·5 times. After 25 minutes treatment the drop in speed is about ten times.

To accelerate the action add 2 cc ammonia. If the water is not added, reduction takes place four times as quickly.

The photograph must be carefully washed, as reduction continues at a low rate during washing until the oxidizing agent is completely eliminated.

For continuous use, the above solution is too unstable. It is therefore preferable to use two solutions: first, the oxidizing agent, then the hypo solvent. For this the following bleach formula is used:

Water	1000 cc
Ferricyanide	50 g
Ammonia	5 cc

The image is completely bleached in 2 minutes. It dissolves rapidly in 10% hypo.

Ferricyanide-bromide reducer. The bleached image is made up of silver bromide.

Water	1000 cc
Ferricyanide	20 g
Potassium bromide	20 g

The following formula, which was used for the complete bleaching of certain colour films is stablized with disodium phosphate Na_2HPO_4 and sodium bisulphate $NaHSO_4$ which give a stable pH of 6·2. The image is bleached in 6 minutes at 20°C (68°F):

Water to	1000 cc
Ferricyanide	100 g
Potassium bromide	10 g
Sodium bisulphate	35 g
Disodium phosphate	40 g

Ferricyanide-iodide reducer: used to bleach the image to silver iodide (treatment time 2–5 minutes):

Water	1000 cc
Ferricyanide	20 g
Potassium iodide	15 g

172. Proportional reduction

(*a*) *Ferric sulphate* reacts evenly throughout the image. This results in a drop in contrast as well as a general reduction of density.

The silver is oxidized to *soluble* silver sulphate whilst the ferric sulphate $Fe_2(SO_4)_3$ is changed to ferrous sulphate $FeSO_4$. It is not necessary to use a fixing solution.

The stable ferric potassium or ferric ammonium alums are generally used in place of ferric sulphate; they are double salts: $Fe_2(SO_4)_2 . K_2SO_4 . 24H_2O$

Water to	1000 cc
Ferric alum	15 g
Sulphuric acid	10 cc

Ferric chloride $FeCl_3$ can also be used as a reducer in a 1% solution. It is, however, preferable to use the Belitzki mixture which can be used in the presence of hypo.

(*b*) *Iron-hypo reducer* (*modified Belitzki formula*):

Water to	1000 cc
Ferric chloride cryst.	25 g
Potassium citrate	75 g
Citric acid	20 g
Sodium sulphite anh.	30 g
Hypo	200 g

The ferric chloride, the potassium citrate + sulphite, the citric acid and the hypo are each dissolved separately in water. The citrate is added to the ferric chloride, then the citric acid and finally the hypo.

A potassium ferri-citrate is formed—a complex similar to potassium ferri-oxalate (which will be studied in the second part), and which, furthermore, can be used as follows:

Water to	1000 cc
Potassium ferri-oxalate	50 g
Oxalic acid	40 g
Hypo	100–200 g

As with the cuprammonium complex, the metal is sequestered in the ferri-citric and ferri-oxalic complexes; this is why hypo does not precipitate it, and can be present in the same solution.

For removing the silver from colour prints on paper, a bleach-fix solution containing the *ferric salt of ethylenediamine-tetraacetic acid* is used; this is a complex which has the same function as the ferri-citrate in Belitski's reducer (para. 555).

(*c*) *Cerium sulphate reducer*. The formula is the same as that of the reversing bath. It must be diluted since slower action is desired. As with the ferric sulphate reducer, fixing in hypo is unnecessary.

(*d*) *Dichromate reducer*. Same formula (more diluted) as the reversal bath. Clear in sulphite or bisulphite.

Another reducer includes dichromate and potassium bisulphate. This enables it to be packaged in the solid state: potassium dichromate 250 g + potassium bisulphate 625 g. Dissolve 9 g of the mixture in 1 litre of water. For slower action, dilute with an equal volume of water.

(*e*) *Permanganate reducer*:

A.	Water to	1000 cc
	Potassium permanganate	4 g
B.	Water	1000 cc
	Sulphuric acid	2 cc

Just before use take: A, 3cc; B, 3 cc; water, 100 cc.

Rinse and clear in 1% bisulphite.

Contrary to the usual statements in the literature, the dichromate and particularly permanganate reducers are not proportional, but slightly superproportional, and because of this should be included in the following group. Permanganate only appears to behave as a cutting reducer in acetic solutions.

(*f*) *Conversion to chloride in the presence of permanganate or dichromate.* The silver image can be converted to chloride with *permanganate in hydrochloric acid solution*—$KMnO_4+4HCl+Ag \rightarrow AgCl+MnCl_2+KCl+H_2O$ using a bath containing 1% permanganate and 2·5% hydrochloric acid. The same result is obtained with *dichromate and hydrochloric acid*, or dichromate, sulphuric acid and an alkali halide such as potassium bromide. In the latter case a silver bromide image is produced.

(*g*) *Ammonium thiosulphate reducer*. Ammonium thiosulphate attacks the silver image—especially in acid solution and at high temperature. As its action is slow, the dichroic fog and stains of Ag and Ag_2S are removed before the image is affected.⁽¹⁴⁾

Use the following solution:

Ammonium thiosulphate 15% + citric acid 1·5–3%.

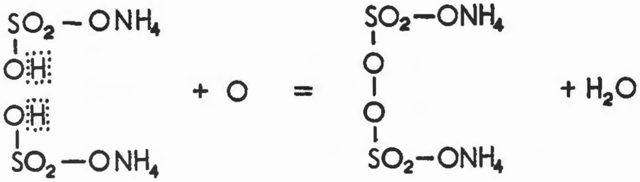
With 3% acid the bath may precipitate sulphur after two days.

For a contrast reduction of 20%, Super XX emulsion must be treated for 10–15 minutes.

173. Superproportional reduction

The action takes place mainly in the dense silver deposits: the shadows are affected before the clear areas which produces, apart from a reduction of contrast, a distortion of the characteristic curve: in other words, the high densities are flatter than the low or medium ones.

(*a*) ***Ammonium persulphate reducer.*** Ammonium persulphate—$(NH_4)_2S_2O_8$—a salt of persulphuric acid $OH—SO_2O—O—SO_2—OH$ is a vigorous oxidizing agent. It is obtained by electrolysis of a saturated solution of ammonium sulphate $(NH_4)_2SO_4$ in sulphuric acid. The oxygen produced at the anode removes two atoms of hydrogen from two atoms of the ammonium bisulphate which is formed, and these are joined via the two oxygens of the two OH groups attacked in this way:



2 molecules of ammonium bisulphate

Ammonium persulphate

Conversely the ammonium persulphate decomposes readily to ammonium sulphate and sulphuric acid in the presence of a substance which can be oxidized, such as silver. Soluble silver sulphate is produced, and removed in the solution. The decomposition of the persulphate appears to be due to catalysis; this is why the reduction takes place in the presence of the greater silver deposit in the dense rather than the light image areas. Furthermore, oxidation of the image takes place more rapidly as more silver sulphate is formed, which is in the more opaque areas. In fact, the addition of small amounts of an alkali halide (sodium chloride for example) slows down image attack by precipitation of the silver salt.

The reducing solution has the following composition:

Water to	1000 cc
Ammonium persulphate	25 g
Sulphuric acid, concentrated	1 cc

The reduced photograph is treated in 10% sulphite solution to arrest oxidation, and is then thoroughly washed.

(*b*) *Quinone reducer.* Quinone, $C_6H_4O_2$ and *sodium quinone sulphonate* $C_6H_3O_2 . SO_3Na$ are related to hydroquinone $C_6H_4(OH)_2$, and are oxidizing agents which, in sulphuric acid solution, reduce photographic images: the resulting Ag^+ ion is dissolved as silver sulphate.

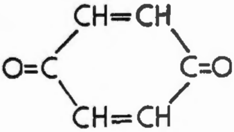
Like persulphate, permanganate and dichromate, quinone reacts more strongly in the dense image areas where more silver sulphate is produced.

For reduction use:

Water to	1000 cc
Quinone	5 g
Sulphuric acid	20 cc

Before washing, stop the oxidation in 10% sodium sulphite or 20% bisulphite.

Quinone is a cyclic diketone prepared by oxidizing aniline with potassium dichromate in sulphuric acid solution


Quinone

It crystallizes in golden yellow needles whose odour is somewhat like iodine; melting point 110°C, very soluble in water, alcohol and ether. It is reduced to hydroquinone—the corresponding diphenol. In time its solutions become brown together with the formation of a precipitate of quinhydrone $OH—C_6H_4—O—O—C_6H_4—OH$.

174. Special reducers

(*a*) *Iodine thiourea reducer*. This reducer which replaces the very poisonous *iodine-cyanide reducer*, was disclosed by Greenhall in 1926.⁽¹⁵⁾ It is prepared by pouring an aqueous solution of thiourea into an alcoholic solution of iodine. This can advantageously be replaced by a solution of iodine in potassium iodide⁽¹⁶⁾: 6 g potassium iodide in 10 cc water and 10 g iodine. Make up to 100 cc with isopropanol. Add two parts of 10% thiourea just before use. Fix in 30% hypo without intermediate rinsing.

(*b*) *Thiourea reducer* to remove dichroic fog: thiourea 12 g, citric acid 12 g, water 1000 cc.

Before using a reducer containing thiourea it is advisable to harden the gelatin with formalin.

(*c*) *Iodine water reducer* for local application to the fogged borders of old paper: potassium iodide 5 g (or bromide 15 g), iodine 2 g, water 100 cc. Then clear in an acid fixer.

INTENSIFICATION

Intensification of photographic images, which enables the contrast to be considerably increased, must only be carried out using methods which give stable images. Furthermore, for even intensification, prior hardening of the gelatin layer should be avoided. Before intensifying, it is advisable to soak the negative in water for 10 to 20 minutes to swell the gelatin.

175. Mercuric chloride intensification

Mercuric chloride, $HgCl_2$, oxidizes the silver of the image, and is itself converted to the insoluble mercurous chloride HgCl:

$$\begin{cases} Hg^{++} + e = Hg^{+} \\ Ag \quad - e = Ag^{+} \end{cases}$$

The silver is converted to chloride so that the bleached image is finally made up of a mixture of mercurous chloride and silver chloride.

To produce a black image again it is sufficient to develop the photograph; the mercury and silver chlorides are reduced to metallic mercury and silver.

The original image is accompanied by an equivalent quantity of mercury.

The blackening methods which use ***ammonia*** or ***potassium argentocyanide***(17) instead of a developer should be avoided as the resulting images are unstable (with ammonia, a mercurosoammonium chloride is formed). Blackening with 10% ***sulphite*** is also of little interest as it results in a minimum intensification. If necessary the bleached image can be ***sulphided*** in 2–10 g per litre ***sodium sulphide.***

Before bleaching with mercury it is necessary to carefully remove any trace of hypo which would produce yellow stains of mercury sulphide HgS. The mercury bath is made up of:

Water	1000 cc
Mercuric chloride	20 g
Sodium chloride	10 g
(or potassium bromide 20 g)	

which can be diluted as desired; or of:

Water	1000 cc
Mercuric chloride	20 g
Hydrochloric acid	3 cc

The water used for washing for the first few changes after bleaching should be acidified with hydrochloric acid (1%) to prevent mercury salts from becoming attached to the gelatin, which would make the image unstable.

It must never be forgotten that mercuric chloride (corrosive sublimate) is a dangerous poison which must be handled with great care. It must be completely removed by prolonged washing. Its solutions are decomposed by light; it is more stable in the presence of hydrochloric acid, or an alkali halide.

176. Mercuric iodide intensification

Mercuric iodide HgI_2 is a red powder, slightly soluble in water, which is produced when a solution of potassium iodide is added to a solution of a mercuric salt:

$$HgCl + 2KI = HgI_2 + 2KCl$$

Mercuric iodide is soluble in potassium iodide (forming potassium mercury iodide), in hypo, and in sodium sulphite. Only the last solution is stable and can be used as an intensifier.

The negative is treated in:

Water	1000 cc
Mercuric iodide	10 g
Sulphite, anhydrous	100 g

in which it is intensified gradually.

Another bath can be prepared by adding to 300 cc of water, alternately and little by little, 100 cc of 2% mercuric chloride and 25 cc of 10% potassium iodide until the red precipitate is dissolved. It is made up with 40 cc of 10% hypo.

The mercuric iodide HgI_2 is reduced to mercurous iodide HgI, whilst the silver is converted to silver iodide AgI. The mercurous iodide is in turn reduced by the sulphite to mercury and mercuric iodide. The latter is redissolved in the sulphite (as a complex) and the sequence of reactions starts again. The final image is made up of yellowish silver iodide and metallic mercury.

To prevent the mercury from being oxidized by prolonged contact with the silver iodide, the latter is developed, after washing, in a developer; stable metallic silver and mercury remain.

177. Indophenol intensification

This method depends on the property of a colour developer to develop an organic dye image together with the silver image. The mechanism of this reaction will be considered in the third part.

At the moment it is sufficient to note that the silver image, bleached and redeveloped is accompanied by a second organic image *in situ* with the silver image; the latter can again be bleached and redeveloped a second time and so on. With each operation the contrast is considerably increased. If such an image is to be used as a negative, its colour must be borne in mind when printing, to obtain the maximum contrast.

A blue-violet image is obtained with the following developer, which is used on a negative *which has been bleached to silver chloride or bromide.*

A	N : N-dimethyl-p-phenylenediamine	6 g
	Sodium sulphite anh.	10 g
	Sodium carbonate anh.	7 g
	Water	1000 cc
B	α-naphthol	14·5 g
	Caustic soda	8 g
	Water	1000 cc
Take:	A	100 cc
	B	33 cc
	Water	200 cc

Printing is preferably carried out on an orthochromatic positive emulsion.

178. Ferrocyanide intensification

Ferrocyanide toning (which we will study in para. 569) results in a great increase in contrast. It can be used for positive images. Toning with *uranium ferrocyanide* in particular enables high-density sepia photographs to be obtained. For negatives, lead intensification is preferable.

Lead ferrocyanide is white. By treating with *sodium sulphide*, brown-black images which are greatly intensified are obtained. Toning is carried out in the following solution after washing the negative in *distilled water.*

Distilled water	500 cc
Potassium ferricyanide	40 g
Lead nitrate (or acetate)	40 g
Acetic acid	5 cc
Distilled water	500 cc

It is washed first with distilled water, then with tap water before sulphiding. The negative must be absolutely free from fog.

179. Physical intensification

Physical intensification with silver is similar to physical development; silver nitrate is reduced by a developing agent in the presence of the particles of silver in the image. The silver from the decomposed silver nitrate is deposited on the image silver, increasing its density.

The solution therefore contains silver nitrate, a developing agent (hydroquinone, pyrogallol, etc.) and an acid inhibitor of spontaneous reduction (citric acid). For example:

Distilled water	900 cc
Silver nitrate	5 g

Distilled water	100 cc
Pyrogallol	3 g
Citric acid	5 g

With thick emulsions, dichroic fog is produced, and intensification is very slow.

Physical intensification with mercury is similar to that with silver. A solution of the double sulphite of sodium and mercury is used together with a reducing agent.

Formula IN.5 using silver:

A.	Water	1000 cc
	Silver nitrate	60 g
B.	Water	1000 cc
	Sulphite anh.	60 g
C.	Water	1000 cc
	Hypo	105 g
D.	Water	3000 cc
	Metol	24 g
	Sulphite anh.	15 g

Slowly add one part of B to one part of A. The resulting white precipitate is dissolved by adding one part of C. After leaving for several minutes, add three parts of D with stirring. The mixed solution keeps for only 30 minutes.

Fix the negative in 30% hypo and wash thoroughly.

180. Chromium intensification

This frequently recommended intensifier results in *only a slight increase.* It is a mixture of dichromate and hydrochloric acid, and forms a deposit of *silver chloride* by oxidation of the metal to Ag^+ and precipitation with the ion Cl^-, together with *chromic oxide* (the amount of which increases as the acidity of the bath is reduced). Example of formula:

Water	1000 cc
Potassium dichromate	10 g
Hydrochloric acid	7 cc

The bleached image is washed and redeveloped in daylight. Rinse, fix 5 minutes and again wash. The bleached image can also be treated with sulphide.

The addition of 5 g of bromide slightly increases the degree of intensification.

The following dry mixture can be prepared:

Potassium dichromate	25 g
Potassium bisulphate	62 g
Sodium chloride	50 g

When required, dissolve 14 g of the mixture in a litre of water.

181. Quinone intensification

This process can be carried out with a mixture of quinone and potassium bromide. It was developed by Hickman and Hecker who used quinone and hydroquinone-thiosulphuric acid. Muehler and Crabtree⁽¹⁸⁾ made a more complete study. The silver is converted to a salt of hydroquinone-thiosulphuric acid, which has a dark colour, in the presence of an oxidizing agent. Other coloured compounds are also produced. The disadvantages of the process are that the image is not completely stable (being destroyed by acid fixers), and that intensification does not take place in the presence of more than 25 p.p.m. chlorides in the water.

A.	Water (chloride-free) to	1000 cc
	Sulphuric acid conc.	30 cc
	Potassium dichromate	25 g
B.	Water to	1000 cc
	Potassium metabisulphite	4 g
	Hydroquinone	15 g
C.	Water	1000 cc
	Hypo	22·5 g

Four g of a wetting agent may be added to B. Take one part of A, add two parts of B with stirring, then two parts of C, and finally, still stirring, one part of A. The mixture will keep for a maximum of 3 hours. Treat negatives one at a time for 10 minutes at 20°C (68°F). Wash 20 minutes and dry.

182. Intensification by dyeing

The image is first converted to copper thiocyanate or other mordant, then dyed (see para. 580).

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1. Verkinderen H.: *Brit. Kin.*, 1948, 37–45.
2. Miller H. A., Russel H. D. and Crabtree J.: *P.S.A. Jl.*, 1949, 382.
3. Dufaycolour.
4. There is another reversal process in which part of the gelatin layer corresponding to the image is dissolved. (See Chapter XXXII.)
5. Potassium permanganate is obtained by alkaline electrolysis of the manganate K_2MnO_4, which is prepared by calcining a mixture of manganese dioxide MnO_2 and potassium nitrate KNO_3, or of natural pyrolusite and caustic potash.

6. Or sulphite (in the case of dichromate).
7. Ville J. G. and Kodak: U.S.P. 2,150,704 (1937).
8. Miller H. A.: *P.S.A. Jl.*, 1948, 103 and *Sci. et Ind. Phot.*, 1948, 216.
9. To avoid unevenness, it is advisable to swell the gelatin in weak alkali before reducing.
10. Perrin F. H. and Altman J. H.: *Jl. Opt. Soc. Amer.*, 1952, 462–467.
11. Wakefield G. C.: *Proc. Engr. Monthly*, 1951, 206–208.
12. The exhaustion of ferricyanide bleach baths is controlled by adding a ferric salt to a sample of the solution. The amount of the resulting Prussian blue is determined colorimetrically.
13. Lal B. B. and Singhal C. P.: *Current Sci.*, 1944, 78–79.
14. Henn R. W., Crabtree J. I. and Russell H. D.: *P.S.A. Jl.*, 1951, 110–113.
15. Greenhall T. H.: *Sci. et Ind. Phot.*, **6R(1)**, 168.
16. Willcock R. B.: *Sci. et Ind. Phot.*, 1950, 459.
17. Potassium argentocyanide is prepared by mixing equal volumes of 4·5% silver nitrate (in distilled water) and 3% potassium cyanide (poison). The argentocyanide gives the maximum contrast with mercuric chloride.
18. Muehler L. E., and Crabtree J. I.: *P.S.A. Jl.*, 1945, 9; *Sci. et Ind. Phot.*, 1945, 222.

Chapter XIII

TONING

183.

Toning is a process for altering the colour of positive prints. Bromide papers only give black images, and it is sometimes desirable to tone them sepia; the *sulphide method* is generally used for this. Toning is unnecessary for chlorobromide papers and lantern plates, as these can be directly developed in warm tones. On the other hand, 'print-out' papers, whose colour is not pleasant, must be toned; *gold toning* is usually used for this, but the precious metals of the platinum group can also be used.

The methods for producing coloured images by *ferrocyanide toning* will be considered in Part III. They are of more interest for colour reproduction.

The colour of an image can be changed by bleaching to chloride in a permanganate or dichromate bath (para. 172 (*f*)) then redeveloping, in, for example, a solution containing 0·75% pyrocatechin and 6% sodium carbonate, followed by clearing in acid hypo.

SULPHIDE TONING

Sulphide toning can be carried out in two different ways:

1. By bleaching to silver halide followed by darkening with sodium sulphide.
2. By direct convertion of the silver image to silver sulphide.

The image colour tends to become more yellow as the silver image grain size becomes finer.

184. Sulphiding after bleaching

This is the process which is generally used.

The image is first bleached in a *ferricyanide-bromide* bath:

Water	1000 cc
Potassium ferricyanide	30 g
Potassium bromide	10 g
Sodium carbonate	16 g

This forms an image of silver bromide and soluble potassium ferrocyanide: the silver, oxidized by the ferricyanide to Ag^+, is precipitated by the bromide, whilst the ferricyanide is reduced to ferrocyanide.

After washing thoroughly, the bleached print is treated in a solution of *sodium sulphide*⁽¹⁾ Na_2S; this results in a change of cations between the bromide and the sulphide: $2AgBr + Na_2S \rightarrow Ag_2S + 2NaBr$.

The following *sulphiding bath* is preferable:

Saturated alum solution	1000 cc
Saturated sodium sulphide solution	5 cc

By diluting, warmer tones are produced. Higher concentrations of sulphide produce colder results.

The sodium sulphide can be replaced by ammonium sulphide $(NH_4)_2S$, barium hydrosulphide BaHS, the alkali sulphoxyphosphates or, best of all, thiourea.

Thiourea NH_2—CS—NH_2, which is a silver bromide solvent, is used in alkaline solution. The tone becomes colder as the pH is raised (coagulation of sulphide particles). A normal bath is composed of:

Thiourea	2 g
Sodium carbonate anh.	100 g
Water to	1000 cc

The carbonate can be replaced by caustic soda at a concentration of 0·4%, and the thiourea doubled: maroon tones.

185. Sulphiding images bleached with metal salts

(*a*) *Sulphiding mercury-bleached images.* By introducing mercury into the bleached image, pleasing tones from warm sepia to gravure black can be obtained. To do this, the following bleach is used:

A.	Potassium ferricyanide	30 g
	Potassium bromide	45 g
	Water	266 cc
B.	Mercuric chloride	4 g
	Potassium bromide	4 g
	Water	150 cc

Colour	*Gravure black*	*Warm black*	*Sepia*	*Warm sepia*
Solution A	10	10	10	10
,, B	30	10	5	0
Water	160	160	120	120

Wash, rinse three times in 1% hydrochloric acid to remove the mercuric chloride (*very poisonous*) which would be retained by the gelatin, again wash in water, then tone in:

Sodium sulphide	9 g
Water	100 cc
Water	800 cc

(*b*) *Sulphiding a copper-bleached image.* When the image is bleached in cupric chloride or bromide, the insoluble cuprous chloride or bromide is formed at the same time as the silver halide. Part of the former is removed by oxidation during washing; the remainder stays in the image. On sulphiding, a mixture of copper and silver sulphides is formed which has a slightly different colour from pure silver sulphide. This method cannot be used on paper as the paper retains some copper salts, which produce a general stain on toning.

(*c*) *Sulphiding chromium images.* The best bleach is dichromate—hydrochloric acid, which gives a deposit of silver chloride and chromium oxide (para. 172 (*f*)). $6Ag+K_2Cr_2O_7+8HCl \rightarrow 6AgCl+Cr_2O_3+2KCl+4H_2O$ which on toning is converted to silver sulphide Ag_2S and chromium sulphide Cr_2S_3.

The bleach has the following composition:

Hydrochloric acid	18 cc
Potassium dichromate	10 g
Water	1000 cc

When thiourea is used for toning, warmer tones than with a ferricyanide-bromide bleach are obtained by replacing the latter with a ferricyanide-dichromate-bromide bleach such as:

Potassium dichromate	22 g
Potassium ferricyanide	30 g
Potassium bromide	16 g
Water	1000 cc

(*d*) *Sulphiding ferrocyanide images.*⁽³⁾ Various sepia tints can be obtained by sulphiding images converted to the ferrocyanides of copper, uranium, molybdenum, titanium, cadmium, etc. A mixture of silver sulphide on the sulphide of the other metal is obtained. The original silver image must be underdeveloped as toning and sulphiding produces considerable intensification.

186. Sulphiding with sulphur complexes

A bleached print treated in:

Sodium thioantimoniate	10 g
Ammonia	1 cc
Water	1000 cc

has a much warmer sepia colour with an orange tinge, than when sodium sulphide is used, due to a deposit of antimony sulphide mixed with the silver sulphide.

Sodium thioantimoniate, or the double sulphide of sodium and antimony $Na_3SbS_4 . 9H_2O$, is commonly called Schlippe's salt, and crystallizes as yellow tetrahedral crystals, covered with a brown layer of antimony pentasulphide Sb_2S_5.

The thioantimoniate can be replaced by a *thiomolybdate*, a *thioarsenate* or a *thiostannate*. The image is yellowish with the thioarsenate and reddish with the thiostannate.

The alkalinity of the bath is important in determining the colour of the image. With *thiostannate* the following shades are obtained:

Warm tones	Sodium thiostannate	10 g
	Potassium bromide	160 g
	Sodium carbonate anh.	3 g
	Water	850 cc

Sepia tones: add 100 cc 10% carbonate.
Cold tones: add 200 cc 10% carbonate.

The double sulphides, together with sodium sulphide, give intermediate colours, becoming a deeper brown as the proportion of sodium sulphide is increased. With equal quantities of thioantimoniate and sulphide, warm brown tones are obtained.

Other combinations can be produced by treating the copper-, chromium-, or ferrocyanide-toned images with the double sulphides.

187. Toning by direct sulphiding

The direct sulphiding of a silver image is achieved with a hypo-alum solution, with colloidal sulphide or with sodium bisulphide. Only the first method is in current use.

(*a*) *Hypo-alum toning*. A photograph treated in a hot solution of hypo and ordinary alum is slowly sulphided to give a sepia image.

The hypo reacts with the alum (potassium aluminium sulphate): on one hand, *aluminium thiosulphate* $Al_2(SO_2O_3)_3$ is formed, which hydrolyses to aluminium sulphate $Al_2(SO_4)_3$ and hydrogen sulphide H_2S is formed, and on the other, a *precipitate* of sulphur and alumina Al_2O_3 with the evolution of sulphur dioxide SO_2. The hypo is, furthermore, decomposed by the hydrogen sulphide to sodium bisulphite, sodium hydrosulphide and sulphur, whilst the combined action of sulphur dioxide and hydrogen sulphide produces pentathionic acid $H_2S_5O_6$. At the boil, the main products are a precipitate of sulphur and alumina accompanied by sulphur dioxide. The various reactions can be summed up as follows:

$$\begin{aligned}
3Na_2S_2O_3 + Al_2(SO_4)_3 &= 3S + 3SO_2 + Al_2O_3 + 3Na_2SO_4 \\
3Na_2S_2O_3 + Al_2(SO_4)_3 &= Al_2(S_2O_3)_3 + 3Na_2SO_4 \\
Al_2(S_2O_3)_3 + 3H_2O &= Al_2(SO_4)_3 + 3H_2S \\
Na_2S_2O_3 + H_2S &= NaHSO_3 + NaHS + S \\
5H_2S + 5SO_2 &= H_2S_5O_6 + 5S + 4H_2O
\end{aligned}$$

The sulphiding of the silver image is therefore due to nascent sulphur together with hydrogen sulphide.

The hypo alum solution is practically an argentithiosulphate in the presence of excess sodium chloride. It is prepared as follows:

To the solution

Cold water	700 cc
Hypo	120 g

add

Hot water (70°C or 158°F)	180 cc
Alum	30 g

Then pour in slowly with vigorous stirring:

Cold water	18 cc
Silver nitrate	1 g
Sodium chloride	1 g

including the white precipitate of silver chloride which is formed; make up to 1 litre.

For toning, heat the bath to 50°C (122°F) and put the previously wetted print in, and leave for 15–30 mins. After toning, first rinse in warm water, then wash in running water.

At 20°C (68°F) toning takes 6–8 hours.

(*b*) *Toning with colloidal sulphur.* An image treated in a colloidal sulphur solution for 20–30 mins. then given a prolonged wash (1–2 hours) is toned warm sepia.

The same result is obtained by treating a print impregnated with hypo in 1% hydrochloric acid for at least 30 mins. The nascent colloidal sulphur formed by the action of the acid on the hypo reacts directly with the image silver

$$Na_2S_2O_3 + 2HCl = 2NaCl + S + SO_2 + H_2O$$

Colloidal sulphur is obtained from hypo solution treated with an acid in the presence of a protective colloid:

Water	1000 cc
Hypo	150 g
25% Dextrine	500 cc
Hydrochloric acid	60 cc

(*c*) *Toning with sodium bisulphide.* Sodium bisulphide Na_2S_2 is prepared by fusing a molecule of sulphur with a molecule of sodium sulphide i.e. 32 g sulphur with 78 g sulphide. It is also obtained by adding 200 cc of hydrogen peroxide(4) to 800 cc 5% sodium sulphide: the sulphide is converted to bisulphide and caustic soda.

A photograph is toned sepia in 30 mins. in a 2% bisulphide solution. The whites are slightly stained with a sulphur deposit.

(*d*) *Liver of sulphur toning.* Liver of sulphur is a crude potassium pentasulphide obtained by heating equal parts of sulphur and potassium carbonate $S+K_2CO_3$. It is in the form of a reddish brown mass, smelling of hydrogen sulphide.

When it is dissolved in water, colloidal sulphur is formed which can tone photographic images.

To tone, treat the previously hardened photograph in a solution of 50 cc of 20% liver of sulphur in a litre of water at 35–40°C (95–104°F) for a few minutes.

(*e*) *Toning with ammonium polysulphide.* Ammonium polysulphide is prepared by dissolving sulphur in ammonium sulphide $(NH_4)_2S$; about 10 g per 100 cc is enough.

The toning solution is prepared by diluting 10–15 cc of the polysulphide stock solution to one litre with water. The speed of toning can be increased by warming to 35–40°C.

188. Selenium toning

A silver image from a chlorobromide material immersed in an alkali selenide becomes reddish, probably due to a deposit of selenium on the black metal. The best results are obtained with underdeveloped images.

Good selenium toning is obtained by using sodium thioselenate $Na_2Se_2O_3$ obtained by the action of a large excess of hypo on sodium selenosulphate. The latter is obtained by dissolving selenium in a boiling solution of sodium sulphite. The toning bath contains about 1 g per litre selenium. It is accelerated by ammonium chloride.

The T.55 formula has the following composition:

Sodium sulphite anh.	150 g
Selenium cryst.	6 g
Ammonium chloride	190 g
Water to	1000 cc

For use, dilute with five parts of water. Toning time 3–10 mins. Wash 15 mins.

The selenium can be used combined with sodium sulphide as the *seleno-sulphide*: 5 g selenium and 135 g sulphide in 200 cc hot water; the solution is stabilized by adding a few cc of sodium bisulphite. For use, dilute with twenty parts of water. A ferricyanide-bleached image is toned to a colder colour in this bath than in monosulphide alone.

PRECIOUS METALS TONING

189. Colloidal silver toning

A silver image, bleached to chloride with cupric chloride can be redeveloped with a reducing agent. Depending on the nature of the latter, the size of the resulting particles will vary giving a wide range of tints.

The image is first bleached in the bath recommended by Formstecher:

Cupric chloride	30 g
Hydrochloric acid	3cc
Ammonium persulphate	10 g
Water	1000 cc

The washed image, formed of silver chloride, is exposed to light and reduced with one of the three following solutions.

A.	Stannous chloride	10 g
	Hydrochloric acid	1 cc
	Water	100 cc
B.	Hydrazine sulphate	10 g
	Water	500 cc
C.	Sodium nitrite	10 g
	Water	500 cc

The *stannous chloride* gives colours from yellow to red. If the print has been washed after exposure, the colour is purplish brown.

The *hydrazine sulphate* gives blue tones, provided the image has been washed after exposure.

The sodium nitrite gives red-violet tints.

Only chloride emulsions give the best results: with chlorobromide emulsions it is preferable to use hydrazine sulphate.

190. Gold toning

Aqua regia(5) readily dissolves gold. By slow evaporation yellow crystals of *chloroauric acid* $AuCl_3 . HCl . 3H_2O$ are deposited, a combination of auric chloride and hydrochloric acid. By heating, the acid is eliminated giving the chloride $AuCl_3$.

Chloroauric acid combines with alkalis to give the *chloroaurates*, crystalline soluble double salts, in which the complex ion is unstable. The most common are the sodium (yellow crystals) and potassium (orange prisms) chloroaurates $AuCl_3 . NaCl . 2H_2O$ and $AuCl_3 . KCl . 3H_2O$.

Auric chloride is decomposed by the silver of the photographic image, giving silver chloride and metallic gold.

Actually, the image is not completely attacked; the majority of the silver remains unchanged.

In addition, the size of the particles of gold deposited depends on the *pH* of the bath. This means that the colour of the image is a function of the acidity or alkalinity, as well as the dilution and toning time. In this way, a wide range of colours, bluish and violet to red, can be produced.

The blue tones result from a coagulated form whilst the red tones are produced by a very dispersed state of the gold.

Neutral and slightly alkaline solutions give blue tones.

Acid baths, without solvent give pinkish tones.

Gold toning is used with citrate or collodion *print-out papers*, whose colour is unpleasant. Printing is prolonged to give a higher density than that required, as the image is reduced later. The print is washed to remove the soluble salts, and is then toned in a fresh bath. After toning, the print is carefully washed to remove all traces of gold salts (which would give a yellow stain with hypo). Fixing is carried out in 10–20% hypo, which is completely removed by a third long wash.

This toning method is used less and less, but is of interest.

191. Gold-toning baths

Gold-toning baths are generally ***neutral, slightly alkaline or slightly acid.*** A solution which is too alkaline decomposes the gold salt to the oxide, which redissolves in excess alkali; too much acid removes the half-tones.

The gold chloride can either be the neutral chloride $AuCl_3$, chloroauric acid or a chloroaurate. In the case of chloroauric acid, it is best to neutralize the hydrochloric acid molecule with chalk.

(*a*) *Neutral baths.* These are prepared from a solution of gold chloride containing an insoluble carbonate (calcium, barium, magnesium) to neutralize the acidity.

Example:

Gold chloride	1 g
Calcium carbonate	20 g
Water to	1000 cc

The addition of a few drops of sodium chloride solution to the bath produces a silver complex which is converted to adsorbed colloidal silver chloride which reduces the action of the auric ions. This slowing down is even more marked with the alkali bromides. The colour of the resulting images tends to sepia.

With potassium iodide distinctly red shades result.

The reverse effect occurs when the gold salt is included in the emulsion (self-toning paper). In this case the halides accelerate toning and produce bluer tones.

(*b*) *Alkaline baths.* Sodium carbonate, borax, sodium phosphate, etc. are used:

Gold chloride	1 g
Sodium carbonate	5 g
Water	1000 cc

or

Gold chloride	1 g
Borax	20 g
Water	1000 cc

(*c*) *Weakly acid baths.* Sodium acetate, benzoate, etc. are used, frequently together with borax or sodium tungstate. Example:

Chloride	1 g
Sodium acetate	10 g
Water	1000 cc

to which 10 g borax or sodium tungstate may be added.

192. Gold-toning baths with solvent

(*a*) *Thiocyanate baths.* Ammonium thiocyanate NH_4CNS is a silver halide solvent. Using a solution containing 10–20 g per litre with 2 g per litre gold chloride, bluish-black, sepia or purple tones are produced according to the dilution.

With 5 g per litre thiocyanate and 0·25 g per litre neutral gold chloride, blue-blacks are produced. By adding 0·5–1·5 g potassium iodide, the image is toned more to violet and red. The toning time is controlled in each case.

The following formula gives purple tones after 5–10 mins.:

A	Ammonium thiocyanate	12 g
	Water	500 cc
B	Gold chloride	1 g
	Water	500 cc

Just before use take 10 cc of A, 10 cc of B and 100 cc water.

Neutral thiocyanate baths, however, have a tendency to deposit. *They are much more stable in the presence of an acid* such as tartaric, and can tone the depths of the image; which is not true of the other baths. The best formula is Namias':

Ammonium thiocyanate	25 g
Tartaric acid	2 g
Sodium chloride	5 g
Gold chloride, 1% sol.	25 cc
Water to	1000 cc

tones violet-black in 20 mins.

This bath enables print-out papers to be toned *after fixing*. It can also be used with *chlorobromide prints*.

(*b*) *Thiourea baths*. We have seen that thiourea is a good silver chloride solvent, with which it forms complexes. In high concentrations, it also attacks gelatin. To obtain bluish tones, the following bath can be used:

Thiourea	3 g
Citric acid	2 g
Distilled water	1000 cc
Gold chloride	1 g
Sodium chloride	25 g
Distilled water	1000 cc

The sodium chloride moderates the action of the thiourea.

Thiourea baths lose their activity more quickly than acid thiocyanate ones.

193. Gold-toning of sulphided images

Silver sulphide images obtained by one of the methods already described can be gold toned.

Red tones are obtained with a bath containing 0·4 g of thiocyanate and 0·2 g gold per litre. Blood red tones are obtained with the yellowish images, preferably obtained with polysulphides, when treated in the above thiourea bath. With sepia sulphide images the tone becomes red-violet.

A	Ammonium thiocyanate	20 g
	Water	1000 cc
B	Gold chloride	2 g
	Water	1000 cc

	Purple-black	*Brown*	*Red*
A	100	25	16
B	100	25	16
Water	1000	1000	1000

The images should be overexposed and developed in a diluted developer.

Nelson toner. Excellent brown tones can be obtained with a single *toning-sulphiding* bath. The sulphiding is produced by the colloidal sulphur resulting from the decomposition of hypo with alum, and whose bleaching action is retarded by silver bromide. The bath is made alkaline and gold chloride is added. The practical method is as follows: boil 450 g hypo and 56 g alum in 4 litres of water. After cooling, the solution is made alkaline with 56 g trisodium phosphate, then the reaction product of 8 g of bromide dissolved in 30 cc water with 4 g silver nitrate in 30 cc water (silver bromide) is added. Finally, just before use, 7·5 cc gold chloride per litre of liquid is added. Toning temperature 32–45° C (90–113°F). Rinse and fix for 5 mins.

The Kodak formula uses: A. Warm water 4 l., hypo 960 g, *ammonium persulphate* 120 g (added after the hypo is dissolved; if the solution becomes milky, warm until it is clear). B. Cold water 65 cc, silver nitrate 5 g, then sodium chloride 5 g. C. Water 250 cc, gold chloride 1 g. Just before use, add 125 cc C to B with rapid stirring, then pour the mixture into A. Tone at 43°C (110° F), agitating the prints. Rinse and fix for 5 mins.

194. Toning-fixing

The toning-fixing bath simplifies the operation of gold toning. It contains both gold chloride and hypo. The washed print is simultaneously toned and fixed in the same bath.

With gold chloride, hypo gives a double thiosulphate of gold and sodium. This is decomposed by the silver of the image, producing metallic gold, which is deposited, and sodium argentithiosulphate which dissolves.

The usual additions to toning-fixing baths are: *lead salts*, a *pH stabilizer* such as sodium acetate, alum, and optionally, a *reducer-solvent* such as ammonium thiocyanate. *Alkalis* such as carbonates, borates, phosphates, etc., can also be included.

The *lead salts* activate the reaction. They are themselves toning agents (PbS formation) and can be used without gold.

Toning-fixer formulas:

Hypo	200 g
Lead nitrate	8 g
Gold chloride	1 g
Water	1000 cc

Hypo	200 g
Alum	10 g
Citric acid	1 g
Lead acetate	1 g
Gold chloride	0·6 g
Water	1000 cc

Hypo	240 g
Ammonium thiocyanate	24 g
Nitric acid	6 cc
Lead acetate	6 g
Gold chloride	0·3 g
Water	1000 cc

Hypo	200 g
Ammonium thiocyanate	2 g
Alum	10 g
Lead acetate	5 g
Sodium acetate	10 g
Gold chloride	10 g
Water	1000 cc

195. Platinum toning

Platinum toning gives black images. *Platinous chloride* $PtCl_2$ is used, which in the presence of an alkali chloride gives a chloroplatinite such as $PtCl_2 . 2KCl$.

The silver of the photographic image displaces the platinum from these compounds: this is precipitated as the metal, whilst the silver is converted to the insoluble halide:

$$PtCl_2 + 2Ag = Pt + 2AgCl$$

The reaction only takes place in acid solution: inorganic acids or acetic or lactic acids can be used. The preferred platinum salt is potassium chloroplatinite. These baths keep well, and can be used almost until they are exhausted. After toning at least 25% of the silver is unaffected.

Example of formula:

Potassium chloroplatinite	0·5 g
Phosphoric acid	10 cc
Water	1000 cc

The chlorides of the metals of the platinum group: iridium, ruthenium, rhodium, osmium and palladium have the same reactions. *Palladium chloride* $PdCl_2 . 2H_2O$ tones sepia.

1. Sodium monosulphide crystallizes with 9 mols. water: $Na_2S . 9H_2O$. It is a white compound, unstable in the air, forming caustic soda, hypo and polysulphide. The solution only keeps at a concentration above 20%. It must be used away from sensitive materials in a ventilated room. It is *caustic*; avoid contact with the skin.
2. Henney and Dudley: *Handbook of Photography* (McGraw-Hill. New York).
3. For ferrocyanide toning, see para. 569.
4. Generally an oxidizing agent.
5. *Aqua regia*: mixture of 1–2 vols. nitric acid with 4 vols. hydrochloric acid; the reaction of the two acids produces chlorine, nitrogen dioxide NO_2, and nitrosylchloride NOCl.

Chapter XIV

SENSITOMETRIC LAWS

DEFINITIONS

Each amount of light can produce, on a sufficiently sensitive photographic emulsion, a fixed degree of *darkening* through the action of the developer.⁽¹⁾

The knowledge of this amount of light, or *illumination* is the first requirement in the study of the relation between the action of radiant energy and the photographic image.

196. Exposure

This is the product of the luminous intensity by the time of exposure

$$E = It$$

The unit of luminous intensity is the *candle-metre* or lux which is the illumination produced by a source of one *new candle* (or 'candela') at a distance of one metre. The unit of duration, or time, is the second so that the exposure It is measured in *candle-metre-seconds*. The characteristics of standard sources will be studied at the beginning of the third part, and for the moment we will ignore the spectral composition of the source, supposing that uniform white light is used.

If the light beam strikes the layer obliquely, the intensity is diminished

$$E = E_0 \cos \alpha$$

where α is the angle between the light beam and the normal to the layer.

197. Opacity

The black silver deposit produced by an exposure E will reduce the intensity of an incident light beam F_0 to a transmitted intensity F.

The relationship between the two intensities F_0 and F is termed the opacity:

$$O = \frac{F_0}{F}$$

The opacity is the reciprocal of the transparency: the lower the intensity of the transmitted beam, the greater the opacity: for example, an opacity of

10 corresponds to a transparency of 1/10 and an opacity of 100 to a transparency of 1/100.

198. Density

Density is the logarithm of the opacity

$$D = \log_{10} O$$

The following table shows the relationship between transparency, opacity and density.

Transmission	Opacity	Density
1/10,000th	10,000	4
1/1,000th	1,000	3
1/300th	300	2·5
1/100th	100	2
1/50th	50	1·7
1/20th	20	1·3
1/10th	10	1
1/5th	5	0·7
1/3rd	3	0·5
1/2	2	0·3

If *a* is the thickness of the sensitive layer(2) and *k* its coefficient of luminous absorption, the effective exposure at the depth x is $E_x = E_e^{-kx}$ which enables the total density to be derived from the relation

$$D_E = \frac{1}{a}\int_0^a f(Ee^{-kx})dx$$

The density can be expressed by an infinite number of different values depending on the measurement method. In practice it is measured by specular or diffuse light. With *specular light* one has

$$D_{\parallel} = \log_{10} \frac{\text{normal incident flux}}{\text{normal transmitted flux}}$$

It is very difficult to measure specular density unless the measuring beam is perfectly collimated.

In diffuse light (by an opal glass for example) the density value is lower than the preceding value.

$$D_{\#} = \log_{10} \frac{\text{diffuse incident flux}}{\text{normal transmitted flux}}$$

The relationship $Q = D_{\parallel}/D_{\#}$ is the *Callier coefficient* about 1·5 (1·25 for fine-grain images and 1·8 for coarse-grain images). As the variations of this coefficient are not well defined the Renwick and Bloch formula is preferred

$$\log_{10} D_{\#} = a \,.\, \log_{10} D_{\parallel} + b$$

in which a and b are coefficients constant for the same opal glass and the same emulsion. L. P. Clerc gives the following figures for a particular example

$$\log_{10} D_{\nparallel} = 1{\cdot}045 \log_{10} D_{\parallel} - 0{\cdot}286$$

The *effective density* $D\phi$ which corresponds to contact printing where the transmitted light is immediately received by the positive emulsion behind the negative. In this case it is the total transmitted light, specular and diffuse, which is effective

$$D\phi = \log_{10} \frac{\text{normal incident flux}}{\text{total transmitted flux}}$$

The effective density is related to the diffuse density by the formula

$$D^{p}{}_{\phi} = kD_{\nparallel}$$

where p is about 1.

If the incident light is, however, diffused, the density is measured with respect to this diffuse light

$$D\psi = \log_{10} \frac{\text{diffuse incident flux}}{\text{total transmitted flux}}$$

and the four densities are mutually related by the formula

$$D\psi = D\phi + D_{\nparallel} - D_{\parallel}$$
$$\text{where } D_{\parallel} > D_{\nparallel} > D\phi$$

In projection printing, the incident and transmitted beams will be parallel if the negative is non-diffusing and if scattering of the light can be avoided. In fact, the effective density in this case is intermediate between $D_{\parallel}$ and $D_{\nparallel}$. This also holds for motion picture 'optical' printing.

The density value also depends on the *image colour*; it is at the maximum with the most strongly absorbed light, that is when it is measured with light of a complementary colour.

Reflection density. The reflection density of an image on paper is obtained by measuring the intensity of the normal diffuse beam, when the incident light is projected at an angle of 45°. This density is defined as the relationship between the light reflected from a pure white and the light reflected by the sample

$$D_R = \log_{10} \frac{\text{normal reflected light from pure white}}{\text{normal reflected light from sample}}$$

The pure white rarely reflects more than 80% of the incident light, and this is the reason why the ratio of incident to reflected light is not used. The densest blacks reflect about 4–6% of the light. This reduces the luminosity range of photographic papers.

When the paper texture is pronounced, the density varies regularly as the sample is rotated about its perpendicular axis.

The densities obtained on matt paper are appreciably lower than those on glossy paper. The luminosity range of the latter appears greater but the elimination of unwanted reflections by using polarized light eliminates this difference. All papers then appear to have the same maximum density, as the reflected light is not diluted with specular reflections.

CHARACTERISTIC CURVE

199. If a series of increasing exposures is given to a photographic emulsion, each different exposure gives, after development, an image, or silver deposit, represented by a specific darkening (Fig. 7).

By measuring the density of each step and drawing a graph with the *densities* on the ordinate and the *log exposures* on the abscissa the characteristic curve(3) of the emulsion is obtained (Fig. 8). It comprises an underexposed region AB (toe), a straight line region BC which is the normal exposure region, an overexposure region CD (shoulder) and a solarization region DE where the densities again decrease. The part A_0A represents the period of photochemical induction, A being the first visible point or *threshold.*

200. Contrast

The gradient of the characteristic curve is measured at each point by the tangent at this point (Fig. 9); we have

$$\tan\alpha = \frac{\mathrm{mn}}{\mathrm{pn}}$$

Now mn = Dm and pn $= \log_{10} E_n - \log_{10} E_p$

therefore
$$\tan\alpha = \frac{D}{\log_{10} E_n - \log_{10} E_p}$$

where Dm $= \tan\alpha\,(\log_{10} E_n - \log_{10} E_p)$.

It is obvious that the value of tan α, low at A, increases up to B, remains constant from B to C, then decreases from C to D until it is zero, then becomes negative from D to E.

When $\alpha = 45°$, $\tan\alpha = 1$.

The tangent to the characteristic curve measures the *contrast* γ (gamma). This varies along the curve; if only the straight line portion is considered, the preceding equation becomes

$$D = \gamma\,(\log_{10} E - \log_{10} i)$$

in which i is an emulsion constant, which represents the exposure corresponding to the point of intersection of the produced straight line with the abscissa. This is customarily (but wrongly) called the *inertia*.

Photographic reproduction is said to be correct when the contrast is unity. Negatives are developed to a much lower γ (0·65–0·8) to take advantage of the increased exposure scale. The positive copies are therefore developed to a γ greater than 1 to restore the true rendering following the equation:

$$\gamma \text{ positive image} = \gamma \text{ negative image} \times \gamma \text{ positive development}$$

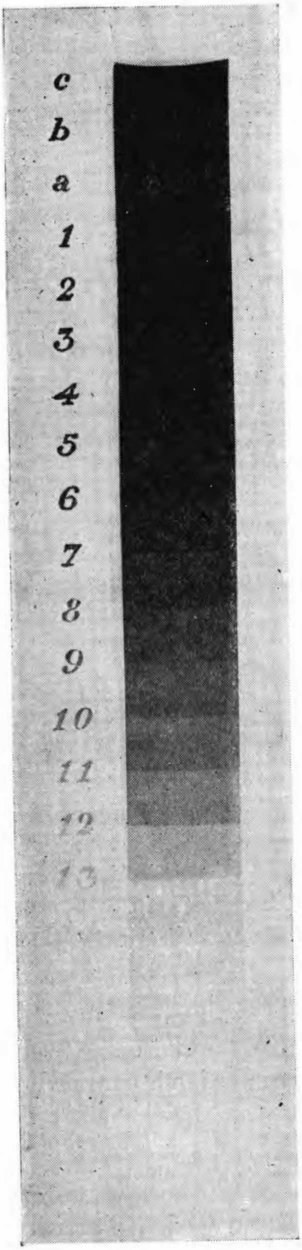


FIG. 7. Scale of increasing densities.

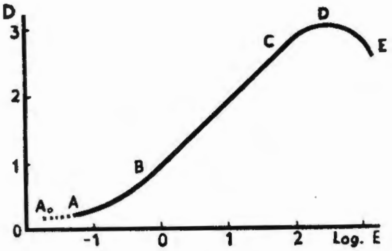


FIG. 8.

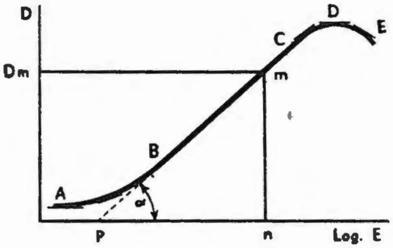


FIG. 9.

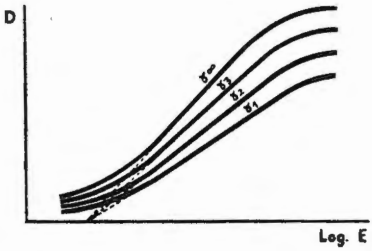


FIG. 10.

For example: to obtain a motion picture positive image with a contrast of 1·4 starting with a negative with a contrast of 0·7, the positive must be developed to $\gamma = 2$ as $1{\cdot}4 = 0{\cdot}7 \times 2$.

201. Effect of developing time on contrast

As soon as an image appears during development, it has a very low contrast. This increases as development proceeds (Fig. 10) until a limiting value is reached—gamma infinity γ_∞. With negative emulsions γ_∞ is about 1–1·6 whilst it can be as high as 4 for positive emulsions.

As we have already seen, gamma infinity corresponds to the complete blackening of all exposed grains; the different densities are therefore composed of completely developed crystals with none in an intermediate condition, and differ from each other only in the number of these grains. In Part II, the relationship between γ_∞ and the emulsion type will be shown.

The straight-line portions of the various curves of the same emulsion coincide at the point *i* if the developer contains no alkali bromide. This condition can never be satisfied in practice for a soluble bromide is formed during development at the same point as the image, and similarly, bromide is added to the developer to reduce fog. The intersection of the straight lines takes place below the abscissa (and sometimes above also), which results in an increase of the whole image as development is prolonged.

If an excess of alkali bromide is added or formed, a *regression of inertia* occurs; the point *i* is displaced towards the greater exposures whilst the point of intersection of the straight lines is pushed still further below the exposure axis. At the same time, the contrast increases.

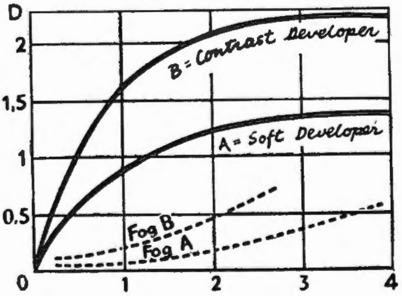


FIG. 11.

Variation in density as function of development time.

Time of development. If D_∞ is the highest density for a given exposure, t the development time to obtain density D with the same exposure (Fig. 11), t_0 the time taken for the image to appear, r a coefficient depending on the developer type and *e* the naperian log base, Sheppard's formula gives the value of D:

$$D = D_\infty (1 - e^{-(t-t_0)})$$

This formula can be compared with Watkins' empirical law:

$$\log \frac{D_\infty}{D_\infty - D} = K_0 \log \frac{t}{t_0}$$

where K_0 is the development velocity constant. After simplifying, it becomes:

$$\frac{t}{t_0} = 2^{\frac{1}{K_0}}$$

where $t = t_0C$ for the production of a normal contrast. C is the '*Watkins Factor*' for the particular developer.

The contrast obtained as a function of the development time t, is given by the exponential equation of Mees and Sheppard:⁽⁴⁾

$$\gamma = \gamma_\infty(1 - e^{kt}) \text{ and } D = D_\infty(1 - e^{kt})$$

k, which is dependent on both emulsion and developer, has a value of 0·3–0·5, being higher for slow emulsions.

Influence of temperature. Both density and contrast increase with temperature. For equal contrast, the development time t as a function of the temperature θ is calculated from the formula

$$t = Ke^{A\theta}$$

where $10A = \log Cr$, Cr depending on the developer. Thus hydroquinone has a coefficient double that of metol; the effect, in an M.Q. developer of an increase in temperature is greater on the hydroquinone than on the metol; the hydroquinone becomes more active than metol. Conversely, at low temperatures, it is primarily the latter which is effective.

202. Equations of the characteristic curve

The characteristic curve of an emulsion results from the properties of the various grains. If v is the number of centres per crystal, the number of grains made developable by an exposure E is:

$$X = a(1 - e^{-v})$$

where a is the total number of grains per cm². A grain becomes developable only after a definite exposure; the nature of the developer is not generally important, except for hydroxylamine and glycin which develop the heavier exposures. If ϵ is the effective coefficient of absorption, σ the average projected area of a grain and n the number of quanta incident per unit area, it is found that the grains σ require at least an effective quanta to become developable by an illumination of n quanta. Only a small proportion $\epsilon\sigma$ of this area is effective in the formation of this latent image By letting y be a variable, a function of the illumination such that $y = \epsilon\sigma n$, there is an inflexion point, and for a number of effective quanta per grain of 2:

$$\frac{D}{D_m} = \frac{y^2(3 + y)}{(1 + y)^3}$$

On Trivelli's supposition that the distribution of grains follows an exponential curve, and putting $\delta = D/D_m$, we have:

$$y = \frac{2}{\sqrt{1-\delta}} \cos\left(60° - \frac{\text{arc.}\cos\sqrt{1-\delta}}{3}\right) - 1$$

The coefficient of effective absorption ϵ is related to y and n by the equation

$$\log \epsilon = 16293 - \log(\lambda\sigma) + \log y - \log E$$

where E is the exposure in ergs/cm^2.

Toraldo di Francia represents the characteristic curve by the general equation

$$n_1 \log c - n_2 \log (C - c) = n_3 \log E + k$$

in which $c^2/C - c = kE$ (*Boll. Ass. Ott. Ital.*, Jan. 1944, p. 75).

If E_0 is the exposure on the front of the emulsion and E_p the exposure at the rear, $\log E_0/E_p$ is proportional to the thickness of the emulsion. Webb has shown that for slow emulsions where this logarithm is greater than 2, the relative gradient γ/D_m is fixed almost entirely by the absorbing power, whilst for rapid emulsions with a relatively low slope, the form of the curve is also dependent on the distribution of light between the grains. In other words, the influence of absorption on the curve shape decreases as the initial value of γ/D_m decreases.

Additivity law. Let I_A be the intensity of a coloured light A necessary to increase by d a density D obtained with this light A, and I_B the intensity of light B necessary to increase by d the same density D obtained with light B, and let I_M be the equivalent intensity obtained by mixing lights A and B. Putting $aI_M = \alpha I_A$ and $bI_M = \beta I_B$, where $\alpha + \beta = 1$; we have

$$\frac{aI_M}{I_A} + \frac{bI_M}{I_B} = 1$$

and for n coloured lights

$$\sum \frac{nI_M}{I_n} = 1$$

E. Katz (Thesis, Utrecht, July 1941, p. 57) found an equation of the form

$$\frac{1}{\underset{B}{I_A}} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \frac{dt}{\underset{B}{I_A(t)}}$$

Van Kreveld's law, put into general terms by Webb is a satisfactory approximation to this function: *If two exposures I_A and I_B, of two radiation bands A and B, each give in t the same density D, this will also be obtained by a mixture of A and B such that the exposure is $\alpha I_A + (1 - \alpha) I_B$.*

SHAPE OF THE CHARACTERISTIC CURVE

203. The characteristic curve of a normal emulsion is generally S-shaped with a straight part between the two regions of underexposure and overexposure. The photographic reproduction becomes more exact when the toe is reduced to the benefit of the central straight part: these emulsions are found in the sensitive elements for colour photography and for photomechanical reproduction (*orthophotic emulsions*).

There are, on the other hand, *anorthophotic emulsions* which have no straight-line portion or which have two.

In the first case the concave toe is very long, only a tangent at the inflexion point marking the transition to the overexposure region (Fig. 12). The image obtained cannot be a precise reproduction of the subject.

The curves having more than one distinct straight line are obtained with emulsions with grains of different sizes (and therefore sensitivities): *these emulsions obtained by precipitation in steps, by mixture or by superimposition of two layers of different sensitivities* (being themselves mixtures) are currently used in the manufacture of plates and films to increase the exposure latitude.

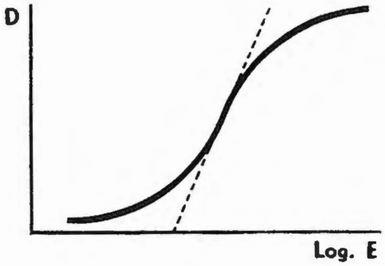


FIG. 12
Anorthophotic emulsion with no straight line.

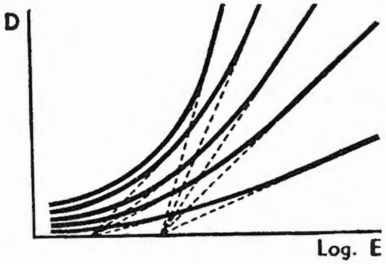


FIG. 13
Anorthophotic emulsion with two straight-line portions.

Each group of straight lines in the family of curves converges at a different point on or below the log E axis (Fig. 13), but frequently the lower part of the curve has no definite slope; this is a simple arc which joins the straight line higher up. These are called long-toe emulsions. Although approved commercially, these emulsions are inferior to the straight-line emulsions from the viewpoints of accurate reproduction and subsequent ease of printing.

The characteristic curve, instead of having a regularly increasing slope as above, can on the contrary, be composed of several straight portions with crossing gradients (Fig. 14) due to the non-correspondence of the constituent emulsions (bad blending for example).

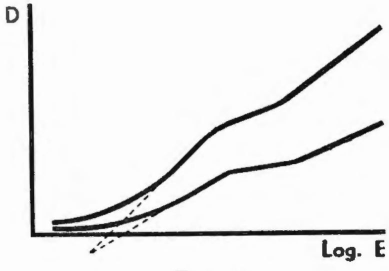


FIG. 14
Anorthophotic emulsion with decreasing gradient.

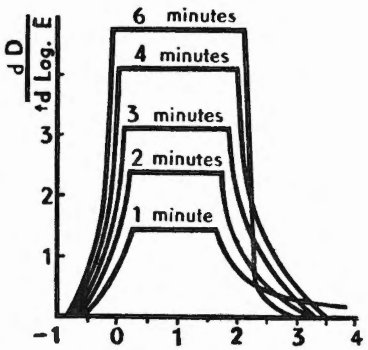


FIG. 15
Derivative curves of a positive emulsion.

204. Variation of contrast along the characteristic curve

The image contrast increases along the curve up to the start of the straight-line part after which it decreases to zero at the beginning of solarization; but the change in slope is not constant along the curve. Starting at the threshold, the increase is at first slow, then it increases progressively up to the straight line when it remains constant; it changes again if there is a break in the curve, then drops after a sharp turn at the beginning of the shoulder. This is shown in the *derivative curves* corresponding to the characteristic curves in which the ordinates are dD/d log E (Fig. 15).

205. Exposure latitude

The latitude is the *brightness rànge* which can be accommodated by a sensitive layer.

A good negative emulsion has a characteristic curve similar to that shown in Fig. 16; the straight-line portion covers a brightness range of 1 : 132. This range is sufficient to accommodate most subjects, but the latitude is in fact much greater, for the brightness range between A and D is 1 : 2,400. With a subject having a brightness range of 1 : 100 the total exposure latitude is 24—12 times for overexposure and 12 times for underexposure. It is obvious that the greater the brightness range of the subject, the lower the exposure latitude; the exposure time must be estimated more accurately.

The measurements of the extreme brightness values of a subject are therefore very useful; they can be made more or less accurately with various photoelectric photometers which are directed successively on the shadows and highlights of the subject. On the other hand the parts which are to be accentuated must be chosen in order to eliminate the extremes which would falsify the calculations: areas of snow, reflections from the sea, dazzling sky, useless shadows, etc., unless the interesting details are situated in the luminosity extremes, when the exposure is reduced or increased accordingly.

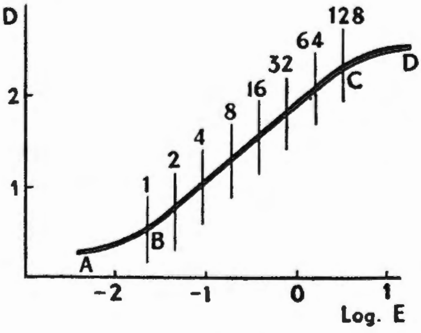


FIG. 16.

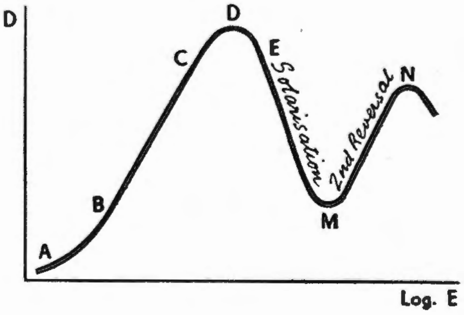


FIG. 17.

The normal brightness range—that is the range covered by the straight line—is reduced somewhat as development proceeds and contrast increases.

Always, and this should be carefully noted, it is the difference between the extreme densities which reproduces a fixed exposure range; if development is continued to $\gamma = 1$, the opacity range obtained will be equal to the exposure range, and consequently, when printing the positive, the negative gives an equal exposure range which the paper cannot accommodate. If, on the contrary, the γ is below 1, an extended luminosity scale will be translated into an opacity range which is much lower, as if it were compressed. The negative therefore has a reduced luminosity range; printing of positive copies will be simplified.

If ΔE is the log brightness range of the subject, and δ the density range which reproduces this brightness range, then

$$\delta = \Delta E \times \gamma$$

Compared with negative materials, *photographic papers* have but a slight exposure latitude. This explains why the negative must not have too great a brightness range. The greatest range is accepted by positive emulsions of low contrast (soft papers) as a low γ corresponds to a high ΔE.

Photographic papers have the following average characteristics:

Paper	*Brightness range*
Soft	30
Normal	20
Hard	10

206. Solarization

Solarization is a *reversal phenomenon* which is produced after a certain exposure when the density decreases instead of increasing ($E = 10{,}000-20{,}000$ threshold value).

Referring to the characteristic curve of Fig. 17, it is seen that after the point C there is a more and more accentuated drop in the rate of density increase as a function of exposure. The contrast drops until it is zero at D whilst the density is relatively constant for a considerable exposure range.

The overexposure region CD, with its characteristic slowing down of the density increase, is already related to the solarization phenomenon which it precedes.

Reversal by solarization takes place in the region DEM of the curve; the density falls as exposure is increased and the resulting image is a *direct positive*. The length of the part DM depends on the emulsion; most frequently it does not reach the exposure axis and leaves a considerable uniform residual density.

With some sensitive layers, a *second reversal* MN occurs, the density rising again. Some authorities state that there are several successive alternating cycles, of decreasing amplitude.

The relationship between solarization and the overexposure region gives rise to the supposition that the development centres are destroyed; that is, two opposite reactions both produced by light: after a certain exposure the destruction process completely predominates over the production of development centres.

The destruction can only take place on the centres already produced. It is admitted that the number of atoms of silver constituting a development centre is diminished below the developability level by *reconversion to silver bromide* by the halogen diffusing from the interior of the crystal towards the surface.

Solarization is enhanced by the presence of iodide ions I^-, whose concentration must be at an optimum, as well as by bromide ions Br^- (Chloride ions Cl^-, have no effect). Conversely, silver ions Ag^+, retard the phenomenon. Solarization is also favoured by *bromine acceptors*, 1% sodium nitrite, acetone-semicarbazone or phenol.(5)

Low temperatures (−160°C) prevent solarization. A static pressure, on the contrary, accelerates reversal:(6) 100 kg/cm^2 for papers and 400 kg/cm^2 for films.

Chemicals such as *sodium arsenite* or *stannous chloride* which can form a latent image in the absence of light, also produce reversal by solarization. Similarly, *hydrogen peroxide* and *ozone* can be used.(7)

The preparation of a solarized emulsion for the production of direct positives consists in producing a uniform latent image corresponding to the critical exposure. This can be produced by light, or can be chemical fog —controlled action of an arsenite for example. The sensitivity of such a material is lower than that of a chloride paper. Maurer and Yule have noted that certain emulsions, easily solarized, produce positives with a very long low intensity second exposure(8) following a relatively short first exposure.

The effect of gelatins with a high reducing power (producing internal fog and an unstable emulsion) is also important in the second reversal following solarization. In this case it assists a photoreduction process.

It should finally be noted that colour sensitization of direct positive emulsions requires higher concentrations of sensitizer than normal. In addition, desensitizers like fuchsine sensitize them to long wavelengths without altering the general sensitivity.

The *rehalogenization theory* which was outlined above was proposed by Luppo-Cramer in 1905, then supported by Webb and Berg (see Webb and Evans: *J.O.S.A.*, 1940, p. 445). It is generally accepted today. *Other theories* propose the interference of *coagulated silver* which loses its catalytic properties (Eggert, Arens, Noddack, Meidinger, von Ardenne); the *coagulation of the gelatin* around the grain (Luther); the *reduction of contact* between the bromide and silver metal by the liberated bromine (Kuhn and Erdos); and finally, more recently (1948), the *blocking theory* when the surface silver which develops quickly blocks the grain and isolates it from the developer (Hautot and Debot). The latter theory appears to have been abandoned by the first of its proposers.

LAWS OF PHOTOGRAPHIC ACTION

207. Reciprocity failure

Plot the characteristic curves of an emulsion first at constant intensity and varying time, then at constant time and varying intensity, in each case having the luminous energies of the two series corresponding to each other.

$$E = I_c t_V = I_V t_c$$

The two curves obtained are different. If low intensities are used, the variable time curve will be less contrasty than the variable intensity curve; but if a high intensity is used, then the variable intensity curve will have a lower gamma than the variable time one. It can be further stated that whatever the intensity used, the variable time curve has practically the same gamma, whilst the variable intensity curve has an appreciably higher gamma at low intensities.

Bunsen and Roscoe stated that the photographic action P is proportional to the product of the intensity of the light and the duration of the exposure: $P = It$. It is seen that this law is incorrect except for very active radiation: γ-, X-, α-, β- and cathode rays.

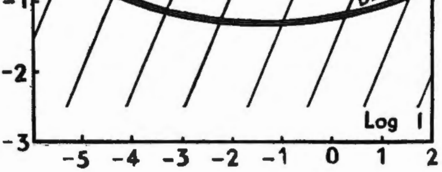


FIG. 18.

Graphical representation of reciprocity failure having the log I values on the abscissa and on the ordinate the log It values which give a constant density at each intensity value (Fig. 18). The exposure times are on the parallel lines which cut the resulting curve diagonally.

It can be stated that the exposure It, necessary to give a certain given density, is at a minimum for an average optimum intensity I_0 (maximum efficiency); with low and high intensities a greater exposure is needed to produce the same density.

At 0°C the minimum of the curve is still visible; at 50°C and with high intensities log It tends to decrease, whilst at —75°C it tends to increase.

The inclusion of silver iodide in an emulsion produces a shift of the reciprocity curve without changing its shape.(9)

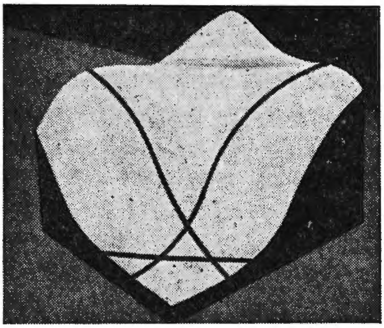


FIG. 19.

Characteristic surface of an Agfa negative emulsion obtained by Arens and Eggert having log 1 and log t horizontally and D vertically. The horizontal region of the front corner, represents the "inertia zone" limited by the threshold of effective exposure (black line): in the upper part the gradient of solarization followed by a further upward curve of the surface will be noted.

To calculate the reciprocity failure with the characteristic curves, these are sometimes represented in three dimensions which correspond respectively to the log intensities, the log exposure times and the densities (vertically). This results in what are known as '*characteristic surfaces*' or rather volumes. The characteristic surfaces are more difficult to interpret than ordinary characteristic curves without considerable experience. They can be replaced with flat representations (Fig. 20).

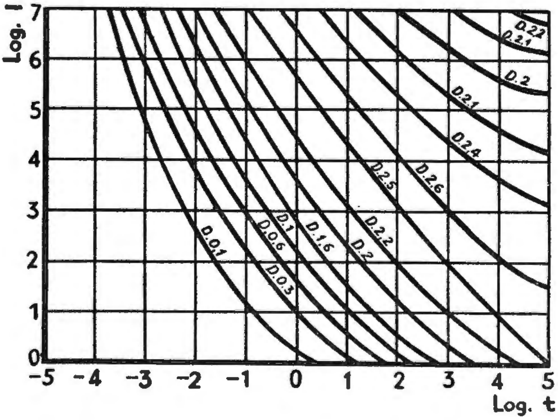


FIG. 20.

Flat representation of the characteristic surface of a negative.

208. Threshold of effective illumination

At low light levels, *no impression is made on the sensitive layer below a critical level of illumination whatever the time of exposure.* This is the true inertia value: the *threshold of effective illumination.*

There is no reciprocity failure with exposure times less than 4×10^{-5} secs. according to Berg's calculations, confirmed by Alentsev.(10) However, at high intensity levels with exposures of 1 μsec. on a panchromatic emulsion, Milne found failure with red light, but not with blue light.(11)

Reciprocity failure is explained by the *delays* which can occur during the concentration of the silver ions Ag^+ around the sensitivity specks. These become saturated with electrons and the electron transfer is retarded. According to Mott, the small centres lose their electrons which recombine with bromine atoms.

At low intensities, thermal decomposition prevents the sub-latent image from increasing by capturing electrons.

Emulsions for Raman effect. The emulsions for the study of the Raman effect must be very sensitive to low intensities of illumination at exposure times as long as 20 hours. Grain sufficiently fine to give a resolving power of 20 lines/mm. Development gamma: 1·5.

209. Schwartzchild coefficient

Schwartzchild has stated that the photographic effect P can be expressed with a satisfactory approximation by the formula

$$P = It^P$$

where p is a variable term about 0·85. It is given by Renwicks formula

$$p = \frac{\gamma t}{\gamma i}$$

where γ_t and γ_i are the contrast factors of the curves obtained with intensity scale and time scale exposures. p, which possess a minimum at average brightness, is lower for slow emulsions and moreover varies with the wavelength.

Krön's formula, on the other hand, represents experimental observations:

$$P = It \times 10^{-\alpha\omega} \text{ with } \omega = \sqrt{1 + \left(\log \frac{I}{I_0}\right)^2}$$

The coefficients a and I_0 depend on the emulsion. a is in general about 0·2. For low illuminations the relation is reduced to that of Schwartzchild where $p = 1/1 + a$ and, for high intensities, to the Bunsen-Roscoe formula.

The Schwartzchild conception is no longer accepted for medium intensities.

210. Intermittency effect

The effect produced by an intermittent exposure is, for equal energies, lower than the effect produced by a continuous exposure; the characteristic curve obtained with intermittent exposures has lower densities especially at the lower It values (Fig. 21).

Intermittency has no effect once the frequency of interruption reaches a critical level which depends on the nature of the emulsion. This critical frequency increases with the square root of intensity and drops with the total exposure time.⁽¹²⁾ This phenomenon is attributed to the fact that the dark periods, becoming very small, become comparable with the intervals which separate the individual quanta affecting each grain.

The critical frequency is proportional to the relationship: time of flash/time of flash + darkness; and is not dependent on the emulsion and the development.⁽¹³⁾

With very active radiation, such as X-rays, a single quantum can make a silver bromide grain developable; interruption of the exposure then has no effect whatever the frequency.

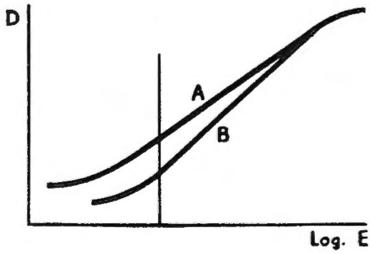


FIG. 21. A: continuous exposure. B: intermittent exposure.

To explain the photographic action of intermittent exposures in the case of moderate intensities two opposing factors must be considered: the formation of the latent image and its subsequent destruction. The latent image can lose electrons to form silver ions Ag^+ which again become dispersed interstitially in the crystal lattice. This regression of the latent image can continue even during the start of the following exposure and is accelerated by raising the temperature and increasing the dark period.⁽¹⁴⁾

REVERSAL EFFECTS

211.

A photographic image can be reversed, that is, destroyed, by a second exposure of long duration when the first exposure was made by the most vigorous photochemical action. This can be with X-, γ- or corpuscular rays (*Villard effect*), or even with visible radiation of extremely high intensity and short duration (*Clayden effect*). In practice, the sensitive layer is first fogged uniformly by one of the methods mentioned, then the fogged emulsion is again exposed at a low intensity for a sufficiently long time. The first exposure produces a strong latent image, but in the interior of the grain. Silver bromide solvents which favour development of the internal latent image must be avoided as they destroy the reversal effect. E. Weyde⁽¹⁵⁾ stated that the Clayden effect can be applied to *printing out* of coarse-grain emulsions; Agfa 'Registrier papier L' has a silver bromothiocyanate emulsion containing halogen acceptors.

212. Herschel effect

A latent image can also be reversed by a second exposure to red or infra-red light. The sensitive layer is first fogged uniformly to its maximum density with blue-violet light, then re-exposed at a wavelength greater than 600 $m\mu$ behind a positive, preferably at low intensity for a long time. After development, a positive is obtained. Similarly, an ordinary latent image loses contrast when exposed to these radiations for a short time. If red light is used, an intermittent exposure enhances the destructive effect; on the other hand, an intermittent exposure has little effect when infra-red light is used.

The reversal effect caused by red and infra-red light depends for its effectiveness on the nature of the emulsion, on the total exposure and on the intensity of the first exposure. Low densities are especially affected when obtained with low intensity blue light.(16) Bromide ions and oxidizing metallic ions such as Fe^{+++} and Cu^{++} favour the Herschel effect.

The influence of *humidity* on the Herschel effect is considerable and explains the difference obtained by many workers.(17) This influence varies with each emulsion and cannot be generalized.

Certain *oxidizing agents* have a favourable effect, especially quinone—0·05%—together with an equal quantity of potassium bromide or iodide, or 0·05% potassium dichromate + 0·5% manganese sulphate.(18) The bathed plate is dried without rinsing, exposed to uniform blue light then to red light. Sensitization with perborate has also been studied.(19)

Emulsions ripened in the presence of *sulphur sensitizers* are more prone to the Herschel effect whilst those treated with gold are inert.(20)

By applying the general theory of Gurney and Mott, and after the work of Hautot and Falla it appears that the Herschel effect is due to the absorption of red light by the metallic silver development centres. The spectral region of this absorption is at about 700 $m\mu$—exactly where the F-band of the alkali halides is found, which as we know, appears after irradiation with ultra-violet. Debot has shown that the affected centres lose their electrons which pass into the conduction levels whilst the Ag^+ ions formed, activated by thermal agitation, migrate towards the interior, or vice-versa. The internal image is intensified by recombination of the Ag^+ ions with electrons re-forming metallic silver Ag. The total mass of the latter therefore remains constant, but is found dispersed in smaller centres. In the solarization region, the effect is sometimes additive, sometimes subtractive. If the latent image is strong, the photo-electrons can return to the silver ions, or be captured by an F-centre where silver ions are found (case of overexposure).

213. Becquerel effect

Contrary to the reversal effects, it is possible to *strengthen* or induce the printing-out of an image by a second uniform exposure to green or orange light (itself inert). The photolytic silver, produced by the first exposure renders the emulsion orthochromatic. Chloride print-out papers bearing an image have been strengthened in this way, whilst a print-out image can be formed in a silver gelatino-bromide emulsion which has previously been exposed to X-rays.

214. Photochemical reversal

A uniformly fogged sensitive layer impregnated with a *dilute solution of desensitizer* (such as safranine) and *potassium bromide*, and dried, will be reversed by a *second exposure* under an image, due to the proportional destruction of the latent fog. Good results are obtained with fine-grain lantern plates and 1 : 5,000 solutions of safranine or Pinakryptol Green containing 1% potassium bromide.

The active radiations are those which are obsorbed by the dye except for a shift of 50 $m\mu$ towards the longer wavelengths. See the notes below.(21)

215. Sabattier effect

Reversal takes place when the material is uniformly exposed (or bathed in a solution of sodium arsenite) *after the image development has started.*

The lines separating the dark and light areas in the first image and which have been affected by the uniform exposure form, after reversal and complete development, clear lines having a 'piped' appearance (application: in spectrography and sensitometry with absorbing wedges, to accentuate the difference between dark and light areas).

To Stevens and Norrish(22) the Sabattier effect seemed to be due to the desensitization of the silver bromide by the silver developed during first development (even very short). The desensitizing effect is, in fact, destroyed when the metallic silver is removed in a bleaching solution.

The Sabattier effect is very pronounced with very low contrast emulsions. According to Arens,(23) these emulsions have only an internal latent image after first exposure. By developing, the superficial sensitivity specks of the unexposed grains are reinforced. The second uniform exposure produces, on the latter grains, an external image, whilst the electrons freed in the pre-exposed grains go to the internal centres. In normal emulsions there is, from the start, a balance between the surface sub-centres and the internal centres of the grains with no surface centres.

The second exposure can be replaced by a solution of hydrogen peroxide or sodium arsenite, or merely by simply adding a fogging agent to the first developer: hydrazine or hydroxylamine salts, thiourea, etc. The image appears first as a negative, then becomes positive under the action of the fogging agent.

ACTION OF POLARIZED LIGHT

216. Weigert effect

Polarized light, diffused by the turbid emulsion, acts anisotropically in two directions at right angles. If Ox is the direction of the incident beam and Oy that of its perpendicular electric component, the corresponding absorption coefficients Δx and Δy will not be equal.

A photographic emulsion exposed to polarized light gives, if the crystals are sufficiently fine, *oriented silver grains* which produce a dichroic effect.(24)

This dichroism is most readily seen with Lippmann emulsions after development, as well as with print-out emulsions whose particles are about 35 mμ in diameter. This dichroism increases as a function of the exposure time up to a saturation value. If there has been a preliminary exposure to non-polarized light, the dichroism has a sharply defined maximum corresponding to an optimum degree of pre-exposure. In every way the appearance of this phenomenon varies with the emulsion type as well as the development method used.

Photodichroism is also produced in single crystals of alkali halides (and also in silver halides), previously exposed until the F-band of absorption appears,(25) the band due to an excess of metal ions in irregular positions in the lattice. By exposing to plane polarized light, the crystals fade and become dichroic.

The Weigert effect on dyes has been studied by Nikitine.(26) The dye molecules diffuse the light anisotropically, this enables them to be destroyed irregularly, by polarization, in two different directions thereby producing dichroism.

FOG

Fog, general or partial, is a more or less intense blackening which can be due to the nature of the emulsion, to development, to aerial oxidation or to ageing.

217. Emulsion fog

This is caused by the presence of silver bromide grains which are spontaneously developable without light action. Over-ripening, excess washing during the preparation, addition of sulphur sensitizers or certain metallic salts, the presence of gelatin degradation products, colour sensitizers, are among the causes of fog.

Fog is measured by its density. Almost absent in positives, it can be tolerated up to 0·2 for negatives.(27) In current measuring technique the fog value is deducted from the other densities. This method leads to incorrect results, for the fog decreases with density, and becomes negligible at high densities. In fact the reduction of relatively large amounts of silver bromide results in the local formation of equivalent quantities of soluble bromide which helps to prevent the development of fog in the dense areas of the photograph.

Uniform fog obtained by pre-exposure leads to an increase in sensitivity. By post-exposure, it is a method of latensification (see para. 31). The maximum density increase is obtained when the image is at the beginning of the straight line of the curve. The increase in sensitivity is due to the fact that the fogging exposure, if taken just to the threshold, leads to the formation of development centres which are very small but sufficient to initiate the rapid increase to larger grains. The sensitization by fogging is used in astronomy for the study of nebulae which are barely visible.

218. Other causes of fog

Development fog is sometimes produced by the developer or desensitizer, by chemical formation of spontaneously developable grains. Hydrogen peroxide, formalin and some resins have a similar action.

Aerial oxidation fog is caused by contact with atmospheric oxygen when the emulsion is removed from the developer. It is said to be an effect of luminescence. Oxidation fog is produced by hydroquinone alone and by metol, glycin and p-aminophenol in the presence of traces of copper salts or by the influence of certain sensitizers.

Age fog is produced when the emulsion is stored for too long. It is produced more rapidly with colour sensitized plates than ordinary ones. Age fog depends on the sensitivity of the emulsion, that is on the presence of sensitivity centres in an unstable state which become spontaneously developable. Hypersensitized emulsions will only keep for a very short time. The storage of emulsion is an important matter which will be examined in the second part (para. 347).

Physical fog is caused by unwanted images which are produced by reflection of the light on the surfaces of the lens. If there are n surfaces, the total number of unwanted images, y, is

$$y = \frac{n(n-1)}{2}$$

For example, in a lens with four separate glasses $y = 28$. These images have the effect of reducing contrast by increasing the clear areas and reducing the dense ones.

---

1. This blackening is due to the liberation of a certain amount of silver by the developer. For a given mass of metal per unit area, it can vary with the size of the particles which itself depends on the emulsion type, the nature of the developer and the time of development. That is, the covering power of the silver can take a wide variety of values depending on the more or less spongy structure of the grains. An average value is 1 g of metal per m^2 for a density of 1.
2. The sensitive layers have a thickness in the order of 30 μ. Some have 6–10 μ. This means, if the grains have an average diameter of 1 μ, a number of crystal layers between 6 and 30.
3. It is often of interest to plot non-logarithmic curves or again with the densities on the ordinate and the exposure (non-log) on the abcissa, by limiting it to the threshold and underexposure region. In this way, the point of limiting effect is shown on the curve. If there is no photochemical inertia, the γ is at a maximum at the origin. If there is inertia the slope is nil at the beginning.
4. During the induction period, $\gamma = \gamma_\infty(1 - e^{-k(t-t_0)})$. If the point is below $D = 0$ $D = D_\infty - (D_\infty + D_0)e^{-kt}$.
5. Loening E. E.: *Bristol Phot. Conf.*, 1950, 126–148.
6. Oyama Y.: *Jl. Soc. Sci. Phot. Japan*, 1947, 115–120.

7. A 0·2–0·5 mol./l. solution of hydrogen peroxide, for example.
8. Maurer R. F. and Yule J. A. C.: *J.O.S.A.*, 1952, 402–408.
9. Fujisawa S. and Misuki E.: *Sci. Ind. Phot.*, 1953, 302–308.
10. Alentsev M. H.: *Jl. Exp. Theor. Phys.* (*U.S.S.R.*), Jan. 1947, 75–78 and *Sci. et Ind. Phot.*, **11,** 174.
11. Milne G. G.: Thesis, Univ., Rochester, 1952, 30 pages.
12. Webb J. H.: *J.O.S.A.*, 1933, **23,** 157. Kartuzanskii: *Sc. Ind. Phot.*, 1956, **27,** 20–22.
13. Kartuzhanskii A. L. and Meiklyar P. V.: *Jl. Eksper. Teor. Fiziki*, 1951, 598–609 and *Sci. Ind. Phot.*, 1953, 351–352.
14. Blair J. M.: *J.O.S.A.*, 1942, **32,** 332.
15. *Zeits. Wiss. Phot.*, April 1953, 45–57.
16. Trivelli, Leszynski and Hall, cited by Clerc in 'Structure et propriétés des couches photographiques', *loc. cit.*, p. 106, 1st edition, Paris.
17. Vanselow, Quirk and James: *P.S.A. Jl.*, 1953, 66–69.
18. Kaempf: *Zeits. Wiss. Phot.*, Dec. 1950, 165–173, also Hautot and Sauvenier: *Sci. Ind. Phot.*, 1949, 287.
19. Fortmiller, James, Quirk and Vanselow: *J.O.S.A.*, 1950, 487–496.
20. Sasai A.: *R.P.S. Cent. Conf.*, London 1953; *Bull. Soc. Sci. Phot. Japan*, 1952, 19–30.
21. Luppo-Cramer: *Zeits. Wiss. Phot.*, May 1928, 282–287; *Sci. Ind. Phot.*, 1928, 114. Mauz E.: *Zeits. Wiss. Phot.*, Feb. 1929, 289–294. Carroll and Kretchmas: *Jl. Res. Bur. Stand.*, 1933, 449–464; *Sci. Ind. Phot.*, 1933, 223. Cohen-Solal: *Sci. Ind. Phot.*, 1952, 388.
22. Stevens and Norrish: *Sci. Ind. Phot.*, 1938, **9,** 331.
23. Arens H., *Zeits. Wiss. Phot.*, July 1949, 44–50; Oct. 1949, 172–181; Dec. 1951, 125–134; April 1953, 48–52.
24. Narath and Wasserroth: *Colloque Sci. Phot.*, Paris 1951, 38–46 and *R.P.S. Cent. Conf.*, London 1953.
25. Nikitine S.: *Compt. Rend. Ac. Sc.*, Paris 1941, 32–34.
26. Nikitine S.: *Ann. Phys.*, 1941, 284–348.
27. The fog of new *commercial* negative emulsions should not exceed 0·08. That of positive emulsions should be almost nil.

Chapter XV

SENSITOMETRY

219. To obtain the characteristic curve of a photographic emulsion, it is exposed to a known light source; the sensitive layer receives a series of exposures of either varying time or varying intensity. After developing the 'wedge', the resulting densities are measured with a photometer (or densitometer), and the characteristic curve is plotted, as shown in the previous chapter.

We know that the slope of the curve (Fig. 22) is the *contrast factor* γ:

$$\gamma = \tan\alpha = \frac{a}{b} = \frac{D}{\log E - \log i}$$

or

$$D = \gamma(\log E - \log i)$$

As γ increases with development time, up to γ_∞, several identical sensitometer strips must be exposed, which are developed for increasing times.

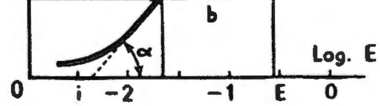


FIG. 22.

The *choice of the light source* is of great importance, for the different sources each emit light of different spectral compositions. The results obtained by exposing a plate to two different light sources cannot be compared directly.

The sources corresponding to practical use are: daylight, normal or overrun incandescent lamps, arc lamps, flashbulbs and U.V. sources.

In sensitometric work it is usual to use electric light, suitably filtered to give the desired spectral composition. The sensitometric sources used in the past were the Hefner amyl acetate lamp, the paraffin lamp and the acetylene burner.

The tests should in every way be related to practical working conditions or the results will have only a limited significance; thus a material intended for use in artificial light should not be tested in daylight conditions and vice-versa.

220. Exposing instruments—sensitometers

The exposure of sensitive layers to obtain sensitometric wedges can be made in two different ways:

(*a*) by varying the exposure time: single or intermittent exposure;
(*b*) by varying the intensity of the light.

The first method is relatively simple to carry out, but does not correspond to practical use where the time is constant and the light intensity varies. Also intermittent exposure introduces a further cause of error.

(*a*) *Time-scale sensitometers.* The simplest type consists of a shutter which uniformly uncovers the plate being exposed. The best types have an automatic mechanism for moving the shutter. A shutter having a series of vertical apertures of different lengths can also be used.

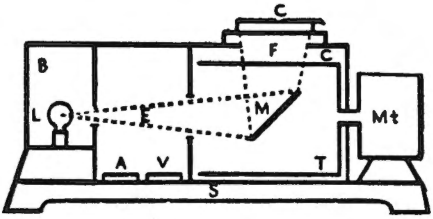


FIG. 23.

More frequently a *sector disc* is used, where openings subtend an increasing angle at the centre following a geometrical progression. By turning the disc in front of a sensitive layer, this is uncovered for time t. If the time for a complete revolution is r, for an angle α one has: $t_1 = \alpha r/360$ and for n revolutions $t_n = n\alpha r/360$.

With a big disc having large apertures, only one revolution need be made: such is the Jones sensitometer in which the ten exposure times increase in a geometrical progression with a factor of 2.

To increase the exposure range, two revolving discs must be used.

The Eastman IIB motion picture sensitometer⁽¹⁾ has a rotating *drum* whose surface is cut in a series of parallel apertures of different lengths increasing in $\sqrt{2}$ steps. The light passes through these apertures via a stationary mirror fixed inside the drum, the film being held outside. (Fig. 23.)

(*b*) *Intensity scale sensitometers.* Intensity scale sensitometers with constant exposure time, consist in principle of a means of modifying the intensity of the light source to be used for the exposure.

The variation of the light can be produced by a *diaphragm* or by *absorption.*

The Roulleau and Lafouasse instrument⁽²⁾ for example, has a series of thirty-eight circular diaphragms. The image of the lamp is projected onto the plate with a simple lens. The plate must therefore be moved thirty-eight times mechanically.

A diaphragm with slotted apertures avoids zonal aberrations. It is also possible to use metallic grills or even the penumbra of a shadow.⁽³⁾ Another system forms, using a cylindrical lens, the image of a series of stepped parallel apertures.⁽⁴⁾

The light absorption can be effected with a polarization apparatus such as Tardy's⁽⁵⁾ where four Glazebrook prisms replace the nicol prisms. Thirty-two $\sqrt{2}$ intensities are obtained.

The most practical sensitometers are those with *absorbing wedges* or preferably *step-wedges*. They have been criticized for lack of neutrality towards the various wavelengths, and for their lack of precision. This however is quite adequate for routine work.

The simplest method is to place a wedge over the material under test and expose it to the selected light source.

A sensitometer similar to the D.I.N. instrument (standard in Germany) and using a step wedge is also very convenient (Fig. 24); the tungsten filament lamp is placed in front of a matt black surface, a filter cell, having one or two layers of filtering liquid, allows light of the required spectral quality to be used. The sensitive layer is 1 m from the lamp and is behind a wedge having thirty steps from zero to density 3. The exposure time (in this case 1/20th sec.) is given by a falling plate with a fixed opening. The guillotine shutter can be replaced by the more accurate pendulum type. The standard Japanese sensitometer N.S.G.⁽⁵ᵇ⁾ is of this type, with an exposure time of 1/50th sec. and the light source is a 500-W lamp operating at 2848° K behind a Davis-Gibson filter. The D.I.N. sensitometer is primarily used to measure the threshold sensitivity.⁽⁵ᶜ⁾

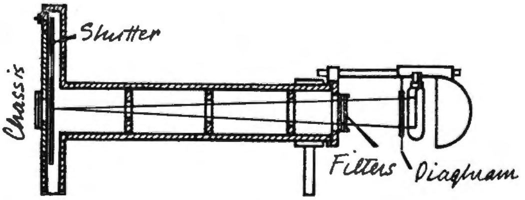


Fig. 24.

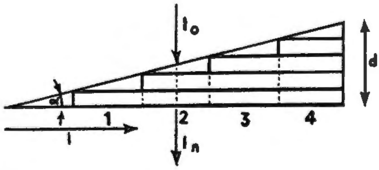


Fig. 25.

221. Photometric absorbing wedges

(*a*) Photometric (or neutral density) wedges are used to progressively absorb the incident light. A wedge can be made from several superimposed layers as in Fig. 25.

If I_0 is the intensity of the incident light, ϵ the transmission coefficient of the single layer, and n the numbers of layers, the intensity of the transmitted light is, for the first layer $I_1 = I_0 . \epsilon$ and for n layers $I_n = I_0 . \epsilon^n$. The intensity of the transmitted light decreases exponentially with n, that is, with the thickness of the absorbing layer.

Fig. 25 shows a step wedge in which the densities of the simple layers are added. In the case of a continuous wedge, the density is a function of the distance l along the wedge, following the formula

$$D = Kl$$

where K is the *wedge constant*. If the unit chosen is the centimetre, for $l = 1$ cm, D = K; therefore K is the value by which the density increases per centimetre. Fig.

26 shows the variation in transmitted light as a function of l, for a constant of 0·4. The value of K can be established by measuring the densities at two points l and $l + x$ (cm) and dividing the density difference by x.

To examine negative emulsions, wedges with a constant of 0·25 and sometimes 0·5 are used; for bromide papers wedges with a constant of 0·25, and for studying halation, 0·75.

When the wedge is made by casting, it can have irregularities in thickness or in pigment concentration; lines of equal density across the wedge are then found by making a large number of measurements.

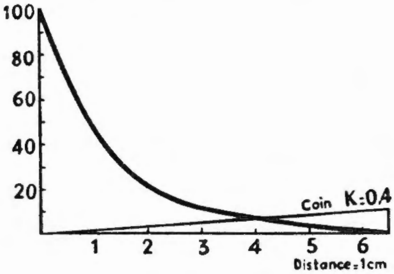


FIG. 26.

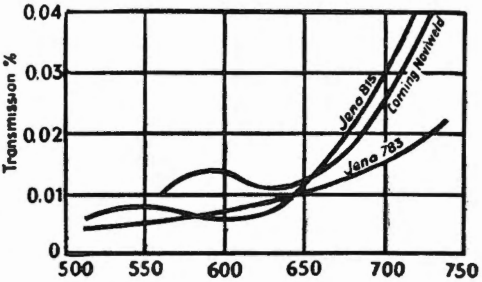


FIG. 27. Neutral glasses

Neutral density wedges are never absolutely neutral; their absorption varies to some extent with the wavelength; this is why precise measurements necessitate a certain correction dependent on the characteristics of the wedge and the light source used. For each gelatin wedge, K can vary, for example, from 0·189 to 0·203 passing from 600 to 440 mμ. The constant can similarly be doubled from 480 to 230 mμ. So-called neutral glasses also have irregular transmission spectra (Fig. 27).

(*b*) *Gelatin wedges* are made by preparing a mould from two inclined pieces of glass separated at one end by a spacer 1 mm thick, and pouring in a 20% solution of coloured gelatin. The lower glass is covered with a very thin layer of albumen to facilitate removal of the dry wedge. The wedge is then mounted between two thin pieces of glass, preferably together with a compensating wedge of colourless gelatin.

The gelatin is usually coloured with reduced silver(6) (in a developing solution) or with graphite. Indian ink (or carbon black) together with dyes has also been used.

Neutral glass wedges are bound up with an identical compensating wedge of clear glass.

Step wedges can be made more accurately than continuous ones as the individual steps can be retouched with an abrasive reducer to obtain the exact density. Two methods are used to make these wedges: the photographic method by successive exposure and development of a photomechanical emulsion, or by casting a suspension of silver in gelatin, using a machined bronze mould which has been waxed (*Sci. et Ind. Phot.*, July 1951, p. 254). Finally the availability of *circular wedges* should be noted.

(*c*) *Preparation of characteristic curves using continuous wedges.* The characteristic curve of an emulsion can be obtained automatically with a continuous wedge.

The emulsion under test is exposed under a wedge so that the minimum exposure given at the dense end of the wedge is known, for example 0·01 c.m.s. ($\log E = \bar{2}$). After development the emulsion has a series of densities corresponding to the gradations in the wedge. The original wedge and the wedge on the material under test are then superimposed at right angles. A print is then made from this combination with an exposure such that the densities above 3 for example give no image. After development, the paper will have two diagonally placed areas in black and white separated by a line following the characteristic curve of the emulsion being tested. Along this line the sum of the densities of the two crossed wedges $D_N + D_W$ is constant; now $D_W =$

Kl where $D_N = C - Kl$. If the limiting density for printing the system is chosen to be 3 then $C = 3$. In addition, it is known that the exposure of the negative varies inversely with the density of the wedge, that is $Kl = \log E$.

Wedges with a constant of 0·4, 8–10 cm square are generally used. For ciné films, a normal 3·5 cm wedge is first used, then for the print on paper, a wedge with a high constant l or $l = 3{\cdot}5$. The curves obtained in this way are flattened, their ordinates having a value 2·5 times greater than their abcissae.

222. Density measurements

The densities of the different steps of a sensitometer strip can be measured with specular or diffuse light. The first method, which is more accurate, is used with materials intended for projection, enlargement, photometry or spectroscopy; the second corresponds to contact printing.

The instruments used for measuring photographic densities are called *photometers* or *densitometers*. When small areas are to be measured, *microdensitometers* are used.

Whatever the instrument, it must contain a light source, photosensitive receiver (which can be the eye) and a measuring device. The density to be measured is placed between the source and the receiver; some type of diaphragm limits the measured area.(6b)

(*a*) *Visual densitomers*. The best-known type is the classic Bunsen photometer in which the brightness of two sources is balanced by varying the distance, until the areas of equal brilliance are obtained. The Fergusson photometer is based on the same principle. These are cumbersome instruments.

The Martens polarizing photometer(7) is inaccurate for high densities.

The light can also be reduced with a sector disc (Jones' instrument).(8) Two revolving adjacent discs were used by Lob and Vodar.

A circular wedge is used to match the two fields in the Capstaff-Purdy densitometer.(9)

The simplest method of varying the intensity of the light is to use absorbing wedges. This is a very convenient method. For measurements of the highest precision the spectral absorption of the wedge must be determined. The most common instrument is the Fabry and Buisson microdensitometer(10) which is a modification of the Hartmann apparatus; the eye sees two adjacent fields provided by the measuring area and the modifying wedge. As the images are formed on the pupil rather than the retina of the eye, graininess is not apparent. The Martin microphotometer is based on the same principle.

The Goldberg *densograph* enables the characteristic curve to be drawn directly; the sensitometric print and the wedge are placed at right angles to each other and are examined by two light sources. The two beams are simultaneously examined with a photometric cube. For each density of the sensitometric print, the wedge, mounted on a movable carriage with a pen, is moved to achieve balance of the two beams. Knowing the densities of the wedge, and hence those of the sensitometric print, a graph is obtained.(11)

The Bull and Cartwright integrating sphere measures the effective density $D\phi$ directly.(12)

Danjon's microdensitometer uses the disappearance of diffraction fringes, produced by polarization.

In Meggers and Foote's instrument, the brightness of the lamp filament is varied.

(*b*) *Thermoelectric densitometers.* The receiving device is a thermopile or thermocouple, a bismuth-silver couple for example, and is connected directly to a galvanometer or to an amplifier (Lyot). The method has the advantage of stability and speed. The optical system must be completely achromatic and the apparatus must be well insulated.

The best-known instruments are those of *Moll*, made by Kipp and Zonen at Delft, of *Harrison* and of *Albrecht* and *Dorneich*. They are recording instruments.(13)

223. Photoelectric densitometers

Various types of photocell are used as receiving devices.(14)

Barrier cells are very easy to use. The current produced by the light is measured with a galvanometer. However, the current is not proportional to the incident light, making individual calibration necessary. Over long periods of use the cell is liable to fatigue and the current drops.

Photoemissive cells are more accurate than the barrier type but even so the current is not exactly proportional to the incident light. The current is generally amplified, before measurement, by what are generally called electron multipliers.

Each cell has its individual characteristics, and this makes it almost impossible to obtain two identical ones.

A sheet of photographic paper moving at a definite distance past the galvanometer beam can record the deflections reflected by the mirror. The accuracy drops at high densities which has led to the construction of log scale galvanometers.

Among the principal barrier type photoelectric densitometers should be mentioned the *Baker* instrument (*Jl. Scient. Instr.*, Oct. 1947, p. 275) and the *Evans Electro-selenium (EEL) Densitometer* made at Harlow, Essex.

The *Kruger and Moeller, Koch, Lambert and Challonge*(15) instruments are recording types using photoemissive cells.

Among recent densitometers are the following:

The Ansco-Sweet Densitometer (*Sci. et Ind. Phot.* (2), **16,** p. 261 and **18,** p. 165 and *J.O.S.A.*, 1947, p.432) in which the cell sensitivity is a logarithm of the applied voltage.

The Baldwin Densitometer, a direct reading instrument made at Dartford, Kent.

The Frayne and Crane Integrating Sphere Densitometer (Electrical Research Co.) which measures the effective density. (*J.S.M.P.E.*, 1940, 184–199 and *Sci. et Ind. Phot.*, 1940, 248).

The Streiffert (Kodak) Densitometer: the light passing through an integrating sphere is measured by two cells to give $D_{\|}$ and $D_{\#}$ (*J.S.M.P.E.*, 1947, 506–522 and *Sci. et Ind. Phot.*, 1948, 119).

Linse A. G. (Berlin) Densitometer designed for use on a rewind table. A portion of the light beam forms an enlarged image of the illuminated part of the film, on opal glass. (*Sci. et Ind. Phot.*, 1950, 291.)

Grabke Densitometer for ciné film has an optical system, an amplifier and a paper recording system (*Bild und Ton*, 1952, 6–11 and *Sci. et Ind. Phot.*, 1952, 265).

The Altmann (Kodak) Densitometer whose optical system gives an extremely small illuminated area (*J.O.S.A.*, 1951, 560 and *Sci. et Ind. Phot.*, 1951, 217).

The Pinoir and Baby Instrument (Kodak), adapted from the Sannié recording microdensitometer, produces a pen-drawn curve (*Sci. et Ind. Phot.*, 1951, 88).

224. Null-reading photoelectric densitometers

As with the visual instruments, two fields are compared with the cell, but successively; two light beams, one via the sample and the other via a known wedge are balanced. The measurement consists of returning the galvanometer to zero each time.

Many methods have been used to produce the two beams simultaneously: revolving discs partly cut away, moving total reflection prisms, nicol prisms, etc.

A simpler method is to superimpose the wedge and the sample. The light passing through the system is reduced or increased by moving the wedge in such a way that the current is constant. Rosenberg's instrument is of this type.

Other instruments use two cells, connected in series and illuminated by the same source. The galvanometer is adjusted to zero, and the sample is placed in front of one of the cells; the needle is then brought back to zero by moving a corresponding wedge. The movement of the wedge gives the density following the formula D = Kl.

In the *Boutry microdensitometer,*(16) the light beam is divided in two, one beam passes through the sample adjusting wedge system, whilst the other passes through a constant comparison density. By moving the wedge a certain amount, the measuring beam is balanced with the comparison beam. The light received by the cell is therefore constant. A revolving toothed disc, placed in front of the cell, enables the two beams to be received successively. Because of the simplicity of its principle the instrument is accurate. E. Vassy has converted it to a recording instrument by mechanically increasing the movement of the wedge and recording the trace on graph paper (made by Kodak-Pathé).

The *Agfa sensitograph* is a development of the Goldberg densograph, having two cells in opposition and a mechanism for automatically drawing the curve. (F.P. 753,809 (1933), *Sci. et Ind. Phot.*, 1934, 77.)

In the *Eckelmann and Schmidt densitometer,* the image of a slit is first projected onto the sample, then onto a screen on which it is enlarged. Two cells in opposition are used. (*Kinotechnik,* 1941, 5–8 and *Sci. et Ind. Phot.*, 1941, 115.)

Wernick's sound-track densitometer has two cells in opposition (*Kinotechnik,* 1940, 31–33 and *Sci. et Ind. Phot.*, 1940, 247).

Hall's microdensimeter uses a logarithmic potentiometer (*Jl. Sci. Instr.*, 1949, 365 and *Sci. et Ind. Phot.*, 1950, 51).

Pinoir's densitometer (Kodak-Pathé). The e.m.f. generated by the cell is cancelled out with an equal e.m.f. to give a constant reading (*Sci. et Ind. Phot.*, 1951, 321).

Goble automatic densitometer has an optical system with two cells, using a circular comparison wedge, an amplifier and a mechanical system. (*Jl. Sci. Instr.*, 1953, 110–113 and *Sci. et Ind. Phot.*, 1953, 279.)

Equal-density curve recorder: two bridged cells receive two beams transmitted by the sample and a reference density respectively. The light source is the spot of a cathode ray oscilloscope. A reading oscilloscope synchronized with the first records the intensity difference of the two circuits (Fowler, Johnson and Billings, *J.O.S.A.*, 1953, 69).

New Kodak densitometer. This very accurate instrument has an optical system with two beams, one for comparison, an amplifier and a galvanometer whose deviation corresponds to the log of the current intensity. (K. G. Macleish: *J.S.M.P.E.*, 1953, 696–708.)

Special densitometers. Some densitometers have been modified for restricted purposes. Among these are:

The Dietert and Schucht *projection comparison densitometer* for spectrographic analysis (*J.O.S.A.*, 1941, 54–57 and *Sci. et Ind. Phot.*, 1941, 116).

The apparatus described by Kirchgessner and made by *Bausch and Lomb* is also intended for spectrography (*Rev. Sci. Instr.*, 1951, 289–292 and *Sci. et Ind. Phot.*, 1951, 373).

Taylor's *direct-reading microdensitometer* for X-ray diffraction patterns (*Jl. Sci.*

Instr., 1951, 200–205) is a variation of Dobson's apparatus (*Sci. et Ind. Phot.*, **3R,** 1923, 182).

Also for X-ray diffraction patterns is the *Brentano recording microphotometer.* The galvanometer spot is received on a photographic plate (*R.P.S. Centenary Conf.*, London 1953, and *Sci. et Ind. Phot.*, 1954, 16).

Densitometer for radiographs by Bruch, Lochet and Valentin is derived from Boutry's constant light apparatus (*Jl. Physique*, 1950, 41, and *Sci. et Ind. Phot.*, 1950, 16).

Photographic densitometers. In this class of densitometer the sensitometer print is placed in contact with a wedge and the combination is illuminated. The wedge produces a graduated illumination of the sample. A print made through this combination has a higher band as the density of the sample decreases. The automatic printing of characteristic curves using crossed wedges is no more than a system of photographic densitometry.

For the densitometry of small samples (3 mm) Abribat(17) made a microdensitometer on this principle. The print, instead of being made by contact is made by enlargement and the wedge is placed in front of the recording plate. Knowing the wedge constant, the corresponding densities can be determined from the height of the printed curve. Graininess caused by the small size of the sample is removed by vibrating the wedge-plate combination vertically.

225. Reflection densitometers

Used for paper sensitometry.

The reflection density increases more rapidly than the transmission density as the light beam has to pass through the silver image twice. It is consequently limited, depending on the type of base, to a density of about 1·6–1·8 for glossy papers.

Among the visual densitometers, that of L. P. Clerc(18) based on the principle of the Fabry and Buisson photometer, should be mentioned.

There are relatively simple paper densitometers:(19) the incident light, after passing through a wedge, is reflected by the paper at 45° and received by a cell. The wedge is moved until the galvanometer returns to its original position (white paper density).

The 'Evans Electro Selenium' and Baldwin photoelectric densitometers, already mentioned among the transmission densitometers, are also available as reflection instruments. The former use a barrier cell and the latter a photoemissive cell.

Another apparatus was described by Nitka and Stammers (I.C.I.) (*R.P.S. Cent. Conf.*, London 1953).

The DuPont model should also be mentioned. It is a modification by Huber and Rakuo of the Frayne and Crane densitometer (*J.O.S.A.*, 1949, 873–876).

Paper surface. The surface of the paper has a great influence on the measurement of reflection densities. The diffusion depends on the grain size, the refractive index of the gelatin and above all on the physical structure of the layer. The diffusion is measured with a *goniophotometer* (that of Hilger for example) and it can be easily seen that the density varies considerably with the angle of incidence, particularly with matt papers. The density is at a maximum in a direction between the incident beam and the normal (Nitka and Stammers); to receive the reflected light under the best conditions the receiver must be in the maximum density position. The angle of the beam must not exceed 10°.

The goniometer measurements are more critical with glossy than with matt papers. E. Sève has estimated the brilliance by comparing the elliptical *reflection spots*, the paper being held on a drum and illuminated by a point source arc. The length of each spot is measured parallel to the source in the incident plane and parallel to this plane. (*Sci. et Ind. Phot.*, 1953, 461).

Two papers, one glossy, the other matt, but otherwise identical, will give totally different figures when their densities are read. They must be considered as equivalent, taking this difference into account in the evaluation (fixed for each type of emulsion). For example, with the same normal contrast emulsion, but different surfaces, the following figures could be obtained:

	D max.	γ
Glossy surface	1·65	2
Matt surface	1·2	1·6

Semi-matt surfaces give intermediate figures.

The characteristic curves of photographic papers are therefore only directly comparable with one type of manufacture. If not, use must be made of relative coefficients.

In current practice it is often considered enough to compare visually two sensitometer step wedges, obtained on different papers. In this way the surface effects are of little importance in judging, which primarily depends on the range between extreme densities.

226. Development

(*a*) A complete sensitometric test must include several sensitometric wedges which are developed for increasing times until γ_∞ is reached. The contrast, that is the slope, of each curve increases with development time.

The type and strength of the developer has a more or less pronounced effect on the numerical value of the densities. Precise comparisons necessitate standardization of the developer solution; unfortunately, a standard developer rarely conforms to all the conditions of practical use, and it is therefore usual to work with a normal working solution, which is after all quite logical.

Among normal developers there are M.Q., p-aminophenol, amidol-carbonate, metoquinone (5 g per litre with 30 g sulphite and 30 g carbonate) and pyro (6 g per litre with 15 g sulphite and 11 g carbonate).

Each developer reacts differently with a given sensitive layer; the speed of γ increase, the threshold and fog density obtained with different baths are never the same. Furthermore, even with the same bath it is impossible to obtain absolutely identical results because of the action of phenomena such as diffusion which is impossible to control.

When must exposed sensitometer strips be developed? In principle, they should be kept for six hours to let the immediate latent image regression following exposure take place. In practice the laboratories, because of the time involved, develop the strips immediately after exposure.

(*b*) *Agitation.* The speed of development depends, in addition to the normal reaction rate, on the rate of diffusion in the gelatin layer of the new developer and of the by-products from the reduction of silver bromide.

The nature of the gelatin, its hardness and also its age influence the swelling properties of the layer and consequently the diffusion of the reaction products, and the inequalities in the thickness of the layer must also be taken into account.

On one hand, the more concentrated the developer the more superficial its action. The surface effect can be accentuated by the addition of certain substances to the developer, a method which has been used for processing colour films. Conversely the addition of silver halide solvents favours development in the interior due to the formation of silver complexes on the surface. Amidol in acid solution is also known to have a similar action as sodium bisulphite is retained at the surface by the gelatin; with the pH being higher in the interior of the emulsion than at the surface, the reducer is more energetic in the interior of the layer (the redox potential drops with pH increase).

The nature of the image is another source of irregularity. The presence of high density areas close to lower density areas can produce an irregular diffusion of bromide, iodide and other by-products towards the low density; the by-products have a local retarding action which results in areas or trails of low density around the high densities.(20) The effect of this can be great in the case of sound records; these irregularities can be produced in opposite directions depending on whether the dense area precedes or follows the light area in the passage of the film through the developing machine.

It is therefore apparent that agitation of the developing solution can have a pronounced effect on the density values and consequently the quality and sharpness of the image; this is troublesome, considering the difficulty of controlling the agitation and reproducing it accurately.

Development in a vertical position gives better results than horizontal development in a dish as the formation of stationary waves is avoided. It is always better to agitate irregularly rather than in a regular manner as the movement of the developer alone is insufficient.

To some extent the diffusion irregularities can be reduced by passing a flat brush across the surface during development. The development of sensitometer tests by shaking in a thermos flask is more convenient. There is in fact no perfect system of agitation especially as it is frequently preferable to use the exact conditions of practical use for the development of sensitometer tests, however bad these may be. In general, each laboratory has its own particular device for agitation in the development of sensitometric tests, and the variety of these devices is infinite. It will be sufficient to note those used in certain important laboratories.(20b)

(*c*) *Eberhard effect*:(21) The local variations in concentration of developer and development by-products produce, in small areas where high and low densities are adjacent, two lines of separation which can greatly affect the image.

The effect is even more pronounced when a large number of different intensities are present in a restricted area. This is the case in stellar spectra whose images contain many density variations per millimetre.

The dense areas contain exhausted developer whilst the light areas still contain active developer. This results in a double flow of developer; the exhausted developer moves towards the clear portion whilst the active developer flows to the dense region. This results on one hand in a density increase in the heavy area at the boundary and on the other, a decrease in the light area at the boundary. The effect is noticed up to 1·5 mm away from the edge; it is diminished by prolonging development when the γ approaches γ_∞. It is evident that this effect becomes greater as the image considered becomes smaller. The normal density does not appear in the centre of the area until its diameter is at least twice the size of the border formed.

(*d*) *Kostinsky effect.*(22) This is produced on two very small images which are close together such as spectrum lines or double stars; the distance between the two developed images is greater than the distance between the exposed areas. The effect is explained by the diffusion of developer exhaustion products to the clear separating areas, the formation of lateral high densities and the outward displacement of the dense parts of the images.

MEASUREMENT OF SENSITIVITY

227. Two emulsions, A and B, are exposed under identical conditions: if, after development to γ_∞, A gives a greater silver deposit than B, it is said that for a fixed exposure, A is more sensitive (or faster) than B.

Consider, however, the curves of the two emulsions A and B shown in Fig. 28; they cross at the point C. To produce a density D, an exposure a_1 must be given to A, which is less than the exposure b_1 which must be given to B: A is therefore faster than B. The same result is achieved if the thresholds s_A and s_B, or the 'inertia points' i_A and i_B, of the two emulsions are compared. But if a minimum density D_2 is to be obtained, which is greater than the density at C, then emulsion B needs the lower exposure, $b_2 < a_2$; B, therefore, is faster than A. This happens in stellar spectrophotography where

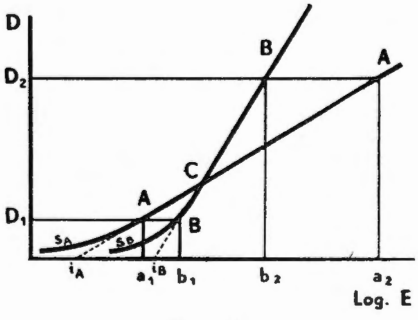


FIG. 28.

a minimum density of 0·6 is required for the detection and measurement of weak emission lines.

Determination of the exposure for the production of a complex image requires knowledge of the contrast achieved on development. Generally the maximum γ obtainable without excessive fog is 80% of the γ_∞.

In astronomy the following definition of sensitivity is used: a quantity inversely proportional to the exposure necessary to produce a density of 0·6 when development is to 80% γ_∞, the plate being 1 metre from a source equivalent to 1 candle.

In practice, the speed of sensitive layers is measured with reference to the *threshold* or *inertia.* Whatever criterion is used, *a complete knowledge of the spectral distribution of the source used is essential.*

It is, in fact, difficult to estimate the speed of an emulsion without considering its specific use, for to have any real significance the sensitometric test must be made under the same conditions. As the sensitivity is dependent on a combination of the properties shown by the characteristic curve it is misleading to indicate it by a single figure. As a general rule, it is best to know the threshold and the inertia point.

Intrinsic sensitivity. To become developable a grain must absorb a certain number of effective quanta r. This number is the same for all the grains of an emulsion. If, of N grains, k become developable with an exposure E, the form of the curve representing k/N as a function of log E is a characteristic of the number of quanta r.

Silberstein defined the intrinsic sensitivity ϵ as the probability that the grain will absorb a number of effective quanta to be made developable after having received a certain exposure related to r. The coefficient of effective absorption determines ϵ; it is lower than the coefficient of absorption of silver halide. ϵ increases as the grains become larger; it can be altered by chemical sensitizers.

Theoretical limit of sensitivity. Bruscagnioli has determined the theoretical limit of sensitivity with the formula

$$\mathrm{It} \geqslant 4\cdot 10^4 \frac{h\nu P^2}{\pi \mathrm{G}\omega\eta}$$

where G is the smallest brightness difference which can be recorded, ω the thermodynamic equivalent of the light in lumen-watts, η is the coefficient of utilization of the light by the sensitive layer, P the resolving power (in lines/cm), h is Planck's constant $6{\cdot}57 \times 10^{-34}$ W. sec.

$$\omega = 4{\cdot}6 \times 10^{-3} \quad \eta = 0{\cdot}4 \quad \mathrm{G} = 2\cdot 10^{-2} \quad \mathrm{P} = 10^3$$

228. Measurement of sensitivity by the threshold method

The *threshold* is the point where the least exposure can give a density which can just be seen in the sensitive layer. It can readily be determined with a photometric wedge which has been standardized for exposures (metre-candles).

As the threshold is visually rather vague, it is preferable to use a *density of 0·1 above fog* which can be measured precisely.

The speed of photographic materials is frequently determined by the threshold method. The figure thus obtained gives no idea of the behaviour of the rest of the curve; it is concerned only with the underexposure region.

(*a*) *Scheiner System.* A time-scale sensitometric exposure is given using a sector wheel. The light source is a paraffin burner. The speed is given in °*Sch.*, after threshold measurement. The yellow light benefits panchromatic emulsions. This method is not used any more except for advertising. In this case, the figures given are very conventional; 33° representing an ultra-rapid emulsion.

(*b*) *DIN System.* Standard German system, it is similar to the preceding one. The lowest exposure capable of giving a density 0·1 above fog is measured using the apparatus shown in Fig. 24. The step wedge has thirty steps from 0 to 3 (interval of 0·1). The exposure time is standardized at 1/20th sec. with a luminous flux of 40 lux of daylight quality.

After development in an M.Q. bath of fixed composition, the negative is examined under a neutral grey filter and the step corresponding to a density 0·1 above fog is found. If, for example, this is the step corresponding to a wedge density of 1·8 the speed is 18/10 DIN. As the scale is logarithmic, the speed is doubled every 3° as with the Scheiner system.

In practice the DIN system can be used for comparative threshold measurements. In this case the spectral composition of the source, the exposure time, the bath and method of development are all adjusted to give conditions as close as possible to those under which the material will be used.

Instead of giving the threshold sensitivities in terms of the wedge density, we prefer to give them in exposure values, as these are simpler and more informative. Thus 23° DIN corresponds to an actual threshold exposure of 0·01 c.m.s. (the density of the wedge is 2·3—giving an opacity of 200 and the exposure transmitted $\frac{40 \times 0{\cdot}05}{200} = 0{\cdot}01$). The figures obtained in this way have the advantage of being proportional.

Neo-DIN System. In the new DIN system, development is carried out in an agitated thermos flask for 4 mins. at 20°C in:

Metol	2 g
Hydroquinone	4 g
Sodium sulphite anh.	50 g
Sodium carbonate anh.	6 g
Potassium bromide	0·75 g
Water to	1 litre

GOST system. In this Russian system, the GOST unit is the unit of sensitivity of an emulsion corresponding to a density 0·2 above fog using an exposure of 1 c.m.s. The sensitivity is the reciprocal of the exposure. Development is at 20°C with a liquid flow of 10–15 cm/sec. Sensitometer of the DIN type with a wedge of twenty-one steps with a 0·15 interval and exposure time of 1/20 sec.

(*c*) *Eder-Hecht system.* The sensitive layer is exposed under a 9 × 12 cm wedge with a constant of about 0·4. A scale in 2-mm squares enables the densities to be located. The threshold is given by the last mark visible after development.

Although speed determination in Eder-Hecht degrees requires magnesium light in the fixed working conditions, comparative measurements with various sources are possible, and even preferable.

The relative sensitivity corresponds to the figures marked on the wedge and a table is provided by the manufacturer (Herlango, of Vienna). They are, however, easy to calculate if the wedge constant is known. The Eder-Hecht wedge, together with its mounting, is an extremely simple and convenient instrument for everyday measurements. It is only used for laboratory tests.

229. Measurements of sensitivity by the inertia method

The inertia method of speed measurement was conceived by Hurter and Driffield. The speed of an emulsion in H and D units is obtained from the characteristic curve in the following way:

The exposure corresponding to the intersection *i* of the straight line with the exposure axis (Fig. 29); the value obtained is conventionally called the *inertia.* The sensitivity is proportional to the reciprocal of the inertia and is given by the expression $S = 34/i$ H and D units, the exposures are given in candle-metre-seconds (c.m.s.). The expression $S = 10/i$ is also used, giving appreciably lower figures.

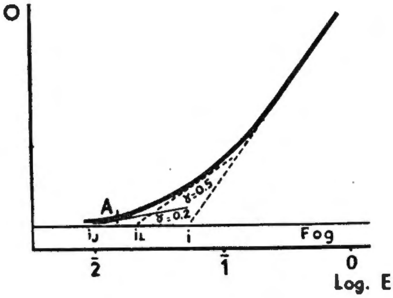


FIG. 29.

S can be easily determined in c.m.s. units, the sensitivity being greater as *i* becomes smaller. This enables the threshold and inertia to be obtained at the same time in figures which are directly comparable without the use of arbitrary units.

For the intersection of the produced straight lines of the different curves of a sensitometric test, to meet at the same point, no bromide is added to the developer. Theoretically the speed value is therefore independent of the development time.

This is not so in practice where the developer contains increasing quantities of bromide. Fig. 30 shows the variations in speed as a function of development time using the inertia method ($10/i$) compared with the Jones and Russel ($10/i_J$) method using a slope of 0·2 (explained later). It is seen that the speed increases rapidly at first, until a maximum is reached, after which it falls slightly.

230. Fixed gradient methods

Instead of using the inertia, the point corresponding to the *minimum useful gradient is measured*, which Jones and Russel found to be 0·2 in the threshold region (Fig. 29).

The exposure A where the slope is 0·2 is used to determine the speed. The expression $S_{JR} = 10/i_J$ can also be used.

(*b*) The sensitivity determined by an old standard of the *Aéronautique Française* is the point where the slopes of 0·2 and 0·4 intersect, the curved toe being likened to a parabola.

(*c*) *Labussière* proposed to use the point where the gradient is 0·5 (Fig. 29). Knowing the exposure corresponding to i_L the speed value is given by

$$S_L = \frac{10}{i_L}$$

(*d*) *Lapeyre system.* A subject with a brightness range of 1·5 is used. The exposure corresponding to a slope of 0·8 gives the sensitivity.

231. ASA system

A system similar to the preceding one was established by Jones by statistical observations, and was approved by the 'American Standards Committee' for the calculation of ASA units (1939).

The subject has a brightness range of 1·5, a point A on the lower part of the curve is found such that the slope γ_A at this point is 0·3 of the average

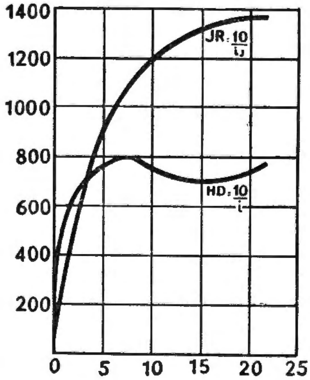


FIG. 30.

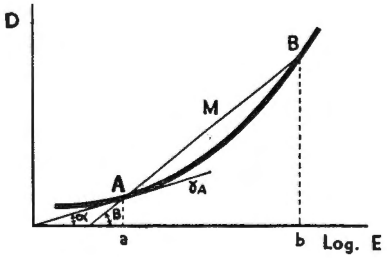


FIG. 31.

gradient M measured from the point A. This average gradient is the chord between points A and B of the curve (Fig. 31). γ_A and M have values corresponding to the tangents of the angles α and β. The average gradient M has a value of 0·7 for films for normal negatives and 0·6 for miniature films.

The exposure corresponding to point A gives the ASA speed:(23) $1/E_A$. The number found is preceded by the figure 0.

To find point A, two transparent rules are used, having on one a line with a slope of 0·6 for example, and on the other, a line with a slope 3/10 of this, i.e. 0·18. A brightness range of 1·5 covered by the line whose slope is 0·6 is found and the slope at the point of intersection A is checked to be 0·18. The Jones and Russell desensitometer(24) gives the point A by examination of two fixed areas of the test wedge without using graphical methods.

Conditioning of samples: atmosphere maintained at 20°C±5° and R.H. 55±5%.

Sensitometer type: non-intermittent intensity scale.

Exposure time: between 1/20 and 1/80th sec. The exposure of one step must not be greater than twice that of the preceding step.

Light source of 2,360°K together with a Davis-Gibson filter (see Light Sources, Part IV).

Development. Wait 2 hours after exposure. Develop at 20°C (68°F) for 4 minutes in

Metol	2 g
Sodium sulphite anh.	50 g
Hydroquinone	4 g
Sodium carbonate anh.	6 g
Potassium bromide	0·75 g
Distilled water (air free) to	1 litre

Apparatus: thermos flask 22 cm long and internal diameter 4 cm, three-quarters full. The test is attached by rubber bands to a strip of glass 20 × 3·5 cm which is fixed to the bung.

Agitation: the flask must be agitated in a vertical plane through an angle of about 45° above and below the horizontal the cycle taking 1 sec. At the same time it must be turned on itself every 5 seconds.

Fixing: after development, in

Sodium thiosulphate	250 g
Sodium sulphite anh.	10 g
Sodium bisulphite	25 g
Water to	1 litre

Temperature 20°±0·5°C (68°F).

Miniature sizes: develop in the following developer for 8 minutes at 20°C.

Metol	2 g
Sodium sulphite anh.	80 g
Hydroquinone	4 g
Borax	4 g
Potassium bromide	0·5 g
Distilled water (air free) to	1 litre

If the average slope is below 0·50, increase the developing time until this value is obtained.

Density is measured by diffuse light.

BSI system (British Standards Institute). This system was originally based on the exposure necessary to obtain a density 0·1 above fog as in the DIN system. It appeared preferable later to adopt the same point for estimation of sensitivity as the ASA method, but with a logarithmic scale: the sensitivity is increased by $\sqrt{2}$ for an increase of 1°, for example:

Exposure	0·01	0·0064	0·005	0·0032	0·0025
log E	2	3·8	3·7	3·5	3·4
ASA speed	0100	0160	0200	0320	0400
ASA index	25	40	50	80	100
BSI index	25°	27°	28°	30°	31°

232. Notes on the choice of a criterion of sensitivity

The great number of methods proposed for the measurement of the sensitivity of a photographic emulsion demonstrates the insatiable character of this objective. It is impossible to express in one figure a physico-chemical system which is controlled by many laws. In a sensitive layer, the practical value of the sensitivity is dependent on the shape of the characteristic curve, on the contrast, the rate of development and the colour sensitivity. Also, the comparison of two emulsions with different properties is meaningless. Two emulsions do not have the same γ in the same development time; their optimum usable γ are rarely the same; the shapes of their characteristic curves are certainly different and each has its individual reaction to various light sources.

It has already been stressed that there are two types of negative emulsion commercially available: those whose characteristic curve has a long straight line and a relatively short toe, and those with a long curved toe. *Only the emulsions with a straight characteristic give correct reproduction.* The existence of curves with long toe regions merely denotes a manufacturing expedient (mixture with a fast coarse-grain emulsion, sensitization with gold, etc.) which in use gives the *illusion* of high sensitivity, for the emulsion always gives in this way a vague image of some sort. It is a great error to think that this type of emulsion with indefinite contrast can help in the artistic rendering of subjects by complete falsification of their tone values.

With a correct emulsion with a straight line the best way to illustrate its sensitivity is to measure at a given contrast (0·8 for example) the inertia point: H and D method, and the position of a density 0·1 above fog (DIN method) together.

In the case of long-toe emulsions, the DIN method gives information about the first usable point but tells nothing of the rest of the curve. There remain the specified gradient methods. The slope of 0·2 is too close to the threshold. But the ASA system was created to help with this type of emulsion. It can always be criticized for its useless complexity giving an illusion of precision. In fact, *an equally good practical estimate can be obtained much more easily, from the exposure corresponding to the point on the curve which has a gradient of* 0·3.

RESOLVING POWER AND GRANULARITY

233. Resolving power

The resolving power of a sensitive layer, is measured by the minimum distance separating the images of two luminous points.

With the images of two parallel lines separated by a distance d equal to their width, the resolving power r is given by

$$r = \frac{1000}{2d}$$

where d is in μ. r also represents the number of lines per millimetre which can be separated. The resolution is much higher if the clear areas are small, relative to the opaque areas of the grid, but r increases ten times more slowly if the ratio—width of clear area/width of opaque area—does not decrease. Finally, the figures obtained depend to some extent on the methods used for printing and examination.

The objects generally used for the measurement of resolving power are the Foucault targets. These are formed of alternate clear and dark lines of the same width. The complete charts contain a series of these targets of decreasing size grouped in four different directions, vertical, horizontal and two diagonal. The chart is preferably used as a transparency, being illuminated diffusely from behind.[25] Many photographs are taken with different exposure times, each series being developed with increasing times. The results are examined with a lens or microscope to find out which lines are only just separated. Another method sometimes used is to find the first patch in which directional lines are visible and to note the number of lines corresponding to it.

The resolving power depends on the object contrast. It also depends on the lens. The resolution of the optical system must be better than that of the layer tested; it is an increasing function of the aperture up to a maximum; it diminishes with the wavelength.[26]

Communication No. 533 from the Bureau of Standards of the 20th March, 1953, gives recommendations for the determination of the resolving power of photographic lenses using printed targets.

Perrin and Hoadley have worked out a special apochromatic objective for measuring the resolving power of sensitive layers, made from two fluorite convergent elements on either side of a divergent element made from Bausch and Lomb S.K.16 glass. It is called 1381.[27] The following are some results obtained with it:

Emulsion	Ord. Fuess Lens	Lens 1381
Super XX	50	95
Panatomic-X	65	105
Tri-X	40	70
Duplicating negative	80	105
Ciné positive	60	105
High-contrast positive	105	170
Duplicating positive	135	170
Sound recording 1357	55	100
Microfile	170	180

234. Diffusion (Irradiation)

The light striking an emulsion is laterally diffused by the minute crystals of silver bromide, reflected many times between the different faces and irradiated in every way, which results in a general spreading of the image:(28) this usually happens with turbid media.

The diameter of the image increases with the amount of light received, or more exactly with the logarithm of the exposure:

$$d = d_0 + \Gamma \log E$$

where d_0 and Γ are constants. Γ, also called 'astrogamma' is a measure of the turbidity of the emulsion. If two measurements of d: d_1 and d_2 with E_1 and E_2, one has

$$d_1 = d_0 + \Gamma \log E_1$$

$$d_2 = d_0 + \Gamma \log E_2$$

$$\text{and } d_2 - d_1 = \Gamma(\log E_2 - \log E_1)$$

$$\text{therefore } \Gamma = \frac{d_2 - d_1}{\log E_2 - \log E_1}$$

Goldberg gives the following average values of Γ for different emulsions:

Grainless emulsions	0 μ
Positive emulsions (lantern)	7 μ
Process emulsions	11 μ
Rapid emulsions	18 μ
Bromide papers	48 μ

The diffusion brings together neighbouring images (spectrum line, double stars) the effect becoming more apparent in underexposed images than with overexposed ones where the Kostinsky effect also comes into play.

If an emulsion is partly covered by a mask with a straight edge in intimate contact, and the remainder exposed to increasing intensities, it is found that irradiation takes place under the mask, starting at its edge and penetrating progressively with the exposure. The shading-off thus formed follows the laws of the penetration of light into an absorbing medium. The characteristic curve in this region of diffusion measured with a microdensitometer as a function of the distance in μ from the edge, is S-shaped.(29) If ϕ is the slope of this curve and K the coefficient of absorption of the emulsion, then $\phi = \gamma/K$. ϕ is a characteristic of the sharpness of the image.(30)

The diffusion of the incident light by the silver halide crystals is the same for all visible λ, for grains up to 1 μ but for larger grains it is greater in the red.(31)

An important factor in the spreading of light by an emulsion, with a drop in its resolving power, is the thickness of the layer. An image at the bottom of the layer is less sharp than one at the surface. This is why U.V. radiation, which does not penetrate far into the layer gives images which are better resolved. A current method of limiting the penetration of light into a sensitive layer, and therefore obtaining a higher resolving power, is to stain the layer. Kowaliski⁽³²⁾ got good results with quinoline yellow and naphthol orange. With a ciné positive emulsion which can resolve 100 lines/mm in the depth of the emulsion and 115 lines/mm at the surface, he obtained, after staining in a 0·1% solution of quinoline yellow, 135 lines in the interior and 150 lines at the surface. Naphthol orange enabled 170 lines to be recorded. The sensitivity is reduced considerably at the same time: 10–25 times for the dyes mentioned above.

235. Granularity

Since diffusion is produced by the granularity of the emulsion, the resolving power must increase as the grain becomes finer. If an image of an illuminated slit is photographed, the negative has an area of apparently uniform density between two clear regions. When examined with a microdensitometer, the deposit in fact shows appreciable variations in density (Fig. 32); the horizontal line AB represents the average density; the relationship between the total area bounded by the undulations between D and E and the length of DE is the mean density Δ of the variations; the quotient of the length DE divided by the number of intersections of the curve by AB represents the average apparent size of the grain g. The distance HG = h from the point H to the geometrical limit separating the two areas can be used to determine the turbidity.(33)

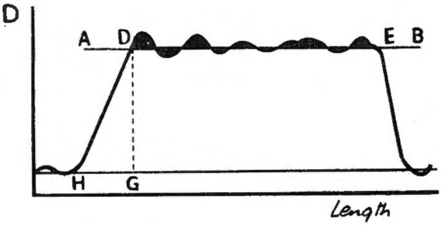


FIG. 32.

The local fluctuations of density of an unexposed or uniformly exposed (and developed) layer, determine the lowest value of the densities difference detected by this layer, and which in sound recording is called 'noise'. Useful densities must be higher.(33b)

The measurement of granularity is made using objective methods in which psychophysical sensations take no part. Generally it is carried out by the methods of Van Kreveld, Goetz and Gould or Selwyn. In each case the statistical frequency of the density fluctuations over a uniform area is approximately determined by the Gaussian function of probable distribution.(34)

For Van Kreveld the *granularity constant* is $G_K = (T_{a1} - T_{a2})$ average where T_{a1} and T_{a2} are the transparencies of two adjacent areas of equal surface.

Goetz and Gould basing it on the distribution equation

$$\frac{2}{G'\sqrt{\pi}} = \int_0^x e^{-(x/G')^2} dx$$

where G′ represents the distribution, fixed the granularity constant by $G = G'/1000$ and constructed an apparatus enabling this constant to be measured.(35) If σ_t is the mean quadratic variation of the relative transparency fluctuations, then $G = \sigma_t\sqrt{2}$ and $G' = 1000\,\sigma_t\sqrt{2}$.

Let the *area* a of the examining light beam be considered. If σ_d is the mean quadratic variation of the density fluctuations as a function of area a, n the number of silver grains covered by the spot, and α the average projected area of these grains on the spot, Nuttings equation, verified by Romer(36) gives the relation

$$D = -\log_{10}\left[1 - \frac{\alpha}{a}\right]^n$$

Selwyn uses, for the measurement of granularity, $G = \sigma_d\sqrt{a}$ where σ_d is the mean quadratic variation in the density fluctuation. Granularity therefore increases with the area of the examining spot.(36b) Ingarden and Minkusinski(37) have verified, by probability calculations, that there is a value for a for which a minimum is, however, attained.

What is the *relationship between granularity and contrast?* Selwyn has shown that the mean fluctuations around the density are of the order of $0{\cdot}6G/\sqrt{a}$; that is, that the measured density D* is

$$D^* = D \pm 0{\cdot}6G/\sqrt{a}$$

but as $D = \gamma(\log E) - b$, it becomes

$$D^* = \gamma(\log E) - b \pm 0{\cdot}6G/\sqrt{a}$$

The error on the evaluation of the exposure is

$$\log E^* - \log E = \pm 0{\cdot}6(G/\gamma)/\sqrt{a}$$

The *practical granularity G* is measured by

$$\mathit{G} = \mathrm{G} - \log\gamma$$

Debot(38) has found, taking $G = \log(\sigma_t\sqrt{a})$

	G	*G*
Pan negative emulsion	2·44	2·65
Fine-grain pan. neg. emulsion	2·28	2·43
Ciné positive	2·35	2·17

An electronic granularometer(39) enables the quadratic mean of the relative transparency variations to be measured continually with the negative moving, to integrate the average value of this transparency, to calculate the deviations, then the square of these, the mean of the squares and finally the relationship

$$\sigma_t = \sigma(\Delta T)/T$$

Another means of measuring the granularity was suggested by Threadgold, then by Kuster and Eggert: it consists of determining the ratio of the specular and diffuse densities, the latter having a value of 0·5

$$K = 100 \log D_{\parallel}/D_{\#}$$

Stricker⁽⁴⁰⁾ found that at increasing gamma in a metol developer:

γ =	0·34	0·48	0·62	0·76	0·92
K =	18	23	26	28	28

236. Graininess

If the fluctuations of the transparency constitute the granularity, the visual sensation of a heterogeneous photographic layer is a psychophysical phenomenon which is usually called graininess.

Graininess can be measured by *the distance at which the unevenness due to grain in an enlargement disappears.* For Selwyn it is a function of the granularity of the negative and the contrast of the printing paper: $\gamma_p . G$. The optical system of the enlarger must also be considered as this can influence the appearance of the enlarged image.

Jones and Higgins⁽⁴¹⁾ who have made many statistical observations on this subject, have come to the conclusion that the retinal cones send nervous impulses to the brain which depend on the sharp variations in excitation, and that consequently the examination area for the measurement of granularity should correspond to the dimensions of the retinal cones.

If Δx corresponds to the distance between area elements (the images of which are formed on the cones contiguous with the fovea), Δx becomes equal to the diameter of these cones multiplied by the amplification coefficient of the retina with regard to the sample, therefore equal to the diameter of the spot of the microdensitometer (10 μ, for instance). The differences ΔD of the densities between neighbouring elementary areas (called 'syzygetic' densities) produce the *graininess* feeling.

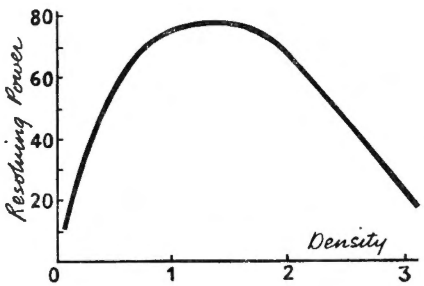


FIG. 33.

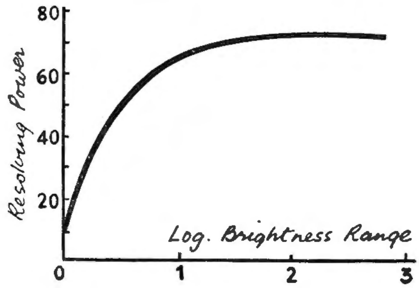


FIG. 34.

$\Delta D/\Delta x$ is the 'illumination gradient', while $S\Delta D$ is the measure of *granularity.*(41b) The value of $S\Delta D$ is obtained with the aid of a microdensitometer having two contiguous spots, which renders possible several hundred readings, thus permitting to trace the distribution curve. The graininess can be determined directly by means of the Jones and Higgins apparatus, assuming that a fovea cone has a 1·5 μ diameter, and that the focal length of the eye lens is 17·5 mm. If H represents the graininess, M the amplification corresponding to the threshold of perception, and ϕ the critical diameter of the exploring area relative to a fovea cone, we have

$$H = 1000/M \text{ and } \phi = 0{\cdot}175\ H$$

The mean granularity $S\Delta D^*$ measures the *threshold of graininess* (with ϕ for the spot diameter); then it can be possible to obtain the curve 'log $S\Delta D^*$ function of D'.

Reduction of graininess. The graininess of an image can be reduced by using one of the following methods:(42)

Shifting the focus.
Interposing a silk or screen.
Vibration.
Successive printing with several identical negatives.

Chemical diffusion. Strauss(43) reduced the graininess by converting the silver to silver bromide, then to silver sulphide in a sulphide-hypo bath (1% sulphide, 0·1–10% hypo).

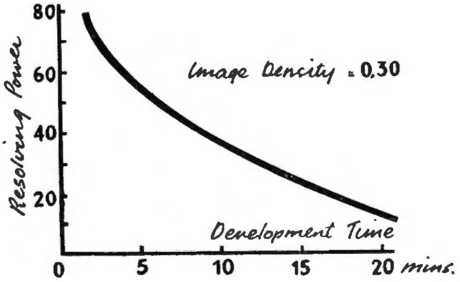


FIG. 35.

Improvement of resolution. The resolution can only be improved by combining, in the same print, the effects of several identical negatives, as has been shown in the experiments of Stevens.(44) This process is only of use if perforations permit perfect registration and if each image is of low contrast. Nothing is gained by superimposing more than four images because of the difficulty of locating them. Application in astronomy.(45)

237. Influence of contrast on the resolving power

The resolving power depends on the subject contrast and upon the density of the photographic image. Thus the curve in Fig. 33 shows the variation in resolving power as a function of the image density for a brightness range of 1·000 and 8 minutes development; in this example, the resolution increases with density up to 1·3, then decreases to become very low at 3·5.

The resolution increases with the brightness range of the subject up to a limiting value. In Fig. 34 the variations in brightness are shown. On the contrary, it decreases with development time (Fig. 35).

1. Another instrument uses, for automatic control, a *metronome* which lights and then extinguishes an electric lamp (Reeves 'Sensitester').
3. Roulleau and Lafouasse: *Sci. et Ind. Phot.*, 1954, **25,** 389–392. The latter model is made by Desgranges and Huot, Paris.
3. King E. S.: *Annals Harvard Observ.*, 1899, **59,** No. 2.
4. Miller O., *Sci. et Ind. Phot.*, 1932, **3,** 81–87.
5. Tardy H.: *IXth Int. Cong. Phot.*, Paris, 1935, 641.
5b. *Sci. et Ind. Phot.*, **6**(2), 264 and 1953, **24,** 349.
5c. E. R. Davies used an instrument with a step wedge having intervals of 0·2 up to 4·3 (*Phot. Jl.*, 1944, 1885). For the sensitometry of variable density sound tracks, the grey scale is produced on a film running in contact with the film wedge over a supporting drum. The image of a slit is projected on the two films giving an exposure time of 1/25,000 sec.
6. Goldberg E.: *Sci. et Ind. Phot.*, 1925, **5M**, 64 and 69.
6b. For a comparative study of the various types of densitometer, see Weaver, *J.O.S.A.*, 1950, 524–536.
7. Martens F. F.: *Ver. deutsch. phys. Ges.*, 1899, **1,** 204; *Arch. Wiss. Phot.*, 1900, **2,** 184.
8. Jones L. A.: *J.S.M.P.E.*, 1931, XVII, 536; *Sci. Ind. Phot.*, 1923, 92.
9. Capstaff J. G. and Purdy R. A.: Trans. *S.M.P.E.*, 1927, **11,** 607.
10. N———, *Sci. et Ind. Phot.*, 1923, 1. A recent modification of this instrument was shown by Gaultier du Marache and Duffiers: *Sci. et Ind. Phot.*, 1952, 359.
11. Lobel L. and Dubois M.: *Manuel de Sensitometrie* (P. Montel, Paris).
12. Bull A. J. and Cartwright H. M.: *Sci. et Ind. Phot.*, 1924, 36.
13. Moll W. H. J.: *Sci. et Ind. Phot.*, 1921, 105; 1930, 89. Thomson K. B.: *Sci. et. Ind. Phot.*, 1935, 398. Harrison G. R.: *J.O.S.A.*, **7,** 999; **10,** 157; *Sci. et Ind. Phot.*, 1924, 34; 1925, 80. Albrecht and Dorneich: *Phys. Zeits.*, **26,** 514; *Sci. et Ind. Phot.*, 1925, 181.
14. Vassy E.: La mesure des densitiés photographiques. (Centre de perfectionnement technique. Presses Documentaires, Paris.)
15. Chalonge D and Lambert P.: *Sci. et Ind. Phot.*, 1925, 94; 1927, 6; 1932, 94.
16. Boutry A.: *Sci. et Ind. Phot.*, 1934, 41. See also the new E. R. Davies apparatus (*Phot. Jl.*, 1944, 185 and *Sci. et Ind. Phot.*, 1945, 77.)
17. Abribat M.: *Sci. et Ind. Phot.*, 1931, 321.
18. Clerc L. P.: *Sci. et Ind. Phot.*, March 1925, 28.
19. Davies E. R.: *Phot. Jl.*, 1932, 118. A new model is semi-automatic. Tuttle made a completely automatic densitometer (see *Sci. et Ind. Phot.* (2), **7,** 309).
20. Another effect noticed by J. Dufay (*Compt. Rend. Ac. Sc. Paris*, 1932, 1898) and studied, among others, by L. Falla (*Sci. et Ind. Phot.*, 1949, 449) is the variation of the characteristic curve as a function of the size of the luminous spot used for exposure; when this is less than 60 μ, areas of different width do not have the same density. There is a *proximity effect* during development giving a higher density to the broader bands.
20b. Bates, Berley and Kowalak (Ansco): *Phot. Eng.*, 1951, 182–191; *Sci. et Ind. Phot.*, 1953, 112.

21. Walenkow N.: *Sci. et Ind. Phot.*, 1930, 51; Junkes J.: *Sci. et Ind. Phot.*, 1938, 16 and 133.
22. Junkes J.: *Sci. Ind. Phot.*, 1938, 16; Ross: *Sci. et Ind. Phot.*, 1921, 89.
23. With exposure meters, an *exposure index* is used equal to a quarter of the ASA speed. A panchromatic negative emulsion will have an index of 100 to daylight and 65 to tungsten.
24. Jones and Russel: *Sci. et Ind. Phot.*, 1935, 325; 1939, 303. The Kodak gradient Meter is a variation of Nelson's apparatus for reading the speed directly from the curve: it is a transparent disc having, at a distance of 1·5 from the centre, a perpendicular to an arc graduated in slopes.
25. Perrin F. H. and Altman J. H.: *Sci. et Ind. Phot.*, 1951, 375.
26. Perrin F. H. and Altman J. H.: *J.O.S.A.*, 1951, 1038–1047; Study of target types, *Sci. et Ind. Phot.*, 1952, 266; *J.O.S.A.*, 1953, 780–790; *Sci. et Ind. Phot.*, 1954, 57.
27. *J.O.S.A.*, 1948, 1040–1053.
28. When the grains are very fine, they also result in diffusion caused by diffraction.
29. Ross F. E.: *Astrophys. Jl.*, 1920, 201. Sandvik O.: *Sci. et Ind. Phot.*, 1928, **8M,** 18 and 27.
30. Clerc L. P.: *Structure et properties des couches photographiques*, p. 148 (Ed. de la Revue Optique, Paris).
31. Breido I. I. and Pruss P. K.: *Doklady Ak.* Nauk. (U.S.S.R.), 1952, 893–896.
32. Thesis: Zurich 1944.
33. Kreveld A. V.: *Phot. Jl.*, 1934, 590; *Sci. et Ind. Phot.*, 1935, 53 and 271. Kreveld A. V.: (Photoelectric apparatus) *Sci. et Ind. Phot.*, 1936, 206 and 243. Raudenbusch H.: (C-R oscillograph), *Physik. Zeits.*, 1941, 208–212.

33b. Clark Jones R. (Polaroid Corp.): *Phot. Sc. Techn.*, May 1955, 56–65.

34. According to Jones and Higgins, this distribution of the fluctuations is not Gaussian.
35. *J.S.M.P.E.*, 1942, 375.
36. Romer W.: *Sci. et Ind. Phot.*, 1953, 312.

36b. The granularity also depends on the shape of the illuminated spot—circular or slit.

37. Ingarden R. S. and Minkusinski J. G.: *Sci. et Ind. Phot.*, 1953, 280.
38. Debot R.: *Sci. et Ind. Phot.*, 1953, 408.
39. *Sci. et Ind. Phot.*, 1952, 148; 1956, 217–222.
40. Stricker K.: *Helv. Chim. Acta.*, 1948, 1487–1496.
41. Jones L. A. and Higgins G. C.: *J.O.S.A.*, 1951, 41–52; *Sci. et Ind. Phot.*, 1951, 178; *J.O.S.A.*, 1951, 192–200; *Sci. et Ind. Phot.*, 1951, 260.
42. Hickman: *Sci. et Ind. Phot.* (1), **6A,** 117.
43. Strauss, *Sci. et Ind. Phot.*, (2), **11,** 185.
44. Stevens G. W. W.: *Phot. Jl.*, 1947, 74–80; *Sci. et Ind. Phot.*, 1947, 303–305.
45. Blair and Stanton: *Amer. Phot.*, 1939, 361. Lyot: *Sci. et Ind. Phot.* (2), **3,** 107 and **14, 185.**

Chapter XVI

PHOTOGRAPHIC REPRODUCTION

PRODUCTION OF THE IMAGE

238. The negative

Very sensitive emulsions with great exposure latitude are used to make negatives. These emulsions are from 100 to 10,000 times as fast as positive paper emulsions and 40 times as fast as ciné positive emulsions.

Negatives are developed to a γ between 0·6 and 0·8.

Fog density. A freshly made negative material should not have a fog density exceeding 0·08. If the emulsion is old the fog may exceed 0·2 (except in the presence of a strong antifoggant). Above 0·2, irregular emulsion fog can alter the low densities of the negative image.

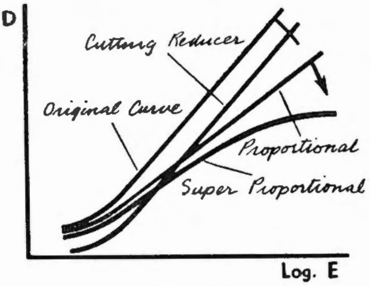


FIG. 36.

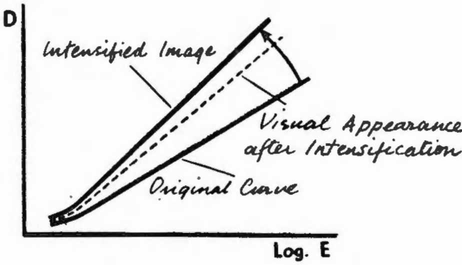


FIG. 37.

In general, *intensification* and *reduction* of negatives should be avoided. If such treatment appears necessary, it is always essential to choose the type of bath which will produce the desired effect; Figs. 36 and 37 show the effect on the characteristic curve of reducers and intensifiers.

239. Duplicate negatives

Duplicate negatives are made in two stages: (*a*) printing a special positive; (*b*) printing the duplicate negative from this positive.

Printing the positive. The positive emulsion must have very fine grain and a characteristic curve with a long straight line with the toe as short as possible. It must have a high contrast with a relatively high maximum density (but little exposure latitude), depending on the brightness range present in the original negative (Fig. 38). A yellow dye can be incorporated in the emulsion to reduce irradiation, whilst the flaws in the base are reduced by colouring it blue or violet (lavender hue).

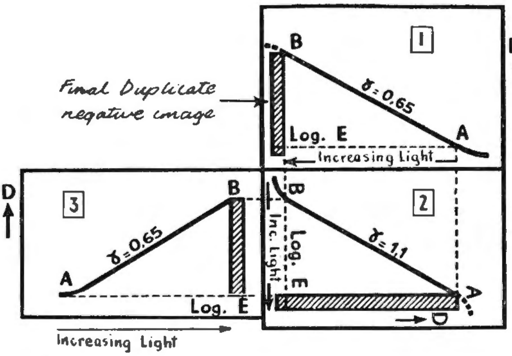


FIG. 38. Preparation of a duplicate negative.

As the original negative is developed to a $\gamma_N = 0{\cdot}65$, the print onto positive material is developed to $\gamma = 1{\cdot}7$.

The image MN is printed only on the straight line in order to avoid distortion. It therefore follows that the print must be overexposed to such an extent that a dense image with no clear parts is obtained. A positive developer is used. If the γ is 1·7 and the negative γ 0·65 then the positive image will have a γ product:

$$\gamma_N \times \gamma_P = 1{\cdot}1$$

Printing the duplicate negative. The duplicate negative emulsion is also slow with very fine grain and a long straight line, but it is less contrasty and the maximum density is lower than the positive.

The dupe negative is developed in M.Q.-Borax to a $\gamma_D = 0{\cdot}59$. The final γ of the dupe negative is the product of the 3γ, negative, positive and duplicate, $\gamma_N \times \gamma_p \times \gamma_D = 0{\cdot}65 \times 1{\cdot}7 \times 0{\cdot}59 = 0{\cdot}65$. In fact, the product $\gamma_p \times \gamma_D = 1{\cdot}7 \times 0{\cdot}60 = 1{\cdot}02$, the contrast of the original is practically unchanged.

To obtain the image on the straight line, the duplicate negative, like the positive, is slightly overexposed. It therefore differs visually from the original as it is more dense, having no clear areas. In addition, it may appear flatter than the original if the image is slightly coloured, due to the finer grain.

It is possible to vary the γ of the three images, provided that the final γ is between 0·6, and 0·8. Thus positive films can be used for duplicating with a γ of only 1·25 and negative films for a γ of 0·65, borax developers being used in each case. The original must have, to compensate for the lower contrast, a higher γ—0·8 if the duplicate is to have a γ of 0·65.

After washing, the films are carefully cleaned with a pad of soft chamois soaked in carbon tetrachloride.

240. Reversal

As we have seen in a previous chapter, the reversal of a negative to a positive can be accomplished in three ways: simple reversal; using a solvent; and controlled re-exposure.

In each case, the contrast of the reversed image is equal to the contrast of the negative image, which must therefore be developed to a high γ (1·4 for films). Actually the reversed image appears slightly less contrasty than the negative, as it is composed of the finer grains (left behind as they are less sensitive); it is known that for an equal mass of silver, fine grains are more transparent than coarse ones.

With *simple reversal* the silver bromide remaining after negative development and bleaching is blackened. As the thickness of the layer is constant, overexposure of the negative produces a positive which is too light and underexposure gives a dense positive (Fig. 39); in the former case detail is lacking in the highlights, whilst in the latter case the shadows suffer. It can be seen in the first two curves the highlights are recorded on the straight line, the clear parts of the reversed positive having correct rendering whilst the dense shadows are on the distorted part of the curve.

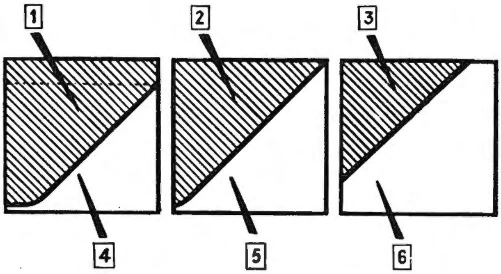


FIG. 39. Simple reversal.

When the negative is developed in a *solvent* developer, a thicker emulsion can be used, the excess halide being eliminated by prolonging development after reaching γ_∞. If the negative image is overexposed there is sufficient latitude, however, to record the whole density scale.

Contrary to the general belief, reversal with solvent does not increase the speed of the layer at all, but only permits overexposure by using thicker emulsions.

It is the same with *controlled second exposure.* The emulsion layer is also thick. If the exposure is normal, that is making best use of the emulsion speed, the excess silver bromide is neutralized by using a low intensity for the second exposure; the larger grains only are affected and the blackening is therefore restricted, the remaining halide being eliminated by fixing; thus the result of normal reversal is achieved. If the negative is overexposed, the major part of the halide is removed by first development and bleaching. There is then a relatively small amount of halide left, and most of this must be used to form the image. In this case a stronger second exposure is given than for the normal exposure (Fig. 40).

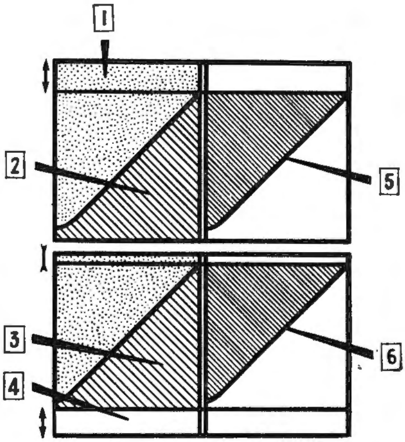


FIG. 40. Reversal with a solvent or by controlled second exposure.

241. Transparent positive copies

Emulsions for transparent positives have characteristic curves which are generally similar to those of negative emulsions, but their exposure latitude is greatly reduced. In compensation, the γ_∞ and maximum density are high. Positive emulsions for transparencies are slow and fine grained.

These positive materials are *printed* by contact or projection. In the former case the effective density has a value close to the diffuse density. In projection printing, the effective density of the negative approaches the specular density. The image itself is diffusing, more so as its grain becomes coarser. A coarse-grain negative produces a much greater difference between contact and projection printing than a fine-grain one.

Ciné positive films are developed to a gamma of 1·8–2·6 so that with a negative developed for example to $\gamma_N = 0{\cdot}7$ a positive image, with a contrast $\gamma_N \times \gamma_p = 0{\cdot}7 \times 2 = 1{\cdot}4$ minimum, is obtained. A tolerance of 0·05 is permissible. When fine-grain positive stock is used the prints are more transparent and to obtain a sufficiently contrasty projected image, the diffuse light control $\gamma^{(1)}$ must be increased to 2·5.

Important note: It must never be forgotten that the characteristics of an emulsion do not only vary from one batch to another, *but also during storage, which makes frequent tests necessary.*

Sixteen-millimetre prints. Prints on 16 mm film from 35 mm originals are made with an optical printer in which stray light is reduced to a minimum.⁽²⁾ The contrast factor inherent in optical printing must be considered, when determining the development.

Positive emulsions for reproduction. These emulsions can be divided into two categories: those for document copying and those for the graphic arts. For the reproduction of documents both ortho and pan *microfilms* are in current use. The microfilm emulsions are generally rapid chlorobromide with extremely fine grain. Bromide types are available but the grain is much coarser. They are made relatively fast by colour sensitizing (in the yellow-orange for ortho). The γ is from 3–3·5. There are films for 16 mm reproductions and positive sheet-films for preparing tracings. The tracing emulsions are also available on translucent waterproof paper; their contrast is very high.

For the *graphic arts* fairly fast emulsions with contrasts varying from 1·6–2·5 are used for half-tone work. Slow fine-grain chlorobromide emulsions with high contrast are used only for line work.

242. Photographic papers

Photographic papers have slow emulsions—bromide, chlorobromide or chloride.

Bromide papers are used primarily for reproductions in large sizes and industrial work. Chlorobromide papers give warm tone images and because of this are used for portraits. The principal use of chloride papers is for printing amateur snapshots.

The gelatin used for glossy papers is well hardened so that they can be hot-glazed.

The emulsion layer is relatively thin and development is to γ_∞ to obtain the maximum black.

The exposure latitude of photographic papers is very small, the more so with more contrasty emulsions; the positive image almost always includes the extremes of the negative.

The support. The paper base is made in two thicknesses: paper and card—two colours: white and ivory (or chamois or cream)—three surfaces: glossy, semi-matt and matt and four physical forms: smooth, grained, silk and velvet.

The paper is deformed by wetting and drying. This is to be expected and results in a shrinkage of less than 0·5%. Drying on a heated drum on the contrary stretches the paper to a greater extent. This deformation is anisotropic, that is different in the two directions. It is noticeable mainly with machine drying where the expansion is greater in the transverse direction. The anisotropy is accentuated further by hot glazing. The variations continue for several days following drying.

White base is always slightly tinted pink blue or yellow. This can easily be seen by rolling the paper into a cylinder and observing the inside. Primarily this tinting is to mask the greyish colour of the gelatin. Ivory papers are sometimes dyed in the mass and sometimes stained superficially.

Sensitivity. Bromide papers are relatively sensitive, about one-hundredth that of a fast negative material. Orthochromatic chlorobromide papers are only half as fast as bromide; unsensitized they are five to ten times slower. The chloride papers (gaslight) are much slower: generally about one-hundredth the speed of a bromide emulsion. They are therefore printed with powerful lamps. In H and D units the following comparative figures can be quoted (in order of speed):

Non-sensitized ultra-rapid negative emulsion	1000
Medium-speed half-tone emulsion	120
Ortho microfilm	60
Process emulsion	18
Normal bromide paper	10
Ortho chlorobromide paper	3–5
Unsensitized chlorobromide paper	1–2
Chloride paper	0·1

The speed (or sensitivity) of a photographic paper depends on the ease with which the *maximum usable black* is obtained, which for glossy papers can be fixed at 1·5, and 1·15 for matt papers. If two different papers require 8 and 4 seconds to give the maximum black, the second is twice as fast as the first.

After the Lilienthal Gesellschaft, the speed has been fixed by the formula

$$S = \frac{10,000}{E}$$

where E is the exposure necessary to give a density of 0·8.

With the ASA standard, which uses the same formula, the density used is determined by a point above the toe such that the slope at this point is ten times as high as that at a lower point which is found experimentally. This controversial method will be discussed later.

Maximum black. We have said that the maximum usable black of a glossy paper is 1·5 and that of a matt paper 1·15. However, the *maximum obtainable black* can reach 1·65–1·7 for a bromide paper and 1·75–1·85 for a chloride paper. It depends mainly on the structure of the silver grains and upon the thickness of the layer. The absolute density of a matt paper generally reaches 1·3; those of semi-matt papers have intermediate values.

A paper poor in silver or having only enough to give grey images easily appears to have a low contrast due to the absence of real blacks. If the paper is made with the minimum of silver, slight differences in layer thickness result in a visible irregularity on development.

Shape of the characteristic curve. Photographic papers have an S-shaped characteristic curve (Fig. 41), very similar to those of negative emulsions. Generally there is a central straight line region which is sharply defined and predominant. The length of the toe and its curvature vary from one type to another and even from one batch to another of the same type because of the presence of a long tail to the toe. Of the many thousands of photographic papers examined by the author there were but two with a badly defined straight line. From all this evidence, and contrary to the opinion unfortunately widespread, the straight line of a paper emulsion is a definite characteristic and even the principal criterion.

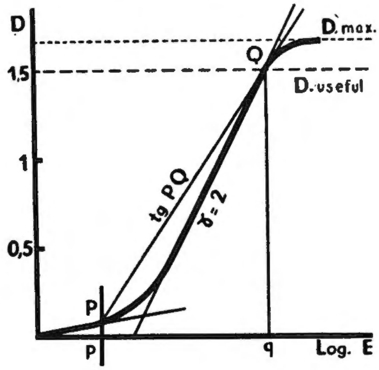


FIG. 41. Normal glossy paper.

243. Gradation of papers

Following the classical conception, the gradation of a paper is determined by the usable extent of luminosities recorded between two points on the characteristic curve situated on the toe and shoulder of the curve corresponding to slopes of 0·2. The lower the brightness range, the more vigorous (in principle) the images obtained. It is true that a normal bromide emulsion can accommodate a range of 1·1–1·2, a soft emulsion 1·2–1·5 and a hard emulsion 0·8–0·5.

In the *ASA system* worked out by Jones and Nelson,⁽³⁾ two points P and Q are taken which are on the toe and upper part respectively such that the slope of the chord joining them (tan PQ) has a value equal to ten times that of the lower tangent passing through P: tan PQ = 10 tan P.

The distance Pq where q is the foot of the perpendicular dropped from Q to the horizontal through P, measures the gradation. Qq is the usable density range.

The tangent PQ can be found by the method of W. Swift⁽⁴⁾ which uses the pivoting of two solid rules, or with Morisson's apparatus.⁽⁵⁾

The determination of gradation using the special gradient methods which have just been described (Chapter XV) has two serious drawbacks: it is not at all reproducible, and does not represent the actual character of the paper. It is not reproducible as it is practically impossible to determine accurately the position of the point where the gradient is as low as 0·1 or 0·2 of an emulsion⁽⁶⁾ whose toe (that is the low density region) varies greatly with slight experimental errors and storage conditions. A simple calculation shows, furthermore, that the thickness of a pencil line in the drawing of the curve is enough to change the gradation. Anyone familiar with the practice of emulsion making knows to what extent they are unpredictable and elusive.

Even if the determination of gradient, by finding low slopes on the toe of the curve, were not subject to errors, it can be asserted that the figure found is not representative of the character of the paper studied. The author has prepared soft, normal and hard positive emulsions which have, however, the same extreme brightness range and therefore, apparently the same gradation.

We have already said that most paper emulsions have a characteristic curve whose straight line is well defined. It is therefore the *contrast* or slope of the central part which should be known to determine the classification. This does not lessen the desirability of finding whether the shape and length of the toe harmonizes with the γ. The toe of a paper emulsion can vary greatly from batch to batch (of the same type), from day to day and from one processing to another; whilst the contrast of the majority of the curve remains relatively stable.

The Deutsche Lilienthal Gesellschaft has proposed that the average gradient should be the γ of the chord joining the points where the density is 0·3 and 1·55 (or 1·3 for papers other than glossy), and the usable range is the distance between the points corresponding to densities of 0·03 and 1·55 (or 1·3).

Apparent contrasts of different paper grades (read on the same densitometer):

	Soft	*Normal*	*Vigorous*	*Hard*	*Extra hard*
Glossy bromide	1·5	2	3	4	5
Matt bromide	1·2	1·6	2·5	3·2	4
Glossy chloride	2	3	4	5·5	7

ASA standard for photographic papers (No. 38, 2nd March 1947). The sample is conditioned at 20° ± 5°C and R.H. 50 ± 5% and exposed in a non-intermittent intensity scale sensitometer for 4–8 secs. A tungsten filament lamp with a colour temperature of 2850 ± 15° K is used.

The exposed paper is developed after 2 hours in the following developer, diluted before use with two parts of water.

Water at 50°C (122°F)	500 cc
Metol	3·1 g
Sodium sulphite anh.	45 g
Hydroquinone	12 g
Sodium carbonate monohydrate	67·5 g
Potassium bromide	1·9 g
Cold water to	1 litre

Temperature: 20 ± 0·5°C (68°F).

Agitation: 2-litre dish, rocked in four directions, fifteen times in 2 minutes.

Development time: 90 secs.

Acid stop bath: 1 minute in

Acetic acid 28%	45 cc
Water to	1 litre

Fixing: 10 mins. at 20°C (68°F) in

Hypo	480 g
Water to	2 litres

to which is added the hardener:

Water	160 cc
Sodium sulphite anh.	30 g
Acetic acid 28%	96 cc
Potash alum	30 g

Washing: 15 mins. at 20 ± 5°C.

Drying: below 40°C (104°F).

Density measurement in diffuse light. For special surfaces, two readings are taken, the second after rotation of the sample through 90° on the measurement axis. The average is used.

Curve: Determine P and Q such that the slope of the tangent at P is 1/10 that of the chord PQ

$$S = \frac{10^4}{E_Q}$$

The Standard Z.38 has been modified in certain respects in *ASA Standard* PH 2.2. 1953. The point *a* where the density is 0·02 is found, then a transparent sheet carrying oblique parallel lines is used. That on the right being the tangent to the toe, and that on the left, the tangent at the shoulder d. The difference $\log E_d - \log E_a$ measures the log brightness range (scale index). $D_d - D_a$ is the usable density range (density scale). The useful black D_d is the maximum evaluated density. Log E_d is the shadow exposure index.

The slope of the oblique lines on the calculator is bar gamma $\bar{\gamma}$.

Remarks. (1) The base density 0·02 is much too low to be indicative of the main character of the curve. (2) The reason for the development time of 90 secs. for all papers is not clear.

244. Reproduction of extreme densities

The extreme density range of a negative is usually greater than the brightness range of the paper. It is sometimes desirable either to reduce the density range of the negative whilst maintaining the contrast of the details, or to reduce the gamma of the paper to match it with the negative.

Reduction of the extreme density range of a negative: this reduction can be effected by two different methods: the first uses unsharp masks using the technique of Yule;(8) the second, which is quicker, is an application of the Herschel effect. The technique described by Miss M. Johnson(9) is as follows: the negative is first printed by contact, using a short exposure to white light. A transparent film is then inserted between the negative and the paper, and a second exposure of long duration to red light is made. The extreme densities of the negative are thus reduced to such a degree that they can be accommodated on the paper. Source of red light: 4 photofloods + 3 Wratten 40 filters to each (ventilated and protected by glass sheets).

The Herschel effect is more pronounced with a desensitized paper. The white source then used is two photofloods, and the exposure 3–9 seconds. The filters for the red light are then Wratten 25 and the second exposure is 30 secs.

Reduction of contrast of papers using the Sterry effect. The Sterry process consists in softening a paper image by treatment, after exposure, with 1% dichromate, for 1 minute. The paper is then rinsed for 20 secs. and developed. For chloride papers, the dichromate concentration is reduced to 0·2%.

The exposure time is adjusted so that the low density details are recorded. The dichromate concentration and treatment time are governed in practice by the difference between the contrast of the negative and of the paper. An empirical rule(10) is to determine the optimum times for the shadows and highlights and to obtain the quotient. The number found, v, is the number of cc of 5% dichromate to be diluted in volume V. 1·5 V then gives the treatment time in seconds.

'High-key' images. High-key images, having most of the subject in light tones, sometimes with dark patches, are generally used for portraits. The simplest method is obviously to photograph a light subject with no strong contrast. Negative and positive are both developed soft. If there are unwanted high densities, the printing time is reduced. A second method is to bleach the positive image in a tanning dichromate bleach which hardens the gelatin in the dense areas. By redeveloping in a dilute amidol developer only the light areas redevelop normally.

245. Industrial papers

Industrial papers are used for document reproduction. There are several types. Generally they have matt surfaces and the emulsion is balanced with the support in such a way that they do not roll up after drying on a hot drum.

Document paper: bromide emulsion on thin paper (90 gramme—no baryta). Sensitivity equal to or less than that of glossy bromide papers. Use: enlargements from microfilms. The same type is made coated on both sides. Some of these papers have chlorobromide emulsions.

Rapid document paper: orthochromatic bromide or chlorobromide emulsion on baryta paper. Ten times as fast as ordinary document paper. High contrast. Use: direct photography of documents on Photostat type machines with lens and reversing prism.

Cardiographic paper: ordinary bromide emulsion on glossy paper slit into laterally perforated bands.

Recording paper: very fast emulsion of negative type, coated on thin non-baryta paper. Use: recording machines with luminous spot.

Reflex paper: extra hard orthochromatic chloride emulsion with very short threshold, coated on a non-baryta coated thin base. It can be handled in weak electric light or very weak daylight.

Use: reflex document copying. The emulsion is placed in close contact with the document and *exposed through the base* using a yellow filter. By rapid development in 30–60 secs. a negative is obtained. After drying, the negative can be printed on the same paper by normal contact to give a positive.

As the foot of the curve is very short the first exposure through the emulsion produces no latent image or fog, but a sub-latent image. The light reflected by the white areas of the document again acts on the emulsion; it augments the action of the incident light to producing a developable latent image, which is very dense as the emulsion is very contrasty ($\gamma : 7$).

Autopositive paper: solarized contrasty orthochromatic chloride emulsion on a thin non-baryta treated base. Use: direct positives by normal or reflex printing. Sensitivity equal to that of diazo paper.

246. Variable contrast papers

(*a*) *Ilford 'Multigrade' paper.* This paper whose principle was disclosed by K. Fischer in 1912 was perfected by F. Renwick in 1940. It consists of a mixture of two emulsions, one with high contrast sensitized to green, the other not colour sensitive and soft. Depending on the predominance of green or violet light, one emulsion or the other is affected which results in a more or less contrasty final image. A range of coloured filters is used in printing. (*Phot. Jl.*, 1940, 266.)

Filter	*Exposure*	*Contrast*
Without filter	½ sec.	very soft
Light yellow	⅔ sec.	soft
Normal yellow	1 sec.	normal
Dark yellow	1½ sec.	hard

(*b*) *Defender 'Varigam' paper* has a chlorobromide emulsion sensitized with a sensitizer such as 1 : 1-diethylpseudocyanine at a concentration below the optimum. This emulsion is washed to remove the excess dye. Potter and Hagaman stated that the dye is adsorbed solely by the larger grains (U.S.P. 2,280,300). By printing with green light, only the sensitized grains are affected which, and owing to their size give a soft image, whilst with violet light the non-sensitized grains are affected giving a contrast 50% higher. Ten filters passing from blue to yellow are used in printing.

(*c*) *Kemart fluorescent paper*. This paper has a fluorescent support and is intended for photomechanical reproduction. It is exposed to an auxiliary ultra-violet source which increases the contrast by excitation of the fluorescent compound.

In the numerous patents concerned with fluorescent substances(11) are: acids derived from amino substituted 4 : 4-diaminostilbene; derivatives of 7-aminomethyl-coumarone; derivatives of 2-styrylbenzimidazole, etc.

Document reproduction on fluorescent paper. This method, which will be returned to, later, in connexion with colour reproduction, enables the maximum contrast to be obtained in ordinary photography of documents. The latter are made on fluorescent paper. Retouching is carried out on the fluorescent layer. The drawing is lit with a mixture of ordinary and ultra-violet light, whilst a U.V. filter is placed over the lens. The areas activated by the ultra-violet become more brilliant, which increases the luminosity scale and therefore the subject contrast.

SOUND RECORDING

247. General properties of sound

Sound is a *vibration phenomena* defined (in simple cases) by a sinusoidal movement.

$$x = a \sin (\omega t + \phi)$$

in which x is the *elongation*, a the *amplitude*, ω the *pulsation* and t the *time*.

The *period* T, or time necessary to complete one vibration is $2\pi/\omega$ and the *frequency*, number of vibrations per second $F = \omega/2\pi$.

The *intensity* is measured by the product of the square of the amplitude a by the square of the pulsation ω

$$I = a^2\omega^2$$

The ratio of two intensities I_1/I_0 is therefore equal to $a_1{}^2/a_0{}^2$.

In practice, two intensities are compared following a log scale where $\log I_1/I_0$ is given in *bels* (or $10 \log I_1/I_0$ decibels). In using the ratio of power in watts one has: $10 \log W_1/W_0$ watts.

Harmonics. When the vibratory movement produces several sinusoidal vibrations whose frequencies are successive multiples of the fundamental frequency, the results are called harmonics. The shape of the wave depends on the amplitude and phase of each harmonic. A periodic function having higher order harmonics of quite high amplitude has breaks in the wave representing it.

Properties of a sound. A sound has the properties: pitch, intensity and quality or timbre.

Frequency produces the *pitch* of a note. A low note has a low frequency and a high note a high frequency. The lowest audible notes have a frequency of about 16, but the musical scale does not begin until $E_0 = 40$. The upper limit for very high notes is about 16,000, but varies with the age of the observer.

To have a clear impression of a note, a minimum duration of one-tenth of a second is necessary; this corresponds to 5 cycles for $A_3 = 435$ and $C_4 = 512$ and 10 cycles for $C_5 = 1024$.

Intensity. The intensity of a note, as we have seen, is a function of the square of the amplitude. The aural sensation is not directly proportional to the intensity; it varies with the log of the excitation. Below a certain threshold no sound is audible. The aural response curve plotted against the log intensity is S-shaped like the photographic characteristic curve.

The voice in average conversation has a strength of 40 decibels. The ear can detect a difference of 2 dB.

Timbre. The timbre or quality of a note is due to the presence of a certain number of harmonics of various amplitude superimposed on the fundamental note; their vibration shape has only a secondary influence. For example, the flute produces notes almost free from harmonics; stringed instruments have five or six, whilst brass instruments mainly emit higher harmonics.

248. Principle of sound recording

As sounds are periodic vibratory movements, they can be recorded by photographic sensitive layers.

The sound is received by a microphone and converted to electrical vibrations. These, in turn, modulate a light beam projected onto a moving film.

The sound is recorded on a track 2·5 mm wide.

There are two systems of recording the change in intensity on the sensitive layer: (*a*) by *varying the width* of a continuous line of even density giving a saw-tooth effect and (*b*) by *varying the density* of a continuous band (Fig. 42a). In each case the result is the same: a periodic modulation of the total light passed through the sound track. This is brought about by projecting the image of a very narrow slit onto the recording film by an optical system. The slit is illuminated by the modulated light.

A. Variable density recording. In this system, the light is varied by means of a light-valve, a Kerr cell or a glow lamp.

The light-valve consists, in principle, of two flat metallic ribbons placed between the poles of an electromagnet. A modulated current passing through the ribbons alters the separation between them and in consequence, the height of a light beam projected by a fixed source (Western Electric System).

The *Kerr cell* is dependent on the electromagnetic properties of light. A light beam is polarized by passing through a nicol prism, then cut out by a second nicol prism at 90° to the first. Between the two prisms is a small cell filled with nitrobenzene containing two electrodes whose purpose is to produce a varying electrostatic field due to the potential difference between the electrodes resulting from the amplified modulations of the microphone current. The field variations in the nitrobenzene produce corresponding rotations, more or less pronounced, of the polarization plane which alters the intensity of the beam transmitted by the second polarizer. (Toblis-Klangfilm System.)

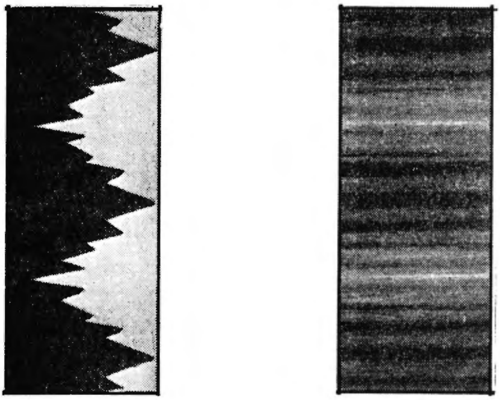


FIG. 42a.
Sound tracks: A. Variable area.
B. Variable density.

The Kerr cell can be advantageously replaced by a thin crystalline layer cut perpendicularly to the geometrical axis, from a crystal of monopotassium phosphate, and placed between two transparent electrodes. With changes in the potential, the layer becomes birefringent and transmits more or less polarized light (Pöckels photoelectric effect).(11b)

The *glow-lamp* produces a variation in light intensity directly, with variations in the current received. The luminous discharge takes place in a rarified gas between a red-hot anode of platinum coated with the oxide of an alkaline earth, and a nickel cathode. The lamp is placed in a quartz tube.

B. Variable area (variable width) recording. The amplified microphone current is received by a mirror galvanometer. This reflects a constant intensity light beam onto the recording film deflecting the beam in proportion to the modulating current (RCA system).

The light modulation can also be carried out, however, with a ribbon valve at 90°. An anamorphic optical system enables the very small ribbon movements to be amplified (Western Electric).(12)

There are several types of variable area track (Fig. 42b).

(*a*)	Unilateral track	Class A
(*b*)	Bilateral symmetrical tracks	
(*c*)	Opposed tracks (push-pull)	
(*d*)	Double unilateral track	
(*e*)	Opposed tracks	Class B

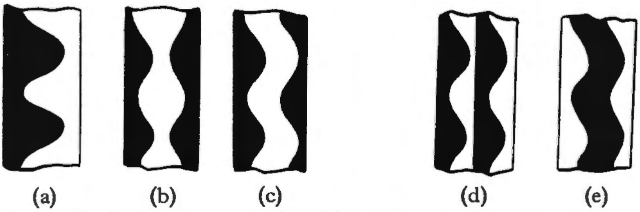


FIG. 42b. Different types of variable area sound track negatives.

Opposed type Ac tracks are composed of two separate 'out of phase' parts. They give the best recording for original tracks (for subsequent re-recording on the final negative) by eliminating even harmonics and reducing background noise. The opposed tracks of type b, one of which records the negative half-wave and the other the positive, have, on the other hand, a high distortion factor.

The double unilaterals track (Ad), which gives excellent results, has the advantage that it is less sensitive to misalignment of the recording apparatus. It is obtained by optically doubling the track image, the ribbon movement being halved.

C. Magnetic recording. Magnetic sound recording has displaced direct photographic recording for the production of originals. The principle of this method is well known: a plastic tape having a layer of iron oxide is passed through a varying magnetic field which affects it permanently. By the reverse process, passing the tape between the poles of an electromagnet produces a modulated current.

The tape is made of cellulose triacetate coated with a layer of ferric oxide Fe_2O_3 whose particle size is less than 1 μ, or polyvinyl chloride containing the oxide.(12b)

Reproduction. One method of applying sound to ciné films is to stick a magnetic tape or coat with a magnetic layer within a narrow band. Stereophonic films have four magnetic sound tracks, on each side of the perforations.

A second method is to re-record the sound photographically on an intermediate negative film. J. G. Frayne (Bell Tel. Co.) has shown that two parallel narrow optical tracks, recorded on a normal 2·5 mm width, are sufficient to produce a stereophonic effect.(12c) The two tracks are separated by an 0·1 mm interval.

For editing, a film carrying both positive photographic (by re-recording) and a stuck-on or coated magnetic track can be used.(13) Some machines use an oscilloscope so that the effect of the magnetic track can be seen, and this enables the photographic track to be dispensed with.(14) Others enable cutting to be performed without visual aid by moving a magnetic head over the stationary drum.(15)

Photographic sound recording is made on a separate *special negative film*. After development, the sound track is printed in the appropriate area of the positive film (which carries both picture and sound). These are developed at the same time in the same operation.

The sound is reproduced by illuminating a narrow slit whose image is projected onto the moving positive film. The periodic light variations produced by the sound track are received by a *photoelectric cell* placed on the other side of the film, and converted to an electrical impulse, which is amplified and fed to the loudspeaker.

Photoelectric cells containing low-pressure gas (such as argon) are much more sensitive than the completely exhausted ones. The former produce, for example, 100 μA per lumen whilst the latter give only 20. The wavelength of optimum sensitivity is at about 700 mμ in the deep red; it can be increased to 840 mμ (near infra-red) for caesium-silver oxide cells, whilst antimony-caesium $SbCs_3$ cells have a maximum response at 460 mμ in the blue.(16)

249. Emulsions for sound recording

A sound recording must be capable of linear reproduction, that is, without distortion, from 40 to 10,000 c.p.s. at a level of 50–60 db.

As the negative film travels at a speed of 456 mm/sec. (length of twenty-four frames), a single cycle of a low note, 120 for example, will cover on the sound track, a distance of 3·8 mm whilst the length of one cycle of a very high note of a frequency of 8,000 occupies only 0·057 mm.

It is therefore evident that for recording high frequencies, a much higher *resolving power* is required than for low frequencies.

Also, the sharpness of the recording depends on the loss of density by diffusion (irradiation). This is why the negative emulsion must have regular and *very fine grain* (0·5 μ). A dye of the complementary colour to the sensitivity can be used to limit the penetration and irradiation of the light in the depth of the emulsion.

Halation, which is particularly troublesome, is avoided by including a thin layer coloured yellow, red or blue, depending on the colour sensitivity, between the emulsion and the base. Anti-halation layers on the opposite side of the base are less effective.

The *speed* of the negative material varies with the recording system, but is generally higher than ciné positive stock. With a movement of 456 mm/sec. and a slit width of 10–20 μ, ultra short exposures of 1/20,000 to 1/50,000 sec. are used at intensities about 100,000 candle-metres. An inertia value of about 0·2 is therefore necessary.

In order to avoid distortion in the reproduction, it is furthermore necessary that the image is produced only on the *straight part* of the characteristic curve.

Because of this, the negative emulsion must have a well-defined straight line with a very short toe. Furthermore, it must be capable of giving sufficiently high densities as we shall see later.

For variable area recording, *contrasty* emulsions are used, whilst for variable density recording, a contrast five times lower is enough.

We note finally that the negative emulsion should have as little fog as possible. However, this is less important than for the positive film. The latter is also used for the picture; it is advantageous to have a long straight line with little irradiation.

To give examples we would quote film characteristics:

Kodak 1372 for variable area recording. Sufficiently slow to dispense with the U.V. filter. Sensitivity limit: 460 mμ. Resolution: 150 lines/mm. High contrast: γ 3–3·5 reached in 4 mins. in D 16. It is usually developed to γ 2·4–2·8. Grey base, density 0·12.

Kodak 1373 for variable density recording. Maximum contrast 0·5. Slow development (6 mins.) for easy control of γ which normally varies between 0·35 and 0·45. Resolving power in borax developer: 90 lines/mm.

Du Pont films. The old film for *positive copies* of sound tracks, *No. 225*, printed in ultra-violet light, the γ obtained being 1·55 (2·3 in white light). The new film *No. 232* enables copies to be made in white light at a γ of 1·6, from negatives of $\gamma = 0{\cdot}85$, destined primarily for ultra-violet light.

For variable density recording *No. 236* is preferably used, developed to γ 0·65 (measured with a IIb sensitometer control), the unmodulated density being 0·52. Copied in white light it has more latitude in print density than the old type 226 which was printed by ultra-violet.

Sound tracks are developed in the same baths used for negative and positive picture images.

250. Development of sound recordings

The development of sound recordings differs with the system (variable area or density) used.

Whatever system is used, the operations are carefully controlled with sensitometric tests. All sensitometric methods are good if used with discretion. Sound recording is always carried out with varying intensity (of high value) and fixed time (very short): these conditions are not produced with normal sensitometers.(17) By careful comparison of the values given by the sensitometer and on the actual recording, coefficients relating them can readily be found, which are adequate for production work.

Variable area recordings. The negative film is developed in an energetic developer to a γ of 2·4–2·8. The recording light is adjusted to give a track density of about 1·5, the fog being below 0·06. For push-pull tracks, the recommended density is sometimes higher.

The positive copy is printed so that the part protected by the opaque track remains quite clear, whilst the unprotected region has a density of about 1·35–1·5. As we know, the positive carrying both picture and sound is developed to a γ of 2–2·6.

The difference in transparency between the dense and clear areas is even greater, and consequently leads to better reproduction, if the clear areas are free from fog. The benefit obtained by increasing the density of the opaque area is much less than the reverse operation of increasing the transparency of the clear area.

To reduce the background noise which masks the low intensities, the 'RCA High Fidelity' system uses a central track, dense in the negative and clear in the positive, with a double row of saw teeth. This track, very narrow in the silent parts, widens when modulated. Thus imperfections in the clear areas have a diminished effect on the reproduction.

Variable density recording. As the modulation is due to variations in the density of the sound track, it is necessary that:

1. The complete density range recorded is on the straight line so that there is no distortion.(18)

2. The effective contrast (with reference to the sensitivity of the photocell) of the picture-sound positive is $1 : \gamma_N \times \gamma_p = 1$.

All effective γ greater or less than 1 lead to distortion.

A variable density sound record consists of a double set of variations higher and lower than an average density of zero level (Fig. 43). This average density corresponds to silence.

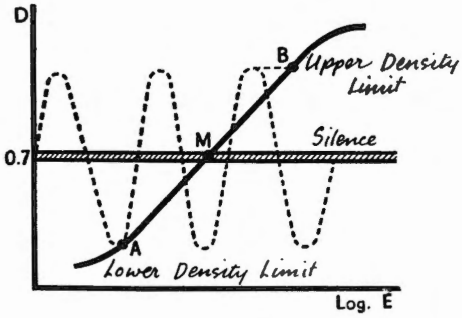


FIG. 43.

Now it can be stated that the background noise is reduced if, during the silent periods, the cell received less light, that is, if the average positive average density is higher (conversely, if the negative track is less dense). As a limit is set by the length of the straight line, the Western Electric 'Noiseless' system can vary the average density automatically depending on the intensity of the sound reproduced. In the silent periods the positive density is maximum; it is reduced during modulation for the high intensities; thus the high density peaks are still found on the straight line below the limiting point B.

A sensitometer strip is developed at the same time as the negative in a fine-grain developer. Now depending on the modulation system used, the interpretation of the control must be varied. The light-valve modulates on a time-scale whilst the Kerr cell varies the intensity. In the former case the gamma does not change whatever the intensity used, and is therefore comparable with the sensitometer control. In the case of intensity variation, the gamma is lower for high intensities, that is, the sensitometer gives values which are apparently much higher. Call γ_N the negative gamma as a function of the openings of the light-valve, γ_{SN} the gamma of the negative sensitometer strip, γ_{SC} the positive copy of the negative sensitometer strip and γ_{SP} the gamma of a positive strip developed at the same time as the positive film.

We know, furthermore, that the ratio of the effective gamma in the optical system of the soundhead and the photometric gamma in *diffused light* is about 1·3. Taking this value in the example equation we have:

$$\text{effective } \gamma = 1 = \gamma_N \times \gamma_{SC} \times 1{\cdot}3$$

$$\text{but } \gamma_N = \text{a} \,.\, \gamma_{SN} \text{ and } \gamma_{SC} = \text{b} \,.\, \gamma_{SP}$$

a and b being the coefficients which show firstly the ratio of the sensitometric and actual negative measurements, and secondly the relationship between the sensitometric measurements and the positive copy. a is determined once and is constant, whilst b must be checked daily.(19) Therefore we have

$$\text{effective } \gamma = \gamma_{SN} \times \gamma_{SP} \times 1{\cdot}3 \times \text{a} \times \text{b}$$

If the negative is developed to $\gamma_{SN} = 0{\cdot}4$ and the positive to $\gamma_{SP} = 2{\cdot}10$ we get

$$\gamma_{SN} \times \gamma_{SP} = 0{\cdot}84$$

Knowing that $\text{a} \times \text{b} = 0{\cdot}91$, we have effectively

$$\gamma_{SN} \times \gamma_{SP} \times 1{\cdot}3 \times \text{a} \times \text{b} = 1.$$

The average density of the negative is 0·6–0·7, and that of the positive 0·5–0·7 depending on the amplitude recorded.

The glow-lamp produces much smaller exposure variations than the light-valve or the Kerr cell. In this case, for maximum volume, the negative is developed to a much higher γ whilst the density is reduced to 0·35.

Development and printing. The control of temperature and composition of the developing solution have a great influence on the constancy of sound track development. Furthermore, inefficient agitation can produce distortion due to the local accumulation of by-products in the region separating the clear and dense areas.(20)

Microdensitometer measurements enable these defects to be detected.(21)

When prints are made, the shrinkage of the negative (which is not constant), must be considered, whilst the shrinkage of the unexposed positive depends on the time it has been stored. Shrinkage can vary between 0 and 1% and the slip of the negative over the unexposed positive can result in more or less pronounced distortions.

The effect of shrinkage can be overcome by using non-slip printers in which the films only touch each other at the exposure point.

Loss in volume due to shrinkage amounts to 1 dB for a difference in length of 0·1%. The other principal losses are: increase of printing speed from 24 to 48 frames/sec. loses 2 dB; increase of the aperture of the optical system, up to 3·5 dB; increase of the height of the exposure aperture, up to 6 dB.

251. Sound tracks on colour films

When the colour print is made with the three subtractive colours and an additional silver key image as in the *Technicolor* process, the development of the sound track presents no special difficulties; the film has a silver bromide emulsion: the sound track and, if desired, a grey silver image, are printed and developed together. The three colour images are then printed by imbibition. Another method used in the three-colour *Supercinecolor* process is to tone only the picture area without affecting the silver image of the sound track.

In the case of films *whose sound track is also coloured* the problem is more difficult to solve; the photocells used in soundheads have their maximum sensitivity in the extreme red or near infra-red (caesium cells). Now most colouring materials are transparent in these spectral regions; it follows that a coloured sound track has no effective absorption on the light beam which it should modulate.

The difficulty can be overcome by using a *blue sensitive photocell* (antimony-caesium) and a red (or more exactly, magenta + yellow) sound track. These cells however are not generally used.

Another simple solution is to use, for the cyan, an iron ferrocyanide image. This is an inorganic pigment, and unlike the organic colouring materials, has a strong absorption in the red and infra-red. The sound is therefore printed in the layer used for printing the red record negative, and after development, both are toned cyan. The contrast and the maximum and average densities are controlled with a spectrophotometer in such a way that the toned positive sound track has the same characteristics towards the photocell of a silver track. The considerable increase in contrast due to iron toning must be considered and the picture-sound record is developed to a gamma two or three times lower, depending on the toning bath. The gamma of the sound negative, and the light used for printing the copy, are adjusted and controlled as a function of the selective absorption of the cyan image compared with a silver track. Iron toning is generally used in two-colour processes.(22) It can also be used for three-colour work as it gives excellent colour rendering, although transmitting part of the orange. However, if the soundhead uses a lead sulphide cell, sensitive between 1 and 3 μ as in some 16 mm projectors, iron toning is unsuitable.

Sound tracks on colour-developed films. When the colour images are obtained by colour forming development, the sound track is composed of silver and dyes. It is usual to remove the silver of the image in a reducer. Now, in the track area, the metal should not be removed.

There are four methods for keeping the sound records on colour films:

(*a*) After bleaching with ferricyanide and superficially drying with an air squeegee, *the sound track is redeveloped locally*, using a narrow roller which applies a vigorous developer rendered viscous (1000 centipoises) by addition of a thickening agent, such as hydroxymethylcellulose, hydroxyethylcellulose, carboxymethylcellulose or a vinylmaleic resin.

The developer can be a hydrosulphite solution (para. 67) or the following: metol 20 g, hydroquinone 20 g, sulphite anh. 40 g, water to 1000 cc. Laurylpyridinium sulphate 1 g (accelerator) and formalin 20 cc (hardener) can be added. An Ansco formula contains 3 g hypo. If the developer is too viscous, it does not penetrate into the layer quickly enough.

Colour films have a yellow filter made of colloidal silver. It is redeveloped with the sound image and produces a yellowish uniform stain which causes a loss of sound volume of only 2 dB. However, it is possible to eliminate it in a very dilute bleach.

The above method has been used with Eastman and Ansco films.

(*b*) The silver of the sound track is not attacked: *the picture area is locally bleached* with a viscous 10% ferricyanide bath, preferably containing a wetting agent such as Nekal BX (5/1000). The jelly is applied to the film, by means of a roller or through a narrow slit, then removed by an oblique scraper. Agfa and Gevaert.

(*c*) *The sound track silver is converted to silver sulphide*, after bleaching (Du Pont), with: sodium sulphide cryst. 63 g, carboxymethylcellulose 20 g, distilled water 100 cc. This method enables the low contrast of the sound record to be increased when the amount of silver in the film layers is too small.

(*d*) The sound track is protected with a *local layer of varnish*, applied after development, or an *adhesive tape*. Not used in practice.

By restricting diffusion, the sound track is located in the two upper layers of the film, but it is possible to print it in all three layers.(23) For variable area recordings, density must exceed 2·4, whilst variable density recordings need much less silver; in that case the upper layers are sufficient.

The dyes which are present in the sound track have no influence upon the sound qualities.

1. Streiffert J. G.: *J.S.M.P.T.E.*, 1947, 506–522.
2. Tutchings A.: *Brit. Kin.*, 1951, 132–139.
3. *Sci. et Ind. Phot.* (2), **16,** 84.
4. Swift W.: *Phot. Jl.*, 1946, 71; *Sci. et Ind. Phot.*, 1946, 339.
4. Morisson C. A.: *J. Frank. Inst.*, 1947, 55–61; *Sci. et Ind. Phot.*, 1947, 102–104.
6. The 1 : 10 tangent ratio is much too low; it should be at least 1 : 3.
8. *Sci. et Ind. Phot.* (2), **16,** 170.
9. *J.O.S.A.*, 1951, 748–751.
10. Marmet: *Phot. Techn. Sc. Wirtsch.*, 1950. 80.
11. See a long list of patents in the advertising pages of *Sci. et Ind. Phot.*, March 1953. An Ilford F.P. 1,074,579 recommends 4-methyl-1·3-diphenylpyrazoline.
11b. Dressler and Chesnes: *J.S.M.P.T.E.*, March 1953, 205–216.
12. Frayne J. G.: *J.S.M.P.T.E.*, 1948, 501–520; *Sci. et Ind. Phot.*, 1949, 113. Browder L. B.: *J.S.M.P.T.E.*, 1948, 521–533; *Sci. et Ind. Phot.*, 1949, 113.
12b. Lovichi and Deriaud: *Onde. Elect.*, March 1954, 241. Kojima: *Konishiroku Rev.*, Sept. 1953, 133–150 (in Japanese). See also *Mitt. Forschungslabo Agfa, Leverkusen*, 1955, **1,** 289–325 (Springer-Verlag).
12c. Frayne: *J.S.M.P.T.E.*, 1955, 303–308.
13. Frayne and Livadary: *J.S.M.P.T.E.*, 1952, 389–397.
14. Miller R. C. : *J.S.M.P.T.E.*, 1953, 304.
15. Hicks W. R.: *J.S.M.P.T.E.*, 1953, 324–332.
16. Sommer A.: *Proc. Phys. Soc.*, 1943, **55,** 145.

17. The Eastman IIb time scale sensitomer is still often used for this purpose. For a theoretical study, see Lovichi, *Sensitometrie des films sonores*, Paris.
18. For a graphical method of controlling the positive parameters, see Lobel and Dubois, *Manuel de Sensitometrie*, p. 199. Paul Montel, Paris.
19. With sensitometers such as the Eastman IIb the gamma given is 1·75 times the actual gamma by exposing for a very short time, and measured in diffuse light.
20. Sewell G.: *Jl. Br. Kin. Soc.*, 1940, 84.
21. The distortion can be measured by recording a high frequency modulated by a low frequency. The variations in the average transparency show the distortion.
22. F.P. 697,095 (1930)—B.P. 360,819 (1930).
23. Evans and Finkle: *J.S.M.P.T.E.*, 1951, 131–139.

PART TWO

Photographic Emulsions

Chapter XVII

GELATIN

252. Colloidal properties of proteins

Gelatin is a *protein* which plays an important part in photographic emulsions where its chemical and physical properties are utilized.

As with most of the *proteins*, gelatin is a colloid, so we will begin with a brief general revue of the colloidal state.

Compounds are usually divided into the *crystalloids* and *colloids*: the first gives true solutions in which the molecules are completely dispersed, whilst the second give pseudo solutions in which the smallest fragments are much larger than those of ordinary molecules.

Colloidal solutions are intermediate between true solutions and *suspensions* of finely divided material in a liquid. It is true to say that there is no well-defined border between solutions and suspensions; only the size of the smallest particles varies resulting in the formation of a solution for the very small ones (simple molecules), a pseudo solution for the medium ones (thirty times as big as the simple molecules), and a coarse suspension for the big ones (insoluble aggregates).

Normal centrifuging cannot separate suspended particles smaller than 0·04 μ whilst molecules vary in size from 0·001 to 0·0001 μ. *Ultra-centrifuging* at a 100,000 r.p.m. enables the protein molecules from 0·02 to 0·003 μ to be isolated. The colloidal particles can be detected with the ultra-microscope down to 0·003 μ. Beyond that the electron microscope must be used.

These particles are subject to '*Brownian movement*' which is a continuous and random vibration with a molecular origin. The vibration is greater as the viscosity of the liquid is lower, and consequently as the temperature is higher. All translatory movement is accompanied by a rotatory movement: whilst the amplitude of the translatory movement is inversely proportional to the diameter of the particle, the speed of rotation is inversely proportional to the cube of the diameter.

Many substances are known which exist in the colloidal state: inorganic substances such as silica, ferric hydroxide, colloidal silver, or organic compounds such as gum arabic, starch, cellulose or albumen. The organic colloids owe their state to a greater or lesser degree of *polymerization*; in other words they occur as associations of more simple molecules. This results in their molecular weight in this complex state being very high: 70,000 for egg albumen and 300,000 for starch, for example, whilst the molecular weight of hydrogen is 2 and alcohol is 46.

Polymerization is therefore an essential factor in the colloidal state of organic substances; it explains the size of their complex molecules which are in fact 'complexes of complexes'. The simple particles of the colloid, or *micelles* formed when these polymers are treated with intermicelliary liquid are made up of two parts: one part is physically inactive and the other plays the part of the contact layer. Colloidal micelles are found in living tissues in various proportions giving therefore biocolloidal micelles. The increasing complexity of the proteins is demonstrated by the fact that their molecular weights are exact multiples, frequently in geometric progression of the molecular weight of a simpler protein. Thus crystalline albumen has a molecular weight of 34,500, that of egg albumen is twice as great whilst blood albumen is three times as great.

253. Isoelectric point

The proteins are amphoteric substances, that is they have both acid and basic functions and can form either *protein salts* with acids or *proteinates* with bases.

Their behaviour depends upon pH. Albumen for example behaves as an acid at a high pH or as a base at a low pH. The equilibrium point of the two phases is termed the *isoelectric point*. It generally corresponds to a hydrogen ion concentration given at a pH of 4·8.

The micelles are electrically charged. When subjected to an electric current (cataphoresis), they migrate towards one of the poles depending on the pH. Thus in an acid solution (low pH) gelatin migrates towards the cathode (—) whilst in alkaline solution it moves towards the anode (+). The neutral point of the electrical properties of the colloid is exactly at the isoelectric point, at a pH of 4·7 to 5 for lime gelatins. The micelles do not then respond to an electric current.

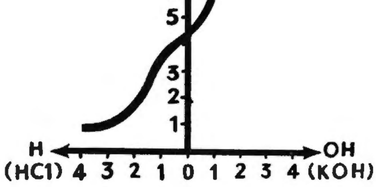


FIG. 44. The titration curve of gelatin.

The titration curve has the shape shown in Fig. 44: the pH is on the ordinate and the amount of acid (hydrochloric for example) and base (caustic potash) on the abscissa, on either side of the ordinate axis. The pH is determined electrometrically after each addition of reagent.

Calf-skin gelatin prepared by the lime method has an isoelectric point from 4·7 to 5·2. Obtained by acid treatment (acetic) it has an isoelectric point between 7 and 9. With pigskin treated with acid, the i.p. is at 8·2. The higher isoelectric point of the gelatins obtained by the second process is due to the treatment time being stopped relatively early (20 hours); if the treatment time is prolonged the i.p. drops to the limit of 4·8.

PHYSICAL PROPERTIES OF GELATIN

253b. Gelatin solvents

The normal solvent for gelatin is warm water. It can, however, be dissolved cold either in concentrated solutions of urea, thiourea, potassium thiocyanate, bromide or iodide, or in organic acids such as acetic, benzoylacetic, salicylic or phthalic. 3N benzene sulphonic acid dissolves gelatin cold without altering it.

254. Viscosity of aqueous gelatin solutions

Due to its complex chemical structure which is easily changed, the internal structure of a gelatin solution becomes more and more rigid on standing; this has the result that the solution does not have a constant viscosity as this increases with time. Agitation on the other hand reduces it.

The increase in viscosity is essentially dependent on the temperature: it is more pronounced at low temperatures when it soon becomes evident. It is important to note that at about 35°C the variations are very small.

If the pH of a gelatin solution is varied, the viscosity is lowest at the isoelectric point, at least when the solution is freshly prepared (max. 10 hours). A solution kept for 25 hours at 52°C shows at the end of this time a sharp viscosity maximum at about pH 7·6.

In acid solution at high temperature (50°C) the viscosity drops considerably on standing for several hours until it is 40% of its original value (after 24 hours). *At the isoelectric point the variations on standing are, on the contrary, very small,* almost negligible. They remain unimportant up to pH 8 (alkaline); beyond this they become appreciable again.

255. Surface tension

The surface tension of gelatin solutions is lowest at the isoelectric point. There are two maxima in acid and basic media respectively.

At a low temperature (16°C) and with solutions of at least 0·5% there is a temporary flocculation of the gelatin after the isoelectric point which is shown by a sharp increase in the surface tension.(1)

Surface active agents readily reduce the surface tension of gelatin solutions.

256. Swelling of gelatin

As with the other properties of gelatin, swelling in water is at a minimum at the isoelectric point. In very acid media the swelling is particularly rapid with a maximum at about pH 2·5, especially in the presence of hydrochloric acid.

The amount of water absorbed increases with the temperature. Furthermore, it is higher with a ready prepared jelly than with dry gelatin, and when the concentration of gelatin is low; a 5% jelly absorbs twice as much water as a 50% jelly (compared with the weight of dry gelatin). We will return to this when emulsion washing is considered.

In the case of dry gelatin films immersed in water at moderate temperatures, the *stretching* due to swelling is preceded by a contraction which is greater as the layer is thinner. A layer 10 μ thick can in this way contract 20% when left in water for an hour, before it assumes its original dimensions after 2 hours and stretches 40% after 2½ hours.

The degree of swelling depends on the temperature at which the film was dried: with slow drying it swells normally, but with hot drying it swells then contracts.(2) It also varies with the dampness of the atmosphere; a high humidity weakens the intermolecular links.

All gelatin swells to an equilibrium with the liquid in which it is treated; the absorption of water is due to the difference between the internal and external *osmotic pressures.*(3) The gelatin therefore swells more as the internal pressure is greater; this internal osmotic pressure increases with the formation of a gelatin salt which can dissociate into ions due to a strongly acid pH (maximum between 2·5 and 2·7); the diffusion of the water from the exterior towards the interior again restores the equilibrium. When the acid is in great excess, reducing the pH further, the exterior pressure increases faster than the internal pressure and swelling is reduced.

By similar mechanism the addition of alkali brings about an increase in internal pressure and the resulting swelling due to the formation of a gelatinate, until the pH reaches a value of 10. An excess of alkali again decreases the amount of water absorbed.

The swelling of gelatin can be *reduced* by adding a *neutral salt* (sodium chloride for example): this gives an increase of external osmotic pressure at the same time as a possible reduction of the internal pressure, by reducing the ionization coefficient of the gelatin salt. *Sodium sulphate* has a stronger action than any of the other sodium salts; this property is used in high temperature development.

257. Gelatin gels

The gelatin gels are distinguished for their hardness and their melting point; the gelatins which are used for their preparation are usually classed as hard or soft gelatins. The 'hard' types are made up of relatively unaltered materials whilst in the 'soft' types the original substance has been attacked and hydrolyzed more strongly thus producing degradation products.

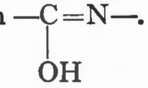
Solutions of hard gelatin therefore appear to contain substances of high molecular weight, making up the gel, which gives them their mechanical strength and their great affinity for foreign materials. This is not, however, the opinion of G. Stainsby⁽⁴⁾ who maintains that the jelly strength is independent of the molecular weight. In fact the stiffness does not increase after a certain molecular weight is reached.

Gelatin gels are made up of two phases; one, solid, formed of a *lattice of joined micelles*; the other liquid, which lubricates the lattice and keeps it soft due to its osmotic pressure.

The lattice which has an oriented structure is made up of stacked simple chains. When a gelatin solution is cooled, the least soluble isoelectric part precipitates first, forming the skeleton of the lattice (organized period) by lateral linking of chains.

The liquid phase is made up of the degradation products of gelatin and by the calcium gelatinate which is always present in commercial gelatins. Contrary to the solid phase which has a large number of chains joined by cross links (*gel form*), the liquid phase (*sol* form), is essentially made up of single chains. From 35°C all the gelatin is converted into a sol. The intermediate systems at various temperatures below 35°C can be detected by variations in *rotatory power* which increases with the appearance of the gel form

$$T < 15°\text{C gel form: } (\alpha_D) = 313°$$
$$T > 35°\text{C sol form: } (\alpha_D) = 141°$$

It has been assumed that when a jelly is liquified, the amide groups —CO—NH— (which are in the keto form) take up the enolic form  $-\underset{\displaystyle OH}{\underset{|}{C}}=N-$.

A gelatin, precipitated with ammonium sulphate from its neutralized sodium solution, does not give jellies.

High frequency treated gelatin will not gel. Substances such as urea and guanidine also prevent gelling.

Melting point. This is the point of total conversion from the gel to the sol form by rapid depolymerization, that is by rupture of the lateral links joining the various strata.

The melting point is naturally higher with gelatins which are only slightly hydrolyzed; it indicates the purest gelatins although it gives no indication of their chemical composition, nor is it an adequate criterion of their photographic quality. It is generally about 32°C at 6% with solidifying temperature around 22°C at the same concentration.

The melting point is highest at the isoelectric point (4·7–5). We have seen that the swelling is, on the contrary, lowest at this same point; conversely there is a melting point minimum (falling suddenly) corresponding to the maximum swelling at pH 2·7. A second weak maximum occurs at about pH 2.

We would finally note that between the isoelectric point and pH 8 (slightly alkaline) the melting point varies only slightly; this is an important matter in the use of commercial gelatin.

The melting point is reduced by adding potassium salts,⁽⁵⁾ and in order of increasing effectiveness (Hofmeister series) are: sulphate < chloride < bromide < nitrate < iodide < thiocyanate.

The melting point is raised by adding to the gelatin solution small quantities of *aluminium* salts (as alum) or *chromium* salts (chrome alum). At the same time the viscosity increases but only when the solutions are relatively concentrated.

The Al and Cr salts produce complex hydrated ions which form *co-ordination complexes* with the gelatin. The reaction is slow (several days). When the carboxyl groups are esterified, the metal cannot form a complex which only seems to take place at a single point in each chain. At the isoelectric point the links are intramolecular as the chains are coiled up (para. 139).

CHEMICAL CONSTITUTION OF GELATIN

The *amino acids* are the basis of the proteins, especially gelatin. These simple groups are joined in long *polypeptide* chains which themselves polymerize to form the *simple proteins*. At a higher degree of polymerization, frequently together with other groups, the natural *complex proteins* are obtained.

258. The amino acids

The amino acids⁽⁶⁾ are compounds which possess two functions: the amino function —NH_2 and the acid —CO.OH. As the amino function is basic the amino acids are amphoteric compounds, both basic and acid.

The simplest member of the series is *glycocol* or glycine or aminoethanoic acid NH_2—CH_2—CO.OH which crystallizes in clinorhombic prisms, melting point 236°C.

In the role of acid, glycocol can give metallic salts such as silver glycocollate NH_2—CH_2—CO.OAg, and in the role of base, salts of glycocol with other acids, for example glycocol sulphate.

Among the other members of the series those usually encountered are *alanine* CH_3—CH.(NH_2)—CO.OH (a derivative of propionic acid CH_3—CH_2—CO.OH), *leucine* CH_3—$(CH_2)_3$—CH.(NH_2)—CO.OH, *isoleucine*, *serine* OH.CH_2—CH(NH_2)—CO.OH or *amino-glyceric acid*, *valine*, etc.

The molecule can have an acid group and two amino groups such as *lysine* and *arginine* or, on the other hand, two acid groups and one amino group, for example *aspartic acid* OH.CO—CH(NH_2)—CH_2—CO.OH and *glutamic acid* OH.CO—CH(NH_2)—$(CH_2)_2$—CO.OH.

An amino acid containing a cyclic nucleus generally has a constitution similar to that of *phenyl-alanine* C_6H_5—CH_2—CH(NH_2)—CO.OH. *Tyrosine* is the corresponding phenol: OH.C_6H_4—CH_2—CH(NH_2)—CO.OH.

If the nucleus is heterocyclic we have *tryptophane*, *histidine*, *proline* and *oxyproline*.

Finally there are sulphur derivatives such as *cystine* with the formula

$$OH.CO—CH(NH_2)—CH_2—S—S—CH_2—CH(NH_2)—CO.OH$$

Properties

The amino acids are crystalline solids which are generally soluble in water but insoluble in ether and the benzene hydrocarbons. They decompose when melted.

When distilled dry in the presence of baryta, they are split into an amine and carbon dioxide. Dehydrated, 2 mols. combine together to form a diketopiperazine or double cyclic amide. When suspended in acetyl chloride and in the presence of phosphorus pentachloride, they give the hydrochlorides of the corresponding acid chlorides. $RCH—(CO . Cl)—NH_2 . HCl$.

Preparation: the simple amino acids can be prepared by reacting ammonia in alcoholic solution on the corresponding chloracid, for example:

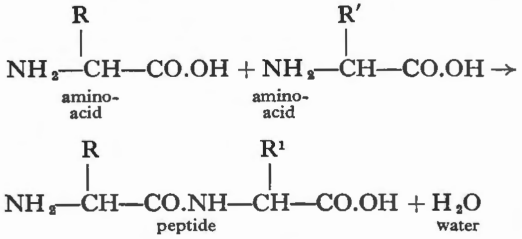
$$\underset{\text{chloracetic acid}}{Cl . CH_2—CO.OH} + \underset{\text{ammonia}}{2NH_3} = \underset{\text{glycocol}}{NH_2 . CH_2—CO.OH} + \underset{\text{ammonium chloride}}{NH_4Cl}$$

They are also obtained by the action of ammonium cyanide on the aldehydes and ketones, by reduction of the nitro or nitroso acids with aluminium amalgam in ether, or reduction of the cyano acids. Other methods consist of attaching NH_3 to ethylene acids, oxidation of amino ketones, etc.

Usually the amino acids are prepared by the hydrolysis of animal or vegetable proteins: gelatin, albumen, gluten, etc. Thus gelatin treated with boiling dilute sulphuric acid gives, on neutralizing with calcium carbonate and evaporation of the filtered liquid, crystalline glycocol. Similar treatment decomposes gluten to glutamic acid, leucine and tyrosine.

259. The peptides

The peptides are polyamides produced by the union of 2 or more amino acid molecules following the general scheme:



$$\underset{\text{amino-acid}}{NH_2—\overset{\overset{R}{|}}{C}H—CO.OH} + \underset{\text{amino-acid}}{NH_2—\overset{\overset{R'}{|}}{C}H—CO.OH} \rightarrow$$

$$\underset{\text{peptide}}{NH_2—\overset{\overset{R}{|}}{C}H—CO.NH—\overset{\overset{R^1}{|}}{C}H—CO.OH} + \underset{\text{water}}{H_2O}$$

The group CO . NH, which is the amide function, is repeated each time a new molecule is added to the peptide chain. This always has the basic and acidic characteristics due to the terminal NH_2 and CO.OH groups.

The peptides are usually soluble in water, acids and alkalis, insoluble in alcohol, decomposed above 200°C. When treated with hydrochloric acid they are hydrolyzed with the regeneration of the amino acids which make them up.

Synthesis (*a*) The union of two or more molecules of amino acids is a dehydration reaction: NH_2 and CO.OH are condensed to CO.NH with the elimination of a molecule of water. This dehydration can be carried out with phosphorus pentoxide P_2O_5 or by heating to a high temperature. In nature the peptides are produced by means of the diastases acting on the amino-acids.

(*b*) The α-halogenated acid chlorides react with the α-amino acids to give *α-halogenated amino acids*, which by the action of ammonia are converted to dipeptides. A dipeptide which is in turn reacted with an α-halogenated acid chloride, then with ammonia, produces a tripeptide, and so on. Examples: chloracetyl chloride reacts with glycocol following the scheme:

$$ClCH_2—CO.Cl + NH_2—CH_2—CO.OH =$$
$$= Cl.CH_2—CO.NH—CH_2—CO.OH + HCl.$$

By the action of ammonia the α-halogenated amino acids produced gives glycocol dipeptide

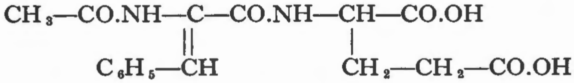
$$\begin{aligned}&Cl.CH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.OH + 2NH_3 \rightarrow\\ &\qquad \rightarrow NH_2\text{—}CH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.OH + NH_4Cl\end{aligned}$$

Similarly bromo-isocaproylglycinic acid chloride $C_4H_9\text{—}CH.Br\text{—}CO.NH\text{—}\text{—}CH_2\text{—}CO.Cl$ is converted to bromoisocaproylglycyl-glycine $C_4H_9\text{—}CH.Br\text{—}\text{—}CO.NH\text{—}CH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.OH$ which treated with ammonia gives leucylglycylglycine $C_4H_9\text{—}CH.NH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.OH$.

(*c*) The methyl ester of a simple peptide is first prepared such as diglycylglycine ester $NH_2\text{—}CH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.NH\text{—}CH_2\text{—}CO.CH_3$.

On heating, this polymerizes to pentaglycylglycinic ester $NH_2\text{—}CH_2\text{—}CO(NH.CH_2.CO)_4NH\text{—}CH_2\text{—}CO.CH_3$.

(*d*) Glutamic acid $OH.CO\text{—}CH(NH_2)\text{—}CH_2\text{—}CH_2\text{—}CO.OH$ reacts with the azolactone of acetamino-cinnamic acid $C_6H_5\text{—}CH = C(NH.CO.CH_3)\text{—}CO.OH$ in the presence of acetone and caustic soda: acetamino-cinnamoyl-glutamic acid is formed



$$\begin{array}{l}CH_3\text{—}CO.NH\text{—}\underset{\displaystyle\overset{\|}{C_6H_5\text{—}CH}}{C}\text{—}CO.NH\text{—}\underset{\displaystyle\overset{|}{CH_2\text{—}CH_2\text{—}CO.OH}}{CH}\text{—}CO.OH\end{array}$$

which can be reduced in the presence of a catalyst (palladium) to N-acetylphenylalanylglutamic acid.

The peptides are the polymers of the α or 2-amino acids. They have the general formula $NH_2\text{—}CH(R^1)\text{—}CO.NH\text{—}CH(R^2)\text{—}CO.NH\text{—} \;.\;.\;.\;.\; CH(R^n)\text{—}CO.OH$.

It is interesting to compare with these the *polyamide resins* obtained from the acids with an amino group with the seven to eighteen positions such as 10-aminodecanoic $NH_2\text{—}(CH_2)_9\text{—}CO.OH$:

$$\text{—}NH\text{—}(CH_2)_n\text{—}CO.NH\text{—}(CH_2)_n\text{—}CO.NH\text{—}(CH_2)_n\text{—}CO\text{—}$$

and with the polyamide resins similar to nylon obtained by condensing a diacid (adipic acid) and a diamine (hexamethylene-diamine) in m-cresol.

$$\text{—}NH\text{—}(CH_2)_n\text{—}NH.CO\text{—}(CH_2)_n\text{—}CO.NH\text{—}(CH_2)_n\text{—}NH\text{—}$$

260. The proteins

The proteins are *nitrogenous compounds* which are produced from the complex polymerization of the *peptides*. We have seen that the latter are polyamides in long chains whose terminal groups are amino and acid respectively.

The nature of the amino-acids from which the peptides are formed is very varied, and this gives an infinite number of combinations.

The proteins are made of a very large number of oriented or coiled peptide chains which are frequently linked together by *secondary valencies* linking certain —CO— of one chain to the —NH— of another chain. Such complex systems result in colloidal micelles. The degree of polymerization, that is the length of the chains and their number, influence the properties of the proteins; these are also dependent on the number of cross-links and their stability. X-ray examination enables the structure of the *reseau* to be deduced as with silk fibres.

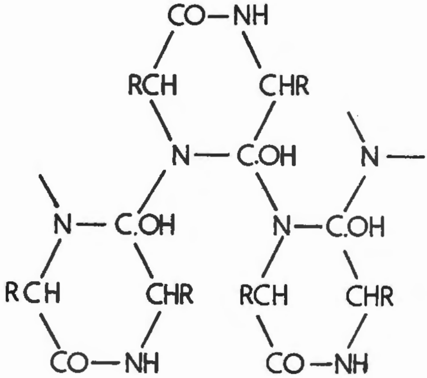
The proteins are divided into two main groups: the *holoproteins* essentially made up of amino-acids for example, the albumens, globulins and protamines; the *heteroproteins* resulting from the union of peptides with other groups such as nucleoproteins, glycoproteins, phosphoproteins. Natural proteins are, however, usually mixtures of various types.

The proteins are also classified as *linear proteins* and *globular proteins* (globulines).

The *linear proteins* have the simple or multiple chain structure molecule; they are either soluble in water at various temperatures such as *gelatin, fibrinogene* and *sericine*, or insoluble due to the presence of extra links as in the case of *ossein* (or collagen), silk *fibroine*, and *keratine* (with sulphur links —S—S—).

The *globular proteins* are made up of linked cyclic or globular nuclei. These globules frequently show no aggregation force because of the absence of negative groups on their surface, as with *albumen* and *haemoglobin*. They have, on the contrary, a tendency to aggregate with *casein* and the *phosphoproteins*, due to the presence of superficial positive and negative groups.

The globulines can be represented by structural formulae similar to the following in which the characteristic nucleus of diketopiperazine is found:



261. Hydrolysis of gelatin

When proteins are treated with an acid, a base or a diastase, they are hydrolized giving the amino-acids from which they are made. If a controlled action is carried out, only partial degradation occurs with the formation of peptides with lower and lower molecular weight.

In practice, hydrolysis is carried out with boiling hydrochloric acid, warm baryta or lime water or with bacterial, fungous, or pancreatic diastases at 55°C and a pH of 6·5–7 (for gelatin). In the case of progressive hydrolysis, the reaction is carried out with the reagents sufficiently diluted or at a sufficiently low temperature to enable the different stages to be readily controlled. The viscosity gradually drops at a fixed pH and concentration as the depolarization or degradation progresses.

The amino acids are then separated chromatographically with a column or on paper, identified with special reactions and estimated colorimetrically.(7) The choice of solvent is very important: Clayton and Strong used a mixture of 75 volumes of methyl ethyl ketone, 25 volumes propionic acid and 30 volumes of water.(8) The separation can also be carried out with an ion exchanger after preparing the dinitrophenyl derivative following the technique of Schroeder, Kay, Le Geth Honnen and Green.(9) Turner and Schmerzler identified the terminal groups of the peptides chromatographically after treatment with acetic anhydride and pyridine.(10) For the colour reactions Muting(11) recommends the use of sodium-1 : 2-naphthoquinone-4-

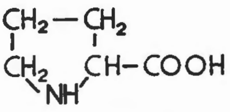
sulphonate which, on filter paper, gives characteristic colorations with 25 amino acids.

High-voltage electrophoresis (10,000 V) is another method for separating amino-acids.(11b)

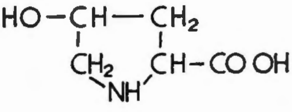
The hydrolysis and separation of the amino acids of gelatin is, however, a very critical task, and even now we have only an approximate idea of the proportion of the various elements, the figures varying somewhat between the different workers. The following list shows the approximate proportions of the amino acids compared to the lowest values found by Neuman (*Arch. of Biochem.*, 1949, **24**, 289).

	Average value	*Neuman*
Glycocol	26%	26%
Proline	15%	15%
Hydroxyproline	14%	14·1%
Glutamic acid	8%	10·2%
Aspartic acid	4·5%	5·5%
Alanine	6·5%	8·7%
Phenylanaline	1·8%	2·2%
Argenine	6·5%	8·6%
Lysine	4·5%	4·1%
Oxylysine	0·8%	1%
Serine	2·5%	3·2%
Leucine	2·3%	3·2%
Valine	1·8%	2·5%
Threonine	1·8%	1·9%
Histidine	0·8%	0·6%
Tyrosine	1·1%	0·5%
Methionine	0·8%	0·6%

We can easily see that the major part of gelatin is made up of glycocol NH_2—CH_2—CO.OH and proline or hydroxyproline.



proline



hydroxyproline

By *electrochemical reduction* of gelatin, piperazines are formed(12) which according to Koperina and Gavrilov provide the *diketopiperazine* rings.

High frequency sound has a destructive action with the liberation of ammonia and aldehydes.(13) At the same time the viscosity drops and the gelling property disappears. It is principally the protein nucleus which is ruptured.

262. Molecular weight of gelatin

Commercial gelatin is a mixture of many gelatins of varying molecular weight from 15,000 to 250,000. The distribution of these component gelatins is obviously dependent on the origin of the raw materials and the treatment which they have received. The least degraded commercial gelatins have a relatively high molecular weight, the average being about 55,000.

Fractionation of a mixture of gelatins by fractional dissolution is unsatisfactory; it is better to work by gradual precipitation for which a dispersing agent such as urea can be used. Some compounds like sodium cetyl sulphate can form addition complexes which are easier to separate. Another method is to precipitate the gelatin with alcohol (coacervation).(14) The addition of alcohol brings about separation into two layers; the lower one containing a large amount of high molecular weight material which is refractionated.

Measurement of molecular weight. This can be done by one of the five following methods.

(*a*) Estimation of the terminal groups chromatographically after reacting with fluorodinitrobenzene and hydrolysis (see Court: *Biochem. Jl.*, 1954, **58,** 70).

(*b*) Ultra centrifuging: mainly applicable to degraded gelatins.

(*c*) Determination of osmotic pressure. The gelatin is first dissolved in a salt solution, in a solution of urea or in anhydrous m-cresol (see: Pouradier and Venet: *Jl. Chim. Phys.*, 1950, **47,** 11).

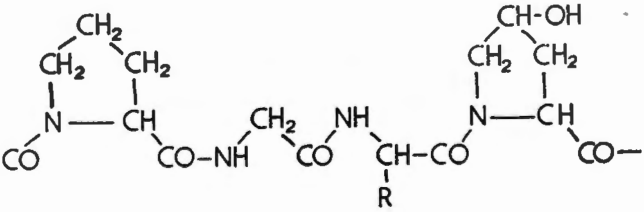
(*d*) Surface tension differences using surface active agents (see: Guastalla: *Cahiers de Physique*, 1943, **13,** 5).

(*e*) Diffusion of light (see: Signer and Mosimann: *Helv. Chim. Acta.*, 1941, **24,** 1058).

263. Structure of gelatin

Thin, dry gelatin films have a two-dimensional crystalline structure which gives them anisotropic characteristics.(15) The plane of the axes is perpendicular to the plane of the gelatin layer and is the direction of maximum elasticity.

X-ray study of the structure of gelatin shows that the peptides chains are made up of 288 amino-acid groups 0·29 mμ apart giving a total chain length of 83·5 mμ.(16) Huggins has suggested that the links are arranged in a zig-zag pattern with a *glycocol* molecule every third group, a proline or *hydroxyproline* molecule, the remainder being divided between the other amino-acids:



Each gelatin molecular chain is, furthermore, *turned-back* on itself when it is at the isoelectric point. It opens up away, from the isoelectric point. The measurements of *optical rotation*(18) have confirmed this mechanism below 36°C. It should be noted, however, that other polypeptides, natural and synthetic, also have the folded and open forms. The *infra-red spectra* of gelatin, however, are sufficiently varied(19) to suggest a particular degree of folding which is also found in the parent collagen.

Recent work by Huggins(20) has shown that the polypeptide chain of collagen is *rolled in a spiral*: each 2·86 mμ spiral having ten groups of three radicals in the order

$$R\,R'R''\,.\,R\,R'\,R''$$

where R″ represents proline, hydroxyproline, aspartic acid or glutamic acid; R R′ representing glycocol and another amino acid. Furthermore, the CO and NH groups produce, by linking —CO . . . NH—, *8-membered cyclic rings.*

264. Conversion of the collagen to gelatin

Gelatin results from conversion of the collagen which makes up the cellular material of the skin and bones (ossein). It is extracted by hydrolyzing the collagen, either with alkali (liming), with acid, with a liquefying agent such as potassium thiocyanate, urea, or with pepsin digestion. It is always finished with cooking, which by hydration separates the gelatin formed during hydrolysis.

Gelatin is formed by *rupture of the amide cross linkages* which cyclise at the same time. Furthermore, some groups are destroyed first by alkali, for example those of guanidine and arginine. These groups—α-amino, imidazol, carboxyl, guanidine—can be evaluated by a technique of Kenchington and Ward.(20b)

Collagen is formed by several constituents and several phases. The fibres are minute rigid rods 1·1 mμ diameter (5 to 7 mμ for other observers), 290 mμ long and having a molecular weight of 300,000 (20°C); they are called *tropocollagen.* From collagen, 10 to 15% of a crystallized protein existing in all living tissues—the *procollagen*—can be extracted. The substance of the fibres, which remains, is *collastromin.*(21)

Collagen is water repellent but after treatment becomes capable of absorbing 35% of its weight of water by hydrogen links.

The structure of gelatin is therefore determined by the method of hydrolysis (in the case of lime process). It is here that the variations in the isoelectric point occur.

265. Photographic gelatin

Gelatin, as we have seen, is made up of a complex mixture of many simple gelatins of different molecular weights, together with degradation products and various animal impurities. These secondary compounds have, from the photographic point of view, as much importance as the structure of the gelatin itself for they have considerable influence on the properties of the resulting emulsions.

The properties of a photographic gelatin depend not only on the treatment received during manufacture but also on the *type and origin of the starting materials:* the breed and age of the animals which provide the skin or the bones, their food, the parts used, all influence the final chemical constitution. It is therefore understandable that the preparation of two absolutely identical batches of gelatin is practically impossible.

It is difficult to *classify photographic gelatins* as they have so many properties. The physical characteristics, especially the viscosity, play an important role, but are not adequate criteria for use. An arbitrary classification based on the *redox potential*(22) can be made but this method although useful cannot give a full picture of the state of the gelatin.

The following groups of substances contained by gelatin are of interest to the photographic chemist.

(*a*) Ripening retarders.
(*b*) Sulphur sensitizers.
(*c*) Desensitizers, contrast modifiers.
(*d*) Ripening accelerators.
(*e*) Aldehydes.
(*f*) Sugars and carbohydrates.
(*g*) Fog inhibitors.
(*h*) Inorganic impurities.

Protein impurities are very numerous as the skin and bones are usually accompanied by flesh, nerve fibres, tendons, cartileges and blood. The impurities are, however, not well known as usually only traces are present.

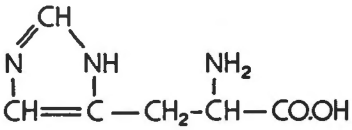
Finally, the possible presence of bacteria should be noted.(22b)

266. Ripening retarders

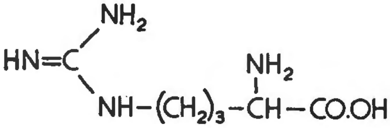
In some gelatins there are substances which retard the ripening of photographic emulsions to a greater or less degree, that is, they prevent the growth of the halide grains on heating. The retarding power of egg albumen and lead salts has been known for some time, but it was Steigmann who first drew attention to the retarding power of gelatin, and disclosed a list of artificial retarders.(23)

Among the *natural retarders* in order of increasing activity are: histidine, arginine, methionine, cystine, cysteine and glutathion. *Cystine*, which is present in gelatin to the extent of 0·1–0·2%, is about thirty times as active as methionine and 100 times as active as histidine. The cystine comes from keratine or the interfibrous protein. The amount of *methionine* is from 0·8–1%; it can be recognized after stirring its acid solution (pH 3·2–5·5) with silver chloride;(24) the filtrate which has dissolved a little halide reacts with Feigl's reagent.(25) In basic solution, the silver chloride is dissolved by other amino acids.

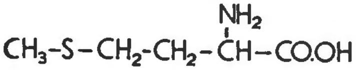
Artificial retarders. Nucleic acid contains no sulphur, its sodium salt is marketed as Inhibitor SN by P.A.C. Chemicals. Egg albumen is also used.⁽²⁶⁾ Among the other compounds which have retarding properties are thioglycollic acid, 2-mercaptobenziminazole, 2-mercaptobenzthiazole, ethyl thiocarbamate, benzotriazole, the indazoles, phenyliodium salts, etc.



Histidine

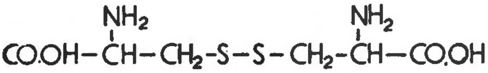


Arginine



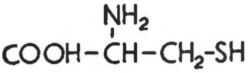
$$CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}\overset{NH_2}{\overset{|}{C}}H-CO.OH$$

Methionine



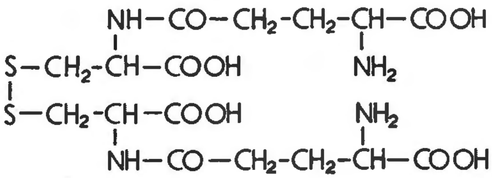
$$CO.OH-\overset{NH_2}{\overset{|}{C}}H-CH_2\text{-}S-S-CH_2\text{-}\overset{NH_2}{\overset{|}{C}}H-CO.OH$$

Cystine



$$COOH-\overset{NH_2}{\overset{|}{C}}H-CH_2\text{-}SH$$

Cysteine



Glutathion

Cadmium and thorium salts, and to a less extent, lithium and lead salts are also ripening retarders.

Lime process hide gelatins are usually rich in retarders, but not acid process gelatins. Bone gelatins are poor in them. The retarders can be eliminated in several ways as we shall see when gelatin manufacture is considered. Gelatins rich in ripening retarders are particularly necessary for the preparation of contrasty positive emulsions, especially chloride ones.

The retarders in gelatin originate from certain collagen polypeptides which are hydrolyzed by liming, these polypeptides being mainly present in the hides. Part of the inhibiting power is also due to imino groups as in proline and arginine.

To explain the *retarding mechanism*, the hypothesis has been put forward that the silver bromide is attached to gelatin via the imino groups and the peripheral Ag ions. Crystal growth is therefore retarded. It is also thought that the action of the imino groups is due to the presence of labile hydrogen. This action varies with the pH. Compounds having no imino group also form *silver complexes* similarly on the crystal surface which, by diminishing the Ag^+ concentration, slow down ripening. These compounds can be broken down by sulphur sensitizers.

The retarders can bring about desensitization of emulsions. Thus cystine, in the presence of a sensitizer, loses sulphur to give the desensitizer cysteine, and H_2S, producing fog.

267. Measurement of the retarding power

A photographic emulsion, precipitated and ripened, becomes more and more opalescent (as a function of the time and temperature) due to the growth of its crystals. With the same time and temperature, an inert gelatin enables the emulsion to ripen more rapidly than a retarding gelatin. Measurement of the *turbidity* of the test emulsion indicates the modifying power of the gelatin under test compared with the standard gelatin (Steigmann's method).

The test emulsion is often made with silver chloride as with the Amman-Brass method.(27) It is preferable to work also with silver bromide emulsions which do not always react towards retarders in the same way as chloride.

The following formula given by Amman-Brass uses cadmium chloride to give a more obvious minimum to the curves.

Stock soln.	Distilled water to	1000 cc
	Sodium chloride	35 g
	Cadmium chloride $CdCl_2 2H_2O$	12 g
Soln. 1 at 77°C	Distilled water	120—x cc
	Gelatin	x g
	Stock soln.	10 cc
Soln. 2 at 77°C	17 g per litre soln. of silver nitrate	20 cc

Eight different emulsions are prepared with the amount of gelatin x, varying from 0·75 to 15 g. Pour solution 2 (silver) into solution 1 (salts) rapidly and ripen for 32 minutes. The emulsions contain respectively 0·5, 1, 2, 3, 4, 6, 8 and 10% of gelatin.

5 cc samples taken at equal intervals are poured into 145 cc cold water and the turbidity of the resulting liquid is measured.(28) Then the *curves of turbidity as a function of the gelatin concentration* are drawn, *each curve corresponding to one ripening time.* This gives a turbidity solid formed by a *group of curves* which shows the characteristics of the gelatin.

A variation has been disclosed by Evva:(29) to a solution of 5 g of gelatin in 25 cc water add 10 cc of a solution of ($NaCl$ 10 g + $CdCl_2 . 2H_2O$ 3·5 g + H_2SO_4 (normal) 125 cc, water to 1000 cc) then 10 cc of 17 g per litre silver nitrate. Ripen for 1, 2, 4 and 8 minutes at 75°C and take 1 cc of each and dilute to 200 cc.

Inert gelatins give curves with horizontal straight lines, almost parallel and descending slightly but the interpretation is complicated in the case of active gelatins as *sulphur sensitizers and contrast modifiers interfere, also due to protective action* which gives families of curves of complex shape. The sensitizers lead to the formation of characteristic depressions marking a minimum of turbidity compared with an optimum concentration. The minimum is even more accentuated when there is little retarder. Gelatins rich in retarders and with an average sensitizer content give a family of undulating curves which drop suddenly at high concentration to a minimum; others, very active but poor in retarders give a family of well-spaced lines marked by a minimum whose location differs with the ripening time. Finally, another system of classification uses the turbidity measured as a function of the ripening time, each curve corresponding to a different gelatin concentration.

To get an even more complete picture of the characteristics of a gelatin it is necessary to work not only with the gelatin as supplied but with the gelatin washed, and filtered through active charcoal or magnesium silicate.(30) The latter especially only eliminates the true protein retarders which enables a decision to be made as to whether the modifying action of the tested gelatin is due to a pseudo retarder such as thiazolidine or the polythionates. A slowing down of ripening followed by speeding up often indicates the presence of a thiosulphate.

The presence of protein retarders shown by the turbidity test with gelatino-silver chloride must be confirmed with a silver sulphite test described below.

If this test is negative when the turbidity test is positive the presence of ripening accelerators is indicated.(31)

Silver sulphite retarder test. This test can be carried out by heating a 10% gelatin solution with 20% of 0·4% sulphurous acid and 20% ammoniacal silver nitrate. It is easier to prepare the following reagent:

17 g per litre silver nitrate soln.	30 cc
Sodium sulphite anh.	2 g
Water to	150 cc

Add 2 cc of the fresh reagent to 10 cc of 10% gelatin solution. Heat the tube for 5 mins. in boiling water. Cool rapidly and note the blackening rate of the liquid (reduced colloidal silver). In the absence of activators, the retarders prevent the solution from blackening too rapidly.

268. Gelatin sulphur sensitizers

By examining the lime liquors produced in the manufacture of gelatin, Sheppard was able to isolate an active substance, *allyl isothiocyanate*, a compound contained in mustard oil. This compound was undoubtedly a degradation product of more complex molecules.

It is certain that the natural active substances in gelatin are sulphur compounds and that their concentration is higher with shorter liming. When lime attacks collagen the main products are *methionine*, *cysteine* and *cystine*, all of which, as we have seen, are retarders: methionine $CH_3—S—CH_2—CH(NH_2)—COOH$; cystine $COOH—(NH_2)CH—CH_2—S—S—CH_2—CH(NH_2)—COOH$; cysteine $SH—CH_2—CH(NH_2)—COOH$.

It is believed that the group R—SH is characteristic of sensitizers whilst the group R—S—S—R′ desensitizes. This is the case with cystine, which desensitizes emulsions and retards ripening. However, cysteine also desensitizes, and even, in some cases, appears to be the cause of desensitizing by cystine, of which it is a half.

We can also detect, in an active gelatin, *active sulphur* and *labile sulphur*, the latter being sulphur which will combine readily with silver to give silver sulphide. The presence of labile sulphur is not in itself a sufficient guide to the sensitizing activity, as the retarders and fogging agents can also contain appreciable amounts. Furthermore, the thiosulphates and the polythionates, which some workers say are the best sensitizers, contain no labile sulphur.

Sulphur content. A photographic gelatin poor in sulphur contains at least 4 mg per kilo whilst a sulphur rich gelatin can contain 30–75 mg per kilo.

What are the sulphur compounds, contained in gelatin, which are actually active? This is a very controversial question. For instance, there is a trend to favour the *thiosulphates* and the *thionates* preferred by Steigmann. Wood has shown, with his chromatographic work⁽³²⁾ that the sensitizer is an inorganic anion which is soluble in water, or which can be converted to the soluble form by heating in alkaline medium. Wood was able to confirm this work by electrophoresis of gelatin extracts⁽³³⁾ and concluded that the active sulphur compounds are the *thiosulphates* and the *tetrathionates.*

$Na_2S_2O_3$	$Na_2S_4O_6$
Sodium thiosulphate	Sodium tetrathionate

The thiosulphates and thionates originate in the cystine (and consequently keratine and the mucoproteins) hydrolyzed by bases, and in the compounds used for depilation of the skin. One could think together with Linderstrom, Lang and Jacobsen that the thiazolidine rings in the animal proteins may be opened by hydrolysis to give mercaptans RSH, which are then converted.

Gelatins of German origin have been reputed to be artificially activated with sodium and ammonium thiosulphate, and even with ammonium polysulphide (although the latter is not a sensitizer, but a fogging agent). The amount of crystalline thiosulphate added to an inert gelatin is 40 to 300 mg per kilo. Another method which has been disclosed is to heat the gelatin solution with colloidal sulphur.⁽³⁴⁾

We would add that it is possible that the addition of thiosulphate to an inert gelatin before emulsion preparation can give interesting results, but the addition to a high-speed emulsion, during preparation, on the contrary generally produces desensitizing and results in fog. The addition of thiosulphates can only give a speed increase with certain slow emulsions.

269. Estimation of sulphur sensitizers

The low molecular weight amino-acids are soluble in a saturated solution of sodium or ammonium thiosulphate. The thiosulphates and trithionates can be separated by absorption on magnesium silicate.

Feigl's reaction. The estimation of the active sulphur with Feigl's reagent is carried out in a graduated test tube with a bent capillary tube. Ten cc of 10% gelatin solution is put in it with 2 cc of 1% borax and 5 cc Feigl's reagent with the formula

N/10 iodine	100 cc
Sodium nitride	2 g

The tube is filled with water and is closed with the cork fitted with the capillary tube. The whole is upended in the water-bath at 65°C. Nitrogen is evolved. After heating for one hour the volume of gas is measured, 0·5 cc corresponding to one Feigl unit, and standards are made using known amounts of thiosulphate.

The Feigl reaction is sensitive to pH. Furthermore, it cannot be used with gelatins containing hydrogen peroxide.(37)

Thiosulphate test.(37) 0·1 g thionine is dissolved in 50 cc ethylene glycol. One cc of this stock solution is diluted to 100 cc with distilled water. One cc of the dilute solution is added to 3 cc of the solution to be tested (filtered through activated carbon and concentrated). 0·4 cc 5N sulphuric acid is added and the tube is heated in boiling water for 8 mins. and cooled in running water for 20 mins. If the thiosulphate content is very low the solution turns from violet to blue. With a higher concentration than 1/40,000 g/mol. it is decolorized. Amounts of thiocarbamide fifty times greater than this also decolorize the solution, but without first turning it blue.

Ammoniacal silver nitrate reaction.(38) When a gelatin solution is heated with ammoniacal silver nitrate, it turns brown. The intensity of the colour enables the active sulphur content to be estimated. Fifty cc of 6% ammoniacal silver nitrate is added to 50 cc of 2% gelatin at 40°C in 15 secs. with stirring. The density of the mixture is measured over 100 hours and D is plotted against time. Ripening retarders slow down the darkening during the first 50 hours, but the density is independent of the gelatin concentration up to 30 hours.

Potentiometric titration with silver nitrate. A silver electrode is used together with a calomel electrode. The curve potential/nitrate volume is drawn. Active gelatins give an inflection point.

Estimation of labile sulphur. 'Labile sulphur' is that which combines directly with silver. It is difficult to assess the importance of this test if the natural sensitizers are thiosulphates and thionates whose sulphur is not labile, and contrary to the work of many writers, Feigl's test does not give the labile sulphur content of gelatin.

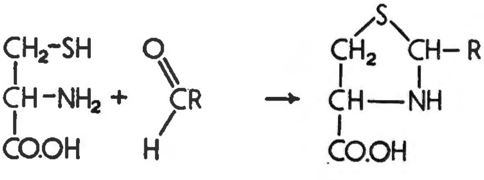
Vogel's reaction has been used to estimate the labile sulphur (formation of lead sulphide with lead acetate in caustic solution), and another method is to convert it to *hydrogen sulphide* by heating the gelatin with alkali, removing the H_2S in a current of nitrogen.(39) The latter method has been used by Sheppard and Hudson(40) in particular, the hydrogen sulphide being estimated colorimetrically with methylene blue.

Abribat(41) has worked out a simpler method, which is to digest the gelatin solution with a known quantity of ammoniacal silver nitrate (as with the method already given) and to back titrate the excess silver nitrate with a sulphur solution of thiourea or allylthiourea. The end point is determined potentiometrically with a silver sulphide electrode, or with an opacimeter.

270. Desensitizers and contrast modifiers

Some compounds found in the liming liquors have the property of desensitizing negative emulsions and increasing the contrast of positive ones depending on the speed.⁽⁴²⁾ They are also found in acid process hide gelatins from which they can be extracted with saturated sodium sulphate solution.

A characteristic type of contrast controlling compound is *thiazolidine-4-carboxylic acid*, which can result from the action of an aldehyde on cysteine.



Cysteine Aldehyde Thiazolidine-4 carboxylic acid

However, the retarders are themselves desensitizers.

Steigmann⁽⁴³⁾ prepared the following derivatives, which are also fogging agents:

(*a*) Seventy cc of 1 : 1000 solution of the sodium salt of cystine + 30 cc 1 : 1000 glyoxal (pH 9) are heated to 90°C and the pH of the solution is then adjusted to 4·5 by adding acetic acid.

Fifty to 100 cc of this solution per kg gelatin increases the contrast of silver chloride emulsions and fogs emulsions containing gold salts.

(*b*) 0·6 g glucosamine hydrochloride and 0·2 g cysteine hydrochloride in 20 cc water (pH 12). Boil until the solution turns brown. Adjust to pH 4·5 with acetic acid, dilute to 40 cc, and 1 g active charcoal and filter. Use 10–25 cc per kg gelatin. The contrast modifying substances give a characteristic reaction with palladium chloride.

271. Ripening accelerators

We have just seen that the aldehydes react with cysteine or cystine, giving thiazolidines which can produce fog. Ripening accelerators can be present in gelatin, and are also fogging agents. Their presence is indicated by an unusual susceptibility to traces of thiosulphate, giving a loss in speed together with fog. As an artificial accelerator, the copper salt of *pseudothiohydantoin* is very active.⁽⁴⁴⁾

Silver halide solvents: thiourea, thiocyanates, thiosulphates are ripening accelerators.

A long list of ripening accelerators for polyvinyl alcohol emulsions has been established by Oh-Yama and Futaki (para. 338).

272. Aldehydes

Photographic gelatin contains 3–15 g per kg of aldehydes. The aldehydes result from the degradation of the mucopolysaccharides. The main aldehyde seems to be similar to reductone CHOH = C . OH—CHO,⁽⁴⁵⁾ which is itself decomposed to formaldehyde and glycolaldehyde or a derivative (in acid process, the formation of the latter negligible). Besides, the presence of an α-acid ketone, such as *pyruvic acid*, has been observed.

The gelatin aldehydes may be fixed to the chain by a labile link.

The mucopolysaccharides which provide the aldehydes are decomposed on liming or by an enzyme, hyaluronidase, to proteins, amino sugars and glycuronic acid. Steigmann(46) has shown the presence of hydroxymethyl-furfuraldehyde which is produced from the latter, themselves formed by bacterial action on hyaluronic and chondroitine-sulphuric acids contained in the skin, cartilage and certain bones.

Detection of the aldehydes. It is carried out *with 2-thiobarbituric acid* or *1 : 3 : 5-triphenyl-tetrazolium chloride.*

Dissolve 1 g 2-thiobarbituric acid in 180 cc glacial acetic acid. Heat until a slight yellow colour appears.(47) Leave and add 20 cc water. For the test, take 1 g powdered gelatin and 5 cc of reagent. Allow to swell for 15 mins. and heat for 30 mins. in boiling water. A coloration from yellow-brown to red is produced. The solution can be diluted to 20 cc, centrifuged, and the transparency measured.(48) It is compared with the colour given by a solution of freshly distilled furfural in 10% acetic acid.

The colour formed by the action of 2-thiobarbituric acid on gelatin has five absorption bands at 390, 455, 495, 535 and 555 mμ.

Triphenyltetrazolium chloride reagent. Dissolve 0·25% in 0·4% caustic soda.(48b) Take 5 cc for 0·5 g gelatin: a red colour is observed after one hour at 20°C, if aldehydes are present.

The aldehydes can also be detected by Schift's test with fuchsine (water 500 cc, basic fuchsine 0·1 g, potassium metabisulphite 2 g, N hydrochloric acid 8 cc, hydrosulphite 0·2 g): 0·5 g dry gelatin for 5 cc reagent—becomes red after two hours, purple with pigskin gelatin.

For *paper chromatography*, with iodine treatment, see (48c).

273. Sugars and carbohydrates

Collagen contains more sugars and various carbohydrates than gelatin—about 1%. These sugars are present as impurities and may cause the colour of gelatin. They can be estimated colorimetrically after heating to 180°C in acetic acid, or by reacting with orcinol.(49)

Acid process gelatins contain more sugars and carbohydrates than lime process ones.

Fats. Gelatin can contain several decigrams of fats per kilo. Extraction with petroleum ether is ineffective, as part of the fat is present as calcium soaps. The best method of extraction is that of Abribat.(49b) This is to saponify the fats and to liberate the corresponding acids. These are then removed by adsorption on calcined alumina.

274. Fog inhibitors

Kameyana(50) prepared gelatin extracts, starting with a wide variety of hides, which had a pronounced anti-fogging action. He was able to concentrate the active material, but could neither isolate nor identify it. However, it appeared to be a nitrogenous substance, probably containing sulphur. The gelatins which were richest in this material were obtained from calves and small animals. A prolonged, but not excessive, liming increases the inhibiting power, but it is reduced by washing and destroyed by excess acid. Treatment with washing waters increases it. The active substance is stable between pH 4·7 and 6·8. It is completely absorbed by active charcoal in acid medium.

275. Gelatin examination

The gelatin to be studied is first treated with sodium sulphate to remove the active agents: 100 g powdered gelatin is added to 300 cc of saturated sodium sulphate at 55°C. After digesting for 20 mins., the solution is decanted, and the gelatin is put into a press; the extract obtained is mixed with the decanted solution. Two g magnesium silicate is added (if the gelatin is a lime process one) and the extract is filtered. The following tests are then made:

(*a*) Add 3 cc palladous chloride reagent(52) to 5 cc of the extract. Heat the tube for 5 mins. in boiling water, then add 2 cc 5N ammonia. These reactions can take place:

Dark brown precipitate (PdS): presence of thiosulphates and polythionates.

Pale yellow coloration: presence of cysteine and thiazolidines.

Slight brown coloration on prolonged heating after adding ammonia: presence of thiazolidines only.

(*b*) Add 3 cc fuchsine reagent(53) to 5 cc of the extract, then 2 cc of cold saturated mercuric bromide solution:

Violet precipitate after more than two hours: traces of thiosulphates.

Purple to blue-violet coloration without mercuric bromide: presence of thiols, if the solution is again decolorized with palladous chloride.

Silver nitrate–methylene blue test:(54)

Gelatin—10% soln. at 40°C	5 cc
Ammonia—·880 + 3 vol. water	0·5 cc
Silver nitrate N/10 (17 g/l)	1 cc
Methylene blue 1 : 5,000	1 cc

Expose the solution to sunlight for 5–10 mins.

No decoloration: Inert gelatin containing $1/10^5$–$1/10^6$ thiosulphate.

Decoloration: Inert gelatin.

Decoloration and formation of brown colloidal silver: active gelatin.

Ammoniacal silver nitrate test. The gelatin solution is heated for 30 mins. in the boiling water bath after adding silver nitrate containing enough ammonia to redissolve the precipitate.

Strong reduction of nitrate: gelatin has a tendency to fog.

Weak reduction of nitrate: contrasty gelatin.

276. Inorganic compounds in gelatin

Estimation of chlorides. The chlorides can be estimated by three principal methods:

(*a*) Burning, and estimating the Cl in the ash.

(*b*) Hydrolysis with hot concentrated nitric acid then precipitation with silver nitrate (gravimetrically, nephelometrically or back-titration of excess silver).

(*c*) Precipitation with silver nitrate, then hydrolysis of the gelatin.(55) AgCl is dissolved in ammonia and titrated with a standard solution of thiourea.

Test for nitrates.(56) First prepare the following reagent: 1 g carbazol and 1·4 g dimethylglyoxime in 100 cc hot isopropyl alcohol. Add 0·2 cc of reagent to a solution of 3 cc concentrated hydrochloric acid and 0·5 cc of guanidine carbonate or arginine hydrochloride, then five drops of the solution of gelatin to be tested. Heat for 20 mins. in boiling water. Traces of nitrates are shown by a pale blue colour.

Conversely, the presence of arginine and guanidine can be checked the same way.

Estimation of sulphur dioxide. The presence of sulphur dioxide, SO_2, in gelatin retards or prevents an ammoniacal solution of argentisulphite containing excess hypo from turning brown. To 100 cc of 15% hypo add 20 cc of 10% ammoniacal silver nitrate. Take 2·5 cc of this solution and add to 10 cc of 15% gelatin. Heat for 30 mins. in boiling water and observe for brown coloration.

To estimate the SO_2, one of the three following methods can be used:

(*a*) Distillation of the SO_2 in the presence of chloroform, in a current of CO_2. The SO_2 is collected for an hour in water, and is estimated with iodine, permanganate or excess hydrogen peroxide.(57)

(*b*) Put 75 cc water, 25 g gelatin and 25 cc dilute H_2SO_4 in a flask with a long neck with a right-angle bend and an opening in the bulb for steam. Connect the flask to a conical flask via a condenser. Put 20 cc of water in the conical flask and steam distil until 100 cc of distillate has been collected. Titrate with N/20 caustic using methyl orange.(58)

(*c*) Heath 15 g gelatin in 150 cc water with 2·5 cc phosphoric acid.The air is expelled with CO_2. 100 cc of distillate is collected in a flask containing 12·5 cc N/20 iodine. Concentrate to 32 cc after adding 2·5 cc hydrochloric acid. The solution is then filtered, brought to the boil and 5 cc N/5 barium chloride is added. The barium sulphate is determined by the usual method.

Estimation of iron. Iron can be detected by coloration of p-phenylenediamine and hydrogen peroxide in strongly acid solution.(59) The same reaction in ammoniacal solution indicates copper.

A colorimetric method is to treat the gelatin, previously dried at 110°C, with concentrated sulphuric acid and 30% hydrogen peroxide. After the organic material is decomposed it is taken up in hydrogen peroxide and excess potassium thiocyanate is added. The colour is compared with that from a standard solution of ferric sulphate.(60)

Estimation of zinc, lead and copper. Zinc gives a red coloration with dithiazone (or dimethylthiocarbazone) in chloroform solution which enables a colorimetric estimation to be made with gelatin ash. Burning must not be carried out above 450°C, and also, if other metals are present they must be converted to complexes by extracting in the presence of thiosulphate.(62)

A more accurate and simpler method of estimating zinc, copper and lead in gelatin is to use a *polarograph* as worked out by Michel and Maron.(63) Twenty-five g of gelatin is ashed at 450°C, and the residue is dissolved in 5 cc of 6N . HCl. Distilled water is added and the pH is brought back to 2·5–3 (thymol blue indicator) with 4N caustic potash. The solution is made up to 50 cc and analysed for copper, lead and zinc with the polarograph.

The method given by the British Standards Institute(64) involves the precipitation of the metals with ferrous sulphide. The lead is estimated colorimetrically as the sulphide; the zinc by precipitation with 8-hydroxyquinoline and copper as the diethyldithiocarbamate or the pyridine complex.

Estimation of Ca, Ba, Al, Mg and Ag in the ash is done by normal analytical methods.

The arsenic can be detected by spotting on mercuric bromide paper, developed in potassium iodide. Its estimation is important for food gelatins.

MANUFACTURE OF PHOTOGRAPHIC GELATIN

277. Raw materials

Photographic gelatins are prepared from *calf skin* or *bones.* They have different properties depending on the raw materials used in their manufacture.

To obtain pure, well-defined and consistent batches of gelatin selected parts of skin and bone completely free from adhering flesh must always be used. For obvious reasons these conditions are not always complied with and to some extent, therefore, commercial gelatins are variable. This leads to difficulties in preparing photographic emulsions of definite properties.

Hides. The hides used for preparing photographic gelatins are calf hides. Kid, rabbit, dog, shark, whale and other skins have also been used or tried. Usually the waste from the tanneries are used as raw materials; these are not the best parts as they include the head, ears, hooves and certain parts of the stomach. The cartilage must be removed as this is converted to *chondrine,* a substance similar to gelatin but having an intense fogging action, and which brings about the rapid coagulation of the latter with chrome alum.

The hair is removed from the tannery scraps with sodium sulphide and chalk. This must be removed by *washing,* preferably slightly acid, together with the sodium chloride used as a preservative by the slaughterhouse.

If the hides are fresh, it is better to remove the hair after pre-liming in 6° Bé. milk of lime for a few days, followed by washing.

The selection of skins is still a purely empirical operation.

Bones. The bones come either from the slaughter-houses (red bones) or ready prepared, and in large quantities from South America and India. The Indian bones which are naturally cleaned and bleached are preferred. Another source is the scraps from button manufacturers. Ten to twelve parts of bone are needed for one part of gelatin.

Bones are mainly composed of *ossein* and tricalcium phosphate: 18% ossein—more from calf head bones—and 71% inorganic matter plus 8% water. The inorganic matter is made up as follows:

Tricalcium phosphate	85%
Calcium carbonate	10%
Magnesium phosphate	1·5%
Calcium fluoride	0·3%
Calcium chloride	0·2%
Other compounds	3%

The sorted bones are first crushed, degreased with trichlorethylene, sifted to remove the tendons and scrubbed with water. They are then *acidified* in 3–6° Bé. hydrochloric acid (for 2–3 weeks or more at 10–15°C) which dissolves the tricalcium and monocalcium phosphates. The gradual demineralizing is followed visually by examination of the texture of the material.

Acidification with sulphurous acid has the advantage of attacking the ossein less.

The bones in which the ossein remains are washed in running water for liming.

278. Liming

The washed skins and ossein are treated with *milk of lime* which hydrolyzes the collagen and solubilizes the other materials, fats, albumens, mucoids, elastine. The action of the lime is due not only to its alkalinity but also to the activity of the Ca ions.

The skins are plunged into 4–8° Bé. milk of lime for two days, then rinsed in batched for 3–8 weeks, at a temperature of 3–12°C.

The bones are limed in vats in milk of lime, 0·8–2° Bé., which is frequently renewed. At the end of the treatment it is reduced to 0·5° Bé. The liming time varies with the temperature and the concentration; it varies from 1–3 months.

The end of liming is judged by touch. A knife should readily pass through ossein. A more precise method is to estimate the tyrosin, which is completely extracted in the waters.

Liming is the most important stage in the manufacture of gelatin. It determines the structure of the gelatin. High temperatures must be avoided (maximum 12°C) as must too long a duration which can cause degradation which produces fogging agents.

Pure gelatins for slow emulsions are preferably obtained at very low temperatures (3–5°C) and for a relatively short time, 2–4 weeks. *Active gelatins* for fast emulsions are obtained between 5 and 12°C for 5–8 weeks depending on the temperature. An optimum time must not, however, be exceeded as beyond it there is a loss of sensitivity.

Samples must be removed at regular intervals and converted to gelatin under fixed conditions.

Reduced liming. Preliminary scalding, by swelling the collagen and removing certain cohesive forces or apolar links (called Van der Waals' forces), enables liming to be shortened.

Another method used by Kincl and Potnis(66) is to treat the collagen first in a solution of 0·1 M calcium chloride for 14 hours. After 4 hours washing, 6 days liming is enough with 3° Bé. milk of lime.

The yield decreases when the concentration of $CaCl_2$ is increased beyond 1·25 M.

279. Neutralization

The limed collagen is washed in running water and then treated in an acid bath to neutralize and dissolve all the lime (to pH 5–7). It ends with a final wash in pure water.

The acid used can be *hydrochloric*, *phosphoric* or *sulphurous*. Concentration: 1–2%, average time 12–24 hours. The neutralization must be neither incomplete nor exceeded.

280. Cooking

Only the cooking shows the chemical effect of liming. At its best it can be considered as a physico-chemical hydration action.

Cooking must be carried out at a *relatively low temperature* to avoid degradation by hydrolysis (rupture of the normal chains).

The mass is broken up and heated in water with agitation. The operation is repeated four or five times giving extracts whose quality drops with successive extractions. Only the first three extracts are suitable for photographic use. These extracts can be mixed but it is better to group them separately. When the temperature of cooking is very low, only the readily hydrated, slightly polymerized fractions are attacked which gives low melting point gelatins.

Photographic gelatin	1st extract at	60– 70°C	3 hrs.	gelatin conc. 8%
	2nd ,,	70– 80°C	3½ hrs.	—
	3rd ,,	80– 85°C	4 hrs.	—
Glue	4th ,,	85– 90°C	5 hrs.	
	5th ,,	90–100°C	(optional).	

The pH is kept between 5 and 6 for the complete duration of cooking. *Concentration is not necessary* except for the glue which is evaporated at reduced pressure. Similarly only the last extracts are clarified (by forming a precipitate which carries down the impurities using albumen or aluminium sulphite and lime salts).

Some manufacturers add, before or after cooking, a small quantity of sulphurous acid as a preservative (15 l. of saturated solution for 500 kg gelatin).

Filtration on a cellulose bed keeps back the ossein residues and the coagulated substances, also traces of fat. The cellulose paste is regenerated by boiling in an alkaline solution.

Gelification. The gelatin solution is set on an endless belt made of stainless steel and dried on metal grids or cotton nets until a maximum moisture content of 15% is reached. The jelly can also be noodled before drying.

Photographic gelatin is generally sold in small flakes produced when the sheets are broken up, more rarely as a powder.

Many runs are mixed by the manufacturer to make batches of several tons.

281. Acid process gelatin

The hydrolysis of the collagen can be carried out just as well by acid treatment as by basic treatment. Acid treatment has the great advantage of being much faster. However, the properties of the gelatins produced in this way differ greatly from those produced by liming, as they contain a large number of intact amide groups. Furthermore, the free or liberated proteins are not dissolved and remain in the mass. The *isoelectric point* of acid processed gelatins is at a pH between 7 and 9 instead of 5. With pigskin which is usually treated this way the i.p. can reach 8·2. We have already noted that by greatly prolonging the acid treatment the i.p. can be reduced to 4·8.

Acid treatment of hides is carried out in 3% hydrochloric acid for 24 hours. The excess acid is eliminated by washing and the gelatin is extracted by cooking at a pH of about 4.

282. De-activation of gelatin

Gelatin is de-activated to make it inert from the photographic point of view, that is, to eliminate or destroy the sulphur compounds, the retarders, and the desensitizers or fogging agents. Many methods have been disclosed to do this. The choice of the raw material is also important: gelatin prepared from hard bones, with extended liming is naturally more inert than hide gelatin.

A. *De-activation by prolonged washing*, eliminates part of the sulphur sensitizers and a small proportion of retarders. The action of washing is more effective if the water is made slightly ammoniacal. Irregular results.

B. *Treatment with active charcoal* at a pH of 4–4·5, or better, with a mixture of carbon and kieselguhr (Steigmann).

The sulphur sensitizers are eliminated together with the cysteine and the thiazolidines; but the retarders still remain.

C. *Treatment with inorganic absorbers*, such as tricalcium phosphate (retarders) or magnesium silicate (retarders and proteins). Activated alumina removes the arsenic.(67)

D. *Extraction with sodium sulphate* in a saturated solution or 10% sodium chloride, of powdered gelatin. The retarding proteins dissolve. They can be extracted, following Steigmann's process, by precipitation with 5% zirconyl basic sulphate (Zircotan N— Rohm and Haas). The precipitate is then ground up in 1% soda solution which dissolves it.

E. *Treatment with ion exchangers* (cations plus anions). The gelatin is *demineralized* and at the same time loses its retarders and some of the sensitizers.

F. *Oxidation treatment* with hydrogen peroxide.(68) It has also been proposed to use calcium hypochlorite, bromine water(69) and sodium peroxide. The excess oxidizing agent is destroyed with SO_2. The after ripening of the emulsion and the appearance of fog are retarded but not suppressed. The writer has observed that, contrary to certain indications in the literature, fogging substances are not destroyed by hydrogen peroxide.

G. *De-activation with powdered metals*,(70) such as Ni, Co, Pb, Pt.

H. *De-activation with silver salts.*(71) Silver nitrate is added to the gelatin before emulsification to 'block' the sensitizers. The amount of silver nitrate necessary is equal to ten times the weight of sulphur present in the gelatin. Yellowish colloidal silver sulphide is formed. Amman-Brass has modified the process using a silver chloride thread 0·07 mm in diameter. The tangled mass of threads is kept for 30 mins. in the gelatin solution. The retarders are not affected.

The mass of AgCl thread is obtained by the action of chlorine water on silver thread.

283. Demineralization of gelatin

We have seen that gelatin solution can be demineralized by treatment with an ion exchanger: Permutit or synthetic resins.(72)

The calcium is substituted by sodium in the first case. All the cations are replaced by hydrogen in the second.

The calcium can also be dissolved and eliminated by a 12-hour wash in water containing carbon dioxide.

Cooling a 0·5% gelatin solution to 15° flocculates the isoelectric fraction. After centrifuging, calcium gelatinate remains in solution. The isoelectric gelatin obtained in this way contains less than 0·026% ash.

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Chapter XVIII

GENERAL PRINCIPLES OF EMULSION PREPARATION

284. Formation of photosensitive silver halides

The crystals of silver bromide, AgBr, are formed by the action of *silver nitrate* $AgNO_3$ on an alkali bromide—potassium or ammonium bromide—in a *gelatinous solution.* Whilst the Br^- and Ag^+ ions precipitate together, an equivalent amount of soluble alkali nitrate is formed.

$$\underset{\text{Silver nitrate}}{AgNO_3} + \underset{\text{Potassium bromide}}{KBr} \rightarrow \underset{\text{Silver bromide}}{AgBr} + \underset{\text{Potassium nitrate}}{KNO_3}$$

Silver chloride is similarly precipitated when silver nitrate is reacted with sodium or ammonium chloride.

As a general rule, the silver nitrate solution is poured into the solution of gelatin and bromide (which may include a small proportion of *potassium iodide*). To prepare silver chloride, either the silver nitrate solution is added to the alkali chloride, or the chloride may be added to the silver.

Whatever the method, an *excess of alkali halide must be used.*

The quantities of the reactants are readily calculated from their molecular weight:

$AgNO_3$: 170	AgBr: 180	AgCl: 143·5	AgI: 235
Ag: 108	KBr: 119	NaCl: 58·5	KI: 166
	AmBr: 98	AmCl: 53·5	

This shows, for example, that 170 g of silver nitrate, containing 108 g silver, requires 119 g of potassium bromide to give 180 g of silver bromide.

One g of silver nitrate corresponds to 0·7 g KBr, 0·58 g AmBr and 0·98 g of KI. It gives, respectively 1·1 g AgBr, 1·38 g AgI and 0·63 g Ag.

In practice, 1 g KI replaces 0·7 g KBr or 0·6 g AmBr. The *function of the iodide* is to modify the emulsion's characteristics, particularly by increasing the sensitivity. The amount necessary rarely exceeds 5% for negative emulsions. It is much less than this for positive ones.

The silver halides crystallize in the *cubic system.* They are found as *hexagonal tablets,* often reduced to triangles (Fig. 2), or as *cubes with rounded peaks* (Fig. 45). The tablets are formed by precipitation in neutral or acid solution, the cubes with ammonia.

285. Silver bromide without protective colloid

Tablet crystals of silver bromide with no protective colloid can be obtained by evaporating an ammoniacal solution of silver bromide. These crystals are relatively large—10 to 40 μ and can be used for studying the action of light.⁽¹⁾

Gelatin-free plates can also be obtained by sedimentation on a layer of rubber from a suspension of silver bromide.⁽²⁾ The images obtained by developing such plates are grey, weak and of low contrast. By adding 0·1% gelatin to the suspension, the reduced silver assumes the normal black colour. The influence of the gelatin is very definite.

Another method is to grind up silver bromide containing 0·001% Ag_2S and up to 5% AgI, fused at 430°C, in an atmosphere of 95% nitrogen and 5% oxygen. The resulting product can then be dispersed in gelatin.⁽³⁾

Loening⁽⁴⁾ has studied the behaviour of silver bromide sols.

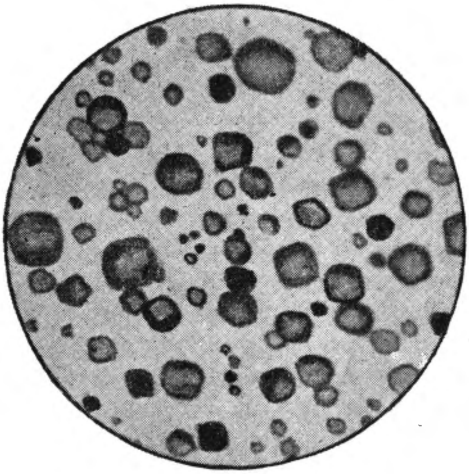

FIG. 45. Silver bromide crystals (ammoniacal emulsion); compare with Fig. 2.

286. Mechanism of precipitation

The precipitation of the silver halide is the most important stage in the preparation of an emulsion. On it depends the future behaviour. It is also the most critical process to operate, for it is most subject to a large number of factors which are difficult to control.

According to classical theories, a mixture of alkali iodide, bromide and chloride is first supposed to give a precipitate of silver iodide, then of bromide and lastly of silver chloride, because the iodide is the least soluble of the three halides:

Silver iodide: 10^{-8} mol. per litre (0·0025 mg).

Silver bromide: 5×10^{-7} mol. per litre (0·9 mg). Gledhill and Malan⁽⁵⁾ found the solubility to be one-fifth of this.

Silver chloride: 10^{-5} mol. per litre (1·5 mg). Davies and Jones⁽⁵ᵇ⁾ found the solubility $1{\cdot}334 \times 10^{-5}$ mol. per litre at 25°C and the solubility product $1{\cdot}765 \times 10^{-10}$.

The silver halides are, however, much more soluble in the *alkali halides, present in great excess at the beginning of precipitation*, which changes the data of the problem, for complex salts are formed whose constitution is dependent on the concentration of soluble halide. These complexes are of the form $[Ag_nBr_m]^{(-)(m-n)}$, for example $[AgBr_3]^{--}$ and $[AgBr_5]^{----}$. Chateau and Pouradier(6) have verified that in the presence of a mixture of supersaturated halide silver salts, the *mixed crystals are precipitated from the start*. However, the first crystals contain most of the iodide and are of the hexagonal type. The following, with a lower iodide content are cubic. The first ones take part in the formation of the later ones, and are changed, perhaps bringing about dislocations in the crystal lattices.

The formation of mixed crystals is favoured by a low concentration of soluble halides. It is inhibited by the presence of neutral salts with polyvalent ions such as Al^{+++}. Chateau(6b) has deduced certain rules for the operation of silver analyses, for which mixed crystals are a source of error: stop the titration before the first end point; boiling and cooling before finishing the operation.

By using the radioactive isotope Ag^{111}, Jonte and Martin(7) were able to study more closely the complex solutions of silver chloride. They were led to the conclusion that there are *non-ionized* AgCl molecules in solution. It had already been shown that several types of centre are formed in the same operation, and that they are not all equally effective in bringing about crystallization. As the most active centres are rapidly used, the crystallization rate is changed. Loveland and Trivelli said that fractions of particular dimensions correspond to particular types of centre, controlled by the Laplace-Gauss law, which explains the anomalies in the grain size distribution curves.

The unstable state of the Ag^+ and Br^- ions during the supersaturation period means that the equilibrium will easily be disturbed by external factors, particularly variations in temperature, degree of agitation and type of agitation. It should also be understood that the slightest change in concentration during the course of precipitation has repercussions on the emulsion characteristics.

Kolthoff has put forward the hypothesis that the first crystals which are formed are spongy, and that having a large contact area they redissolve giving rise to smaller compact homogeneous crystals.

In fact, the faces having a rapid rate of growth, in the circumstances the [100] faces of the octahedral AgBr crystals, disappear to the benefit of the [111] faces which grow more slowly. If growth takes place primarily in two dimensions, tablets which are hexagonal, or may appear triangular, are formed.

The silver halides crystallize in the cubic system with offset faces, that is, in octahedra. The faces of the cube contain both the Ag^+ and X^- ions, whilst the octahedron faces only have one or the other.(8) The former, which are less strongly charged, grow more slowly than the latter, which attract ions with opposite charge strongly. The growth of the crystals depends on the concentration of silver ions; it becomes more rapid as the silver ion concentration falls. This is explained by the fact that at low Ag^+ concentrations the silver complexes are readily dissociated, and consequently provide a regular source of Ag^+ ions.

Precipitation in ammoniacal medium. The emulsions known as ammoniacal are prepared by adding a solution of ammoniacal silver nitrate to a gelatin solution of alkali bromide.

The ammoniacal silver nitrate is obtained by pouring ammonia into a silver nitrate solution; a brown silver hydroxide is formed first, which readily redissolves by adding just enough excess ammonia. Argentoammonium complex ions are formed: $[Ag(NH_3)_2]^+$ and $[Ag(NH_3)_3]^+$.

These ammonium complexes reduce the potential barrier which surrounds each precipitation centre and each crystal. They therefore bring about a more intimate contact between the Ag^+ and Br^- ions. Crystal growth therefore takes place in a more regular way, in three dimensions. This results in the grains having the form of cubes with rounded peaks and with similar dimensions, which has the effect of giving high contrast emulsions.

Adsorption of gelatin. A thin layer of gelatin is adsorbed to the surface of the silver halide crystals. During crystal growth, this envelope is enlarged like a growing cellular bag.

The gelatin layer surrounding each grain is only attached by a few active groups, the majority of the hydrophilic groups ($—CO.OH$ and $—NH_2$) remaining in contact with the liquid. It is not very probable that there are two layers of gelatin joined by their hydrophobic groups.

The adsorbed gelatin cannot be removed by washing. For 1 g of silver bromide, 1–3 g is found,(9) the layer thickness being in the order of 28 Å. If the surface gelatin is removed with hypobromite(10) the residual gelatin can be recovered, after dissolving the bromide in hypo, by concentration. Davis in this way found 0·5 microgram of gelatin per gram of silver salt.

287. Precipitation methods

A precipitate of silver iodide, bromide or chloride formed in a solution of the corresponding alkali halide *adsorbs* the excess negative ions I^-, Br^- or Cl^-, to form an equilibrium electric system with the positive metal ion. For example, with silver chloride, precipitated in potassium chloride, a system will be formed represented by

$$AgCl\,.\,Cl^- \,\vdots\, K^+$$

An ionizable dye, such as fluorescein, added to this medium, will retain its original yellow colour, for the negative fluorescein ion will remain free. This continues until the precipitation of silver chloride by silver nitrate is complete. But as soon as an excess of silver nitrate is present, the silver chloride does not adsorb the Cl^- ions, but the positive Ag^+, to give $AgCl\,.\,Ag^+$ which carries with it the negative organic ion: $Ag\,.\,Cl\,.\,Ag^+ \,\vdots$ fluorescein$^-$.

The colour of the dye changes immediately; from yellow it becomes pink, indicating the completion of precipitation.

Similar phenomena are observed when silver bromide is precipitated in the presence of eosin, or silver iodide in the presence of eosin or fluorescein.

Conversely, a silver solution can be titrated with potassium bromide in the presence of Rhodamine 6G as indicator.(11)

The adsorption of halide ions ($^-$) by the resulting precipitate becomes stronger as the concentration of soluble halide is increased. The result of this is that the higher this concentration, the more compact the precipitate due to a very rough texture.

It is, in fact, easy to show that the globule of silver bromide, precipitated in contact with a drop of silver nitrate in a gelatinous solution of ammonium bromide (in excess) breaks up with more difficulty as the bromide solution becomes more concentrated. A very dilute solution, on the contrary, gives a precipitate which disperses easily with simple agitation into a homogeneous milky suspension.

We have made the following tests: to 3% gelatin solutions kept at 38°C (100°F) we added, respectively, increasing amounts of ammonium bromide, then to each test solution, one drop of normal silver nitrate solution, and we noted the ease with which the resulting silver bromide globule was dispersed:

100 cc of 3% gelating solution to which the ammonium bromide was added, followed by one drop of silver nitrate.	1 g NH_4Br	Rapid dispersion.
	1·8 g ,,	Fairly rapid dispersion.
	2·8 g ,,	Dispersion by agitating.
	3·7 g ,,	Flocculation when agitation stopped.
	4·6 g ,,	Vigorous continuous agitation.
	7·4 g ,,	Flocculation despite agitation.

The same experiment was tried with 1% gelatin solution, giving the following results:

1% gelatin solution to which ammonium bromide, then one drop of silver nitrate is added.	0·5 g NH_4Br	Flocculent ppt. dispersing rapidly.
	1·0 g ,,	Less rapid dispersion than in the first experiment, accelerated by agitation.
	1·8 g ,,	Compact ppt. only dispersed with vigorous agitation.
	2·8 g ,,	Compact ppt. dispersed with extremely vigorous agitation.
	3·7 g ,,	Total dispersion difficult.

A high *gelatin* concentration therefore favours dispersion by forming floccular globules. With 1% gelatin, the emulsion becomes difficult to prepare.

A high *temperature* also favours dispersion. With 1% gelatin containing 1% ammonium bromide, a very compact precipitate of silver bromide is formed at 25°C, which only breaks up with agitation, whereas at 50°C the precipitate is light, and disperses without agitation.

On the other hand, the product which is precipitated and dispersed at a low temperature is more transparent, indicating finer grain.

The addition of *potassium iodide* to the bromide solution increases the compactness of the precipitate.

Ammonia, on the other hand, considerably facilitates its dispersion, by forming a very loose-textured precipitate, the Br^- ions adsorbed by the AgBr being neutralized and displaced. Thus with 1% gelatin and 3·7 g bromide a flocculent precipitate is obtained without ammonia, but this disperses immediately in the presence of the latter. The speed of dispersion increases with the amount of ammonia.

The speed of dispersion of the silver bromide precipitate also increases with the dilution of the *silver nitrate* solution.

Conclusions

(*a*) The precipitation of the silver bromide must be carried out at high temperatures when a neutral solution is used, and at a moderate temperature in ammoniacal solution, the temperature being lower as the ammonia concentration is raised.

(*b*) The precipitation temperature must be higher as the gelatin concentration is reduced and the iodide concentration is raised.

(*c*) Neutral precipitation in dilute gelatin, or with concentrated solutions requires more vigorous agitation.

(*d*) Neutral emulsions can be prepared at relatively low temperatures without forming a 'curd' by adding the alkali bromide at the same time through separate jets, so that there is always a slight excess of bromide, as constant as possible, which should never exceed a given limited value.

(*e*) The *topographical distribution of the grains* depends on the precipitation conditions, that is, on the dispersion difficulties. This is an important consideration in the case of fine-grain emulsions (see para. 72).

In practice, photographic emulsions are prepared in neutral (or acid) solution, and in ammoniacal (or semi-ammoniacal) medium. There are many intermediate varieties, depending on whether the whole or part of the grains are precipitated in neutral or ammoniacal medium, then ripened in neutral or ammoniacal medium.

Type A

1. *Neutral emulsions.* These are prepared at about 70°C (158°F). They are more stable than ammoniacal emulsions and have coarser grain and lower contrast.

2. *Acid emulsions.* These are prepared as neutral emulsions, but in the presence of a small quantity of inorganic or organic acid. In the case of silver chloride, the soluble halide is frequently poured into the nitrate-gelatin solution.

3. *Borax emulsions.* These emulsions are prepared in neutral medium, borax being added finally to bring the pH to 8.

4. '*Double-jet*' *neutral emulsions* can be precipitated at temperatures as low as 45°C (113°F) using two simultaneous streams of bromide and nitrate, the former always being a little ahead of the latter.

5. *Mixed emulsions.* Precipitation is carried out in neutral or acid solution, but ammonia is added before ripening.

Type B

6. *Ammonia emulsions.* Precipitated at 65–70°C (149–158°F) in a gelatin-bromide solution containing a certain amount of ammonia. With high alkali concentrations the temperature can be reduced to 45–55°C (113–131°F).

7. *Partly ammoniacal emulsions.* The first part of the silver is added in the neutral condition (one-third or one-half for example). The remainder is

added in the 'converted' form. The temperature can be higher at the beginning.

8. *Completely ammoniacal emulsions.* All the silver nitrate is converted to the ammoniacal salt. Temperature 45°C (113°F). This is the most common method.

9. *Acid-ammoniacal emulsions.* The ammoniacal silver nitrate is added to a gelatin-bromide which is acidified with a small amount of an organic (tartaric, citric, lactic, etc.) or inorganic (nitric, perchloric, etc.) acid. The first crystallization centres, formed in acid solution, are different from the normal ammoniacal ones, and this influences the final characteristics.

288. Working conditions

Precipitation is the most important operation in the preparation of an emulsion. Its future is decided at this moment. That is why the physicochemical medium and the working conditions must be examined carefully.

Little is known about the initial state of the crystallization centres, but it is certain that for reproducibility the same operating conditions must be observed each time.

Grain size. The grains formed during precipitation are finer as the addition is made more quickly, as the concentrations of nitrate and bromide are reduced, as the gelatin concentration is increased (to a certain limit) and as the temperature is reduced. In other words, the grains are fine when the reaction between the consituents is least violent; if the precipitation time must be short, it is only to prevent the first formed crystals from ripening while the others are being formed.

The sensitivity of the emulsion is a function of the size of the grains. The contrast depends on their fineness and their uniformity.

Precipitation time. We have seen that the grain size, and hence the emulsion characteristics are dependent on the concentrations of the reactants taking part. Now if a volume A of nitrate is poured into volume B of gelatin-bromide, it is obvious that the first drop of silver nitrate reaches a medium of high gelatin and bromide concentration, whereas the last drop enters a solution diluted by the same nitrate solution. Therefore the first drop produces finer grains than the last, the mass passing through all the intermediate sizes.

The ionic state of the solution varies gradually with the disappearance of the soluble bromide during the reaction. Furthermore, the majority of the potassium iodide is precipitated at the beginning. It follows that the later parts of the precipitate are formed in the presence of pre-existing grains, whilst the first ones are in a fresh solution.

The gelatin concentration can also be reduced to one-half—from 5% to 2½% for example—whilst the soluble bromide concentration falls from 18% to 1·8%.

It can therefore be seen that a system involving such variable factors will be difficult to control, and even impossible to reproduce twice in an absolute way.

Negative emulsions, however, whose exposure latitude must be as great as possible, must have a wide range of grain sizes (and therefore of different sensitivities): to this effect, *stepped precipitation* can be used, by adding the silver solution in several separate fractions, separated by periods of time. The first grains grow by ripening, whilst those from a later addition remain small having less time to ripen.

For the preparation of identical successive batches of emulsion, average values are expected. In fact, stepped precipitation introduce new factors causing dissimilarity, in addition to those of simple precipitation: the fractions which are successively precipitated are each produced in a different medium, which results in the formation of grains which are characterized, not only by their size differences, but also by structural differences due to changes in the colloidal and ionic condition of the solution.

It is preferable to substitute a mixture of several emulsions of the same type, with different, but well-defined grain sizes and structure, for stepped precipitation. The preparation of each emulsion is then carried out by *fairly rapid mixing* of the two reagents with vigorous agitation, enabling the maximum homogeneity and constancy of results to be obtained. We have also used a second method, which is to divide the gelatin between the bromide and the silver solution in equal concentrations: thus during the whole precipitation time, the gelatin concentration remains constant. If a double jet method is used to introduce the bromide and silver into a pure gelatin solution a medium of constant ionic composition can thereby be obtained. The temperature must be kept constant, and it is advisable to bring all solutions, including the silver nitrate, to a definite precipitation temperature, and take into account the heat produced by the reaction itself.

289. Physical ripening

This operation has the object of increasing the size of the silver halide grains, and consequently their sensitivity. The precipitated emulsion is kept at a fixed temperature, between 45° and 70°C in the *presence of excess soluble bromide.* During the whole of the ripening operation, the emulsion is constantly and regularly stirred.

The sensitivity increases with prolonged heating of the emulsion: the crystals formed by precipitation increase in size, the larger ones increasing at the expense of the smaller, under the influence of slight supersaturation. Finally the smallest grains disappear because of their greater solubility in the excess silver bromide solvent.

The phenomenon is accelerated in the presence of *ammonia* which is a silver halide solvent. This ammonia can be used as ammoniacal silver nitrate, or can merely be added before or after precipitation.

Ripening is essentially dependent on the solubility of the silver bromide in the bromide solution due to the formation of a complex. In neutral emulsions this solubility increases with the Br^- concentration, but in ammoniacal emulsions it increases at first, then decreases when an optimum value has been exceeded.

According to Lyalikov's measurements(12) the velocity of growth V of a crystal, for a radius r and a ripening time t is related to the concentration c of the silver bromide in solution and the solubility Sr, by the equation

$$V_{r,t} = A\frac{(C - S_r)}{r}$$

where A is a coefficient of proportionality equal to the coefficient of diffusion.

The rate of growth is a linear function of $1/r^2$. For short ripening times the function is somewhat hyperbolic.

The rate increases with temperature:

$$\log V_r = F - \frac{H}{T}$$

where T is the absolute temperature and F and H are constants.

The number of grains n after time t, compared with the number of grains n_0 initially present is given by Lambert and Sheppard's equation, verified by Lyalikov:(13) $n = n_0/1+kn_0t$ where k is the constant of crystallization rate.

What is the *mechanism of crystal growth?* Two are assumed:

(*a*) Progressive growth of crystals at the expense of the finest (Ostwald ripening).

(*b*) Joining of several crystals by *coagulation*.

Progressive growth takes place in low concentrations of gelatin and silver halide as well as in the presence of inert gelatins.(14)

Dimensions of ripened grains. The size of the grains increases with time, temperature, concentration of soluble halide, concentration of ammonia (if any), the dilution of the gelatin and the rate of agitation.

The increase in size of the grains is shown by an increase in the *turbidity* of the emulsion. With negative emulsions the diameter easily reaches 3 μ, but there is, in actual fact, a wide range of smaller diameters. For slow emulsions the average diameter is 0·6 μ, 'process' emulsions 0·3 μ and positive emulsions, 0·1 μ.

The sensitivity of an emulsion increases with the time of physical ripening, but only up to a certain limit.

Contrast. Coarse-grain emulsions are less contrasty than fine-grain ones. Those having a wide range of grain size have an average contrast, resulting from the contrasts of the different groups of grains. Separation of an emulsion into two layers by sedimentation gave Renwick the following significant figures:

	Relative sensitivity	Contrast	Fog density
Initial emulsion	100	1·14	0·14
Coarse grains	170	1·10	0·22
Fine grains	25	1·76	0·10

To obtain a high-contrast emulsion it is consequently necessary to precipitate the grains so that they are as nearly as possible of the same size, and to avoid long ripening. Commercial process emulsions for line work, which need very high contrast, have, even so, a fair range of grain size whose relative areas are 10 : 1. This ratio goes to 100 : 1 for negative emulsions.

290. Retarders and accelerators of physical ripening

Crystal growth during ripening is, as we have seen, inhibited by *gelatin.* This contains a greater or less quantity of natural retarders; also the ripening rate is in inverse proportion to the amount of gelatin present.

Gelatins rich in retarders are generally obtained from hides. Gelatins poor in retarders are obtained from bones or by deactivation (inert gelatins).

Artificial retarders. The introduction of *egg albumen* can, to some extent, make up for the lack of retarders in gelatin. *Cystine* which is sometimes recommended is only effective in fairly high concentrations and also desensitizes. It is better to use *imidazoles*, *thiazoles* or *thiolactic* acid; for example, a concentration of 0·2–2% of the weight of dry gelatin of *4-thiazolidone* (Steigmann). Excellent results can also be obtained with *dithiopyrimidine* and *dithioquinazoline.*(15)

Cadmium ions Cd^{++} retard the ripening of silver chloride, onto which it is adsorbed. Their effect drops with the pH. Cadmium salts are often used in the preparation of contrasty chloride and chlorobromide emulsions.

Ripening accelerators. Sulphur sensitizers generally accelerate crystal growth. The turbidity diagrams established to determine the retarding power of gelatin have inflection points due to disturbances introduced by natural sensitizers which are present. However, a gelatin rich in labile sulphur does not necessarily bring about grain growth by coagulation.(16)

Ohyama and Futoki have studied several very active accelerators:(17) *1-thio-2-ethyl-1:2-dihydrobenzoxazole*, *rhodanine*, *sym-N:N-dioctadecylthiourea*, *N-octadecyl-N-allylthiourea* and *N-octadecylrhodanine.*

291. Distribution of grains after physical ripening

The distribution of grains in an emulsion is shown by a *frequency* curve (Fig. 46). The dimensions in μ are plotted on the abscissa and the frequency per 1000 grains on the ordinate.

The frequency curve can be represented by the equation

$$y = y_0 e^{-k(z-\alpha)^2}$$

in which y is the frequency per 1000 grains, y_0 the maximum ordinate value, α the abscissa value corresponding to this maximum, Z the average diameter of the group of grains considered, k is a constant and e is the Naperian logarithm base. The values of y_0, k and α for three emulsions are shown in the table below:

Emulsion	Millions of grains per cm²	mg of Ag Halide per cm²	Percentage Ag Halide in dry emulsion	Diameter μ	Projected area in μ²	Volume in μ³	Mass in 10^{-12} g	Area in μ² of the largest grains	Constants of the frequency equation		
									y_0	k	α
Process	668	1·37	33·6	0·844	0·560	0·317	2·05	1·6	340	8·95	0·55
Rapid	940	1·30	32·5	0·799	0·502	0·213	1·38	6·2	277	4·27	0·53
Extra-fast	478	1·47	33·7	1·67	2·198	0·476	3·08	12·6	{200	2·78	0·76
									30	6·45	2·05

The evaluation of emulsion grain sizes is made with photomicrographic enlargements of these emulsions which have been previously diluted to a known extent in a larger quantity of gelatin solution, then coated in very thin layers.(19) To simplify measurements specially graduated rulers which directly show linear measurements and area in μ^2 can be used. Loveland used three different graduations for triangular grains, hexagonal grains and substantially circular ones: he measured respectively the height of the triangle, the distance between opposite sides of the hexagon (average value when the hexagon is irregular) and the diameter of the circle.

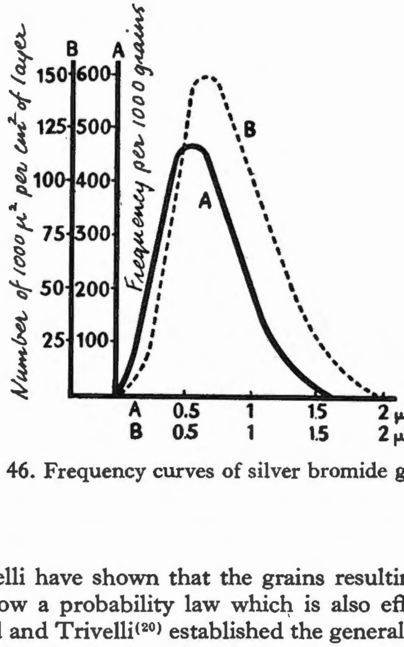

FIG. 46. Frequency curves of silver bromide grains.

Sheppard and Trivelli have shown that the grains resulting from the collision of ions and particles follow a probability law which is also effective with their initial distribution. Loveland and Trivelli(20) established the general equation $y = cf^a$ where y is a characteristic of the distribution of grains by dimensions such as the total number of grains, the average diameter or the dispersion around this average diameter; f is a variable ripening factor (for example, the concentration of soluble bromide): a and c are two parameters.

Another method of representation is to express the area of the grains logarithmically, and use its function Z, called the normal frequency function, in place of the frequency itself:

$$Z = \frac{1}{\sqrt{2\pi}} e^{-x2/2} . dx$$

In practice the cumulative frequencies are plotted on a graph of the logarithmic probabilities. A distribution like that of the function of the cumulative frequencies will be a straight line on a graph of probabilities and can be expressed by:

$$y = A_n x^n \exp[-k(\text{Log}_e x - \alpha_n)^2] \, dx$$

where y is the frequency, x is a property of the size, A, k and α are constants and n is a whole number.

This equation has the same form as the Gauss one:

$$f(x) = f_m \exp[-C^2(x - x_m)^2]$$

where f(x) is the number of grains with an area between

$$x \text{ and } x + dx$$

$f_m = f(x_m)$ being the maximum ordinate and C^2 is a positive constant. A modification suggested by Loveland and used by Kapteyn represents the phenomenon more exactly by replacing x by log x in the Gauss formula:

$$f(x) = f_m \exp[- C^2 \log^2 (x/x_m)]$$

where the preceding Loveland and Trivelli formula is again found.

Silberstein, however, prefers the empirical equation:

$$\log [(f(x)/f_m] = - k(x - x_m)^2/(x - q)^{\frac{1}{2}}$$

where q is a constant, k a positive constant, x_m and f constants which define the maximum of the curve.(21) For example, if $x_m = 0{\cdot}65\ \mu^2$, then $q = 0{\cdot}261\ \mu^2$, $x = 0{\cdot}082\ \mu^2$ and $f_m = 760$ for a total of 3,830 grains measured.

Kottler,(22) referring to recent work of Pearson and Fisher, has made many criticisms of calculations based upon the Gauss error function as well as Kapteyn's transformation. Kottler substituted algebraic for graphical analysis(23) by introducing the principle of the minimum square, ($\chi^2 = \Sigma\, \delta^2/s^2$ where δ is the individual error, and s the average quadratic error). The time of growth is related to a parameter a and the rate of growth to a parameter b.

292. Setting and washing

Dry gelatin is added to the precipitated and ripened emulsion, and dissolves after 15 minutes. The liquid is then rapidly *cooled* and set in vessels placed in a refrigerator at 5–6°C (41–43°F), so that it is turned into a *gel*. The amount of gelatin added must be such that the concentration of gelatin in the emulsion before cooling is 7–10% (of the total amount of water, the evaporated water being replaced). A minimum of 7% is necessary so that during washing the gel will not swell and absorb too much water. If, for example, the gelatin concentration *after* precipitation is 3% for a volume of water equal to 900 cc, that is 27 g, 6% or 54 g of gelatin must be added to bring this concentration up to 9%.

The setting time depends on the volume of the emulsion. Small quantities can be coated on trays at a thickness of 0·5–1 cm which enables them to be thoroughly set in less than 2 hours.(24) It is, however, preferable to keep the set emulsion in a refrigerator for 12 hours.

The solid block of emulsion is shredded into noodles 3 or 4 mm diameter in a press, or with a knife if setting has been carried out in a dish. For small quantities muslin or a net can be used.

The shredded emulsion is then washed in running water. *The purpose of washing is to remove all the soluble salts*, particularly the excess bromide and the alkali nitrate which is formed during the reaction. The time of this operation depends on the concentration and nature of the gelatin, the thickness of the shreds, the total volume, the agitation,(25) the hardness of the water (120 mg CaO average), the rate of flow and mainly the temperature. Hard water, a low rate of flow and a low temperature lead to slow washing. Generally this varies from 3 to 6 hours.

Washing is limited on one hand by the softening, swelling and water absorption of the shredded mass, and on the other by the risk of fog in over-washed emulsions. The elimination of the soluble salts must be controlled by *analysis* (Nessler's reaction) and *measurement of the* Br^- *ion concentration* or by *measurement of the resistivity of the water*. The purity of the water used must also be checked. In experimental work a circuit of distilled water is sometimes used but as it tends to swell the noodles too much, 200 mg of anhydrous sodium sulphate is added per litre.

It is important to know the *quantity of water absorbed* by the emulsion shreds: the emulsion is weighed before and after washing; it is, however, difficult to obtain constant results because of the large number of influencing factors.

This increase in weight due to absorption of washing water is measured after *draining* for 30 mins. to 2 hours or even after blotting.

The emulsion noodles swell in water, this action being more rapid as the noodles are made smaller. They also swell more as the water temperature becomes higher. Furthermore, in the presence of ammonia, weak gels absorb more water than concentrated ones. Ammonium bromide also increases swelling; its action is stronger than that of potassium bromide.

The bromide is removed twice as quickly as the ammonia. This is checked with a few cc of liquid in which a few pieces of the noodles have been crushed by adding a few drops of Nessler's reagent (potassium mercury iodide), which gives a brown precipitate in the presence of ammonia. Riegler's reagent of p-nitrodiazobenzene hydrochloride can also be used; this turns red. The tests are of course carried out after filtering the sample liquid.

A current method of controlling wash-water is by its electrical resistivity. G. G. Blake has disclosed a special system in which a variable resistance is connected in parallel with the condenser of an electrical oscillator.(26)

Washing technique. In practice two different methods are used:

(*a*) Washing in racks in stagnant water, which is renewed every 15 or 30 minutes, with periodic stirring of the noodles.

(*b*) Washing in running water in a tank or in a trough similar to that used for making paper paste.

Contrary to what might be thought, the old method of washing in racks is the quickest and most efficient, and a smaller number of noodles are broken by agitation.

The *washing time* is 3–4 hours for slow emulsions and 5–6 hours for fast ones.

The *water temperature* should not exceed 12°C (54°F) or the noodles may swell and form a mass from which the soluble salts cannot be removed.

The water should have the lowest possible calcium content. Calcium salts make the gelatin opaque and the resulting coatings are matt and grainy. Town water containing 120 mg CaO produce a definite matt surface. This is quite a serious disadvantage which can only be overcome by purifying the water with a permutit or resin ion exchanger. The effect of these should, however, be very carefully checked, for with improperly treated organic resins an intense fog can be produced in the emulsion. A more costly method of purification is to add 2 g per litre of sodium hexametaphosphate to the wash water; this sequesters the calcium and magnesium (the use of Sequestrene or ethylenediamine tetraacetate is even more expensive). Finally, small batches of emulsion can be washed with distilled water obtained from a thermo-compression apparatus; 200 mg per litre of anhydrous sodium sulphate should be added to this water (or 484 mg of $Na_2SO_4 . 10H_2O$).

The wash water almost always contains *organic substances* which have not been properly identified. These organic substances vary in type and quantity depending on the source (spring, river, well, and according to the seasonal variation in rain and drought). They can cause 'inexplicable' variations, by their action on the sensitivity and other properties of the emulsions.

293. Treatment of emulsions without washing

Three methods can be used to separate the ripened silver halide crystals (or at least, the majority of them) from the gelatin:

(*a*) *Centrifuging.*

(*b*) *Sedimentation* of grains precipitated in the presence of very little gelatin and ripened without the addition of further protective colloid. The grains, freed from their salts can then be redispersed in fresh gelatin. This method has been used commercially, but large AgBr grains from which the liquid can be readily decanted are necessary.

(*c*) *Coagulation* with sodium sulphate. An equal quantity of an 80–90% solution of sodium sulphate decahydrate is added to the emulsion. The coagulum is washed, then redispersed in water to which gelatin solution has been added. This method is the most interesting of the three.

We would note here the *washing of an emulsion by dialysis* through a membrane (parchment or cellophane). This enables the soluble salts to be removed from the warm liquid emulsion. This process can be used with polyvinyl alcohol emulsions.(27)

294. After-ripening

The digestion of an emulsion *after washing*, or chemical ripening, has the object of *forming sensitivity specks* on the surface of the silver halide crystals, whose effect is to increase their sensitivity.

After-ripening has no direct effect on the size of the grains except for possible coagulation.

The *after-ripening temperature* depends on the emulsion type: it is about 45°–50°C for ammoniacal emulsions, but may go up to 65°C for neutral emulsions.

After-ripening time. The chemical ripening of an emulsion during digestion is more rapid as the temperature is raised. For extreme speed ammoniacal negative emulsions, it is about one to one-and-a-half hours at 50°C.

The general sensitivity of an emulsion increases with the after-ripening time. It increases to an *optimum value* after which it starts to drop. The *appearance and increase of fog follows the increase in speed* but in a different way. The fog starts to be appreciable around the point of optimum sensitivity; this is why *after-ripening is stopped when the fog becomes appreciable* (but acceptable), say 0·06 for a negative emulsion.

An emulsion which is not digested up to the optimum point will continue to ripen slowly when cold, unless this action is stopped by the addition of a powerful antifoggant.

To follow the progress of after-ripening and to be able to stop the process at the required time, it is necessary to remove samples at equal intervals, coat them rapidly on glass or paper and expose and develop them *wet*, so that the sensitivity and fog can be known.

After-ripening principally increases the sensitivity of emulsions which have had little first ripening. The gamma is, at the same time higher, and the grain finer. As an example, the sensitivity and gamma obtained with an ammoniacal emulsion at varying first and after-ripening times are shown below. The corresponding fog values are also included.

Time of first ripening	After-ripening 30 mins.	After-ripening 60 mins.	After-ripening 90 mins.
0	S = 19·5 γ = 2·1 F = 0·02	S = 26 γ = 2·85 F = 0·04	S = 26 γ = 3 F = 0·1
10 mins.	S = 72 γ = 2·1 F = 0·03	S = 71 γ = 2·45 F = 0·05	S = 57 γ = 2·4 F = 0·25
20 mins.	S = 107 γ = 2·3 F = 0·04	S = 98 γ = 2·2 F = 0·13	S = 75 γ = 2·1 F = 0·4

From this table we see that:

(*a*) For the same after-ripening time, the sensitivity increases regularly with the first ripening time.

(*b*) For the same first ripening time, the sensitivity does not necessarily increase with second ripening time, but reaches an optimum, then drops.

(*c*) The highest contrast is obtained with a short first ripening followed by a long after-ripening.

(*d*) For a short after-ripening, the fog only increases slightly with first ripening, but with extended after-ripening, the fog increases considerably.

(*e*) Whatever the first ripening time, the fog increases quickly when the optimum after-ripening is exceeded.

(*f*) For a practically useful emulsion, either the first ripening must be brief, followed by fairly long digestion (fine grain, low sensitivity, low fog and high contrast) or a fairly long first ripening must be followed by a relatively short digestion (fairly coarse grain, high sensitivity, low fog, moderate contrast).

Influence of ammonia. The addition of a small quantity of ammonia before after-ripening accelerates the rate of chemical ripening. In addition, the fog also increases rapidly, and the ammonia must be neutralized at the end of the operation. This ripening method is not widely used in practice.

Many organic bases have been proposed in place of ammonia: anilines, morpholine, piperazine hydrate, N:N-dihydroxyethylpiperazine, N-hydroxyethyl piperidine, and especially pyridine.

Influence of antifoggants. They are strong ripening retarders, and can even prevent ripening completely.

295. Sensitivity specks

The increase of sensitivity by chemical ripening is due to the formation of specks on the *surface* of the halide crystals.

The sensitivity specks consist of either *silver sulphide* or metallic *silver.*

The sulphur compounds contained in gelatin are indisputably the source of these specks. It is, however, difficult to understand the mechanism of their action. Does the silver sulphide produced remain finally in this form? Some workers, notably Chibissov and his collaborators(28) think not. They grant that if the sulphur compounds effectively accelerate the after-ripening by the formation of adsorption compounds, it is the *autocatalytic reduction of silver salts* to silver which brings about the increase in sensitivity.

Whilst it is true that one can produce silver specks during digestion, using for example, stannous chloride $SnCl_2$ (5–100 mg per kg of $AgNO_3$),(29) it is certain that the active compounds in gelatin have a greater influence on the sensitivity of an emulsion. *Silver sulphide in either a simple or complex form must react with surface sensitivity specks which are already present.* We have seen in para. 25 how the study of the formation of the latent image leads us to consider the specks as complex structures formed by the association of a sulphide ion and a positive hole.

Such a conception is entirely in accordance with observations based on the practice of emulsion preparation, the most important of which is: all the characteristics of an emulsion are defined, in a latent form, at the moment of precipitation, particularly if this is carried out in the presence of an active gelatin. The later operations of first and second ripening only result in the development of these characteristics—not their creation.

296. Choice of gelatin

The choice of gelatin depends on the type of emulsion which is required. Furthermore, each phase in the preparation—precipitation, ripening, after-ripening—must be suited to a particular type of gelatin.

Active gelatins. These are suitable for the precipitation of negative emulsions. Some workers use them to sensitize afterwards. Experience, however, has shown that this does not give the best results, for these active gelatins only produce their optimum effect at the moment of precipitation.

The sensitivity of an extreme speed emulsion is not proportional to the amount of sulphur sensitizer; quite a small percentage of active gelatin (10% of the total) is enough to ensure the speed. Any increase in this amount of gelatin only results in an increase of fog.

Added gelatins. This term applies to gelatins added after precipitation, but before after-ripening (second and third gelatins). These gelatins need not be rich in sensitizers, but rather should have a very low fogging tendency. They must retain the latent sensitivity of precipitation, that is, they must not neutralize the precipitation gelatin. They must, furthermore, have another extremely important quality: *not to accelerate after-ripening.* There are gelatins whose optimum ripening time is zero. These are bad gelatins (at least for the chosen emulsion type). To obtain a good high-speed negative emulsion, the *sensitivity and density of the blacks should be very low at the beginning of after-ripening*: they increase very gradually, and only reach their maxima at the optimum digestion time, *before fog becomes objectionable.*

Inert gelatins. These gelatins (mainly from bones) have been de-activated by various processes (which have already been enumerated). Some workers use them together with artificial sensitizers. Other gelatins are said to be inert to gold: these are ones which do not produce emulsion fog in the presence of gold salts.

Retarding gelatins. These are generally made from calf skins. Emulsions prepared from such gelatins are contrasty; when sufficiently active, the emulsions are of the 'process' or 'contrasty' bromide positive types. As they are free from degradation products and sensitizers, they are suitable for the preparation of silver chloride emulsions. The presence of *contrast bodies* can intensify the power of these gelatins.

Gelatin content. The gelatin concentration of an emulsion must be such that it can be coated and set easily on glass, film or paper. The measurement of the viscosity is therefore a very important measurement. The amount of gelatin must be balanced with the amount of water. The emulsion can, however, have a high or low concentration of silver halides. An emulsion containing little gelatin compared with the silver will develop more rapidly, and the γ_∞ will be reached more quickly.

The variations of this limiting development time as a function of R = gelatin/silver are represented by the curve in Fig. 47. From R = 2, the time necessary to reach γ_∞ remains practically constant.

The contrast given by a photographic layer is not the same for each wavelength; but near γ_∞ the differences become negligible; so that for an identical gamma throughout the spectrum *with the same sensitive layer*, development to γ_∞ must be rapidly reached. Under these conditions it is necessary to use an emulsion with a low gelatin content, and this is practiced with reseau colour films.

Gelatin tests. There are many chemical and physical tests which have already been dealt with which can give useful information on the behaviour of the gelatin. However, experience has shown that the best test is still that of preparing a given emulsion and carefully determining all the sensitometric characteristics. It must, however, be borne in mind that the physical and chemical ripening times can be slightly changed without prejudice to the results; several different preparations are therefore sometimes made, and it is advantageous to plot the characteristic curves of the samples removed during digestion and coated on glass or paper.

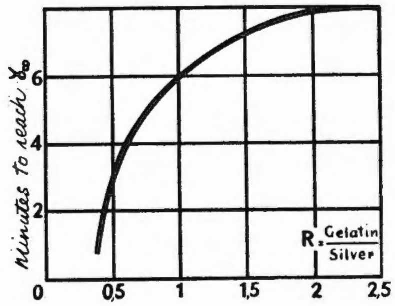

FIG. 47.

CHEMICAL SENSITIZERS

297. Sulphur sensitizers

Gelatin introduces sulphur sensitizers into the emulsion, which bring about the formation of specks during digestion to considerably increase the light sensitivity. What are these natural sensitizers? We have seen that opinions are divided. For some, the *gelatin sensitizers* are thiosulphates and thionates, whilst for others they are *organic substances of relatively high molecular weight*, linked perhaps to the gelatin. Despite the work of the upholders of the thiosulphates, it is the second hypothesis which at the moment, and until absolute proof to the contrary is obtained, appears the most likely. None of the known artificial sulphur sensitizers behave like an active gelatin. Also, it has been wrongly thought for some time that the activity of gelatin is due to allyl isothiocyanate, a compound in mustard oil and discovered by Sheppard in the liming water. What is true, is that *collagen which is limed for too long a time loses its sulphur compounds*, but only the degradation products are found, particularly methionine (1%), cystine, cysteine, polythionates and thiosulphates:

Methionine: $CH_3—S—CH_2—CH_2—(CH—NH_2)—CO . OH$

Cystine: $OH . CO(NH_2) : CH—CH_2—S—S—CH_2—CH : (NH_2)CO . OH$

Cysteine: $OH . CO(NH_2) : CH—CH_2—SH$

The active sulphur, estimated by Feigl's reaction, and the labile sulphur by the sulphiding of silver, can only give results of meagre practical value. *The only effective test is to study the behaviour in an emulsion.* In addition we know that the turbidity curves obtained from physical ripening show inflection points, each of which corresponds to an active substance of gelatin; however, the shape of an inflection zone given by a naturally active gelatin differs greatly from that due to an artificial sensitizer.

Among the *artificial organic sulphur sensitizers* which have been proposed and tried with greater or less success are the following:

Allylthiourea (or thiosinamine) $NH_2{-}CS{-}NH{-}CH_2{-}CH = CH_2$ and its derivatives such as *allylbenzylthiourea, diethylthiourea and allylpiperidylthiourea.* Allylthiourea generally produces intense fog, and is not usable in practice. Concentration 0·1–1 mg per gram of AgBr. The latter quantity can produce image reversal by chemical solarization.

Thiourea $NH_2{-}CS{-}NH_2$ also produces fog. It has, however, been tried by many workers(30) even using the compound with the radioactive isotope S^{35}. Thiourea is most active at pH 8.

Thiosemicarbazide $NH_2{-}CS{-}NH{-}NH_2$. This is produced by boiling a solution of hydrazine and ammonium thiocyanate. Concentration 0·01–0·1 mg per gram of AgBr. Murobushi, Kawaguchi and Ashikowa used *aldehyde-thiosemicarbazones* which are ripening retarders at the same time.(32)

1-thio-2-ethyl-1:2-dihydrobenzoxazole is also a retarder.(33)

Benzothiazole methyl sulphide is only effective with rapid emulsions (concentration 20 mg per litre of emulsion).

Aminothiazole base (in 5 : 1000 aqueous alcoholic solution) increases the sensitivity of fast emulsions but produces fog.

Allylpseudothiohydantoin hydrochloride (5 : 1000 alcoholic solution). Twenty mg per litre of emulsion fogs silver bromide emulsions but increases the sensitivity and contrast of chloride ones.

Thiolactic acid. One hundred mg per litre increases the sensitivity and contrast of chloride emulsions. It desensitizes and increases the contrast of process emulsions and desensitizes fast emulsions.

Ergothioneine hydrochloride only increases the contrast of chloride emulsions.

Thiodiphenylamine (or phenothiazine) increases the contrast of process emulsions but desensitizes.

Thiochrome (vitamin B.1) at a concentration of 0·05 mg per litre of emulsion appears to increase speed when added before after-ripening.(34)

Phenyl-β:β-dimercaptovinylacetone.

Sulphomalic acids.

Dithiolactic and dithioacetic acids.

Potassium dithiocyanate (0·015 mg per g AgBr).

Guanidine thiocyanate.

The thiocyanates generally activate sulphur sensitizers and are anti-retarders.

298. Various organic sensitizers

Gelatin hydrolysis products studied by Bycichin and Vlach, appear to have no practical value.

Slight increase in sensitivity together with considerable fog.	Phenylalanine Tyrosine Glutamic acid Goose haemoglobin

Reduction of sensitivity and fog retarded	Alanine Proline Hydroxyproline Aspartic acid Arginine Glycocol Leucine Albumen Globulin Cholesterin Lecithin Blood serum
Reduction of sensitivity with prevention of fog.	**Cystine**

A gelatin hydrolysis product, however, had increased sensitivity, the fog not increasing until the end of after-ripening.

Betaine and *lecithine* reduce sensitivity and fog.(35)

Creatine and *arginine* have been proposed for increasing the sensitivity of sensitized cellulose films(36) in 1 g per litre baths.

Rivanol is the lactate of 2-ethoxy-6 : 9-diaminoacridine. It has a sensitizing action on some emulsions with a slight increase in contrast. It can be used as a 4 : 1000 solution. Using 1·2 mg per gram AgBr it can increase the speed of slow emulsions by one half. It has the disadvantage of staining the emulsion yellow.

Esculin can increase the sensitivity of moderate-speed emulsions when about 1 mg per gram AgBr is added. The fog rises by 0·03 with no change in contrast.

299. Inorganic sulphur sensitizers

Among the inorganic sulphur sensitizers, the most widely used are the sodium or ammonium *thiosulphates*. We have already seen that these compounds are considered by some workers to be the active substances in gelatin, together with the *polythionates* (which behave like the thiosulphates).

It is, in fact, necessary to discriminate between the action of thiosulphates added to the emulsion (at the end of preparation) and added to the gelatin before precipitation. The best results are obtained when the *thiosulphate is added to the gelatin in amounts of a few mg. per kg.* When added to a completed emulsion, positive results are only obtained with certain slow emulsions; the speed of a slow emulsion, for example, has been increased 2·6 times by adding 1 mg. hypo per gram of AgBr, the fog rising from 0·02 to 0·06. With fast emulsions, however, the speed generally drops, accompanied by an increase in fog. This also occurs when thiosulphate or polythionate is added before precipitation in too high a concentration.

Lorenz,(37) who studied the action of many sulphur compounds, has stated that the *trithionate* $Na_2S_3O_6$ liberates sulphur most easily. In acid solution (pH 3–5) it is 2·5 times more active than thiosulphate. Its activity drops to half in neutral or basic solution. Some commercial sulphiding preparations behave like the polythionates, in particular like the pentathionate $Na_2S_5O_6$.

As far as sodium *thiosulphate* $Na_2S_2O_3$ is concerned, its sensitizing is probably due to only one of the two sulphur atoms. It first forms several *argentothiosulphates* but not all of these dissociate spontaneously.(38) At low

Ag^+ concentrations, and in acid media, secondary reactions can take place, which interfere with the activity of the product.

Sodium sulphide Na_2S. Added to the emulsion it produces fog and an intense yellowing. It sometimes produces a sensitizing action if added to certain gelatins in concentrations below 1 mg per kg.

Colloidal sulphur has been disclosed in F.P. 645,104 and 645,471 (1927) to activate gelatin by heating together. A small fraction of the resulting product is added to the precipitation gelatin.

300. Influence of metallic salts

Metallic salts have very diverse actions on photographic emulsions.

Magnesium as the chloride or bromide. Favours a slight increase in sensitivity with reduction of fog when added before after-ripening.

Ferrous and mercurous salts—slight increase in sensitivity with the formation of fog.

Ferric and mercuric salts—reduction of sensitivity and increase of fog.

Nickel reduces sensitivity, and sometimes increases contrast a little. No increase of fog. Nickel and cobalt are ripening accelerators.

Lithium reduces sensitivity and increases fog.

Lead and thallium reduce sensitivity and increase fog. Thallium was disclosed by Schwarz in 1926. Mueller(39) stated in 1935 that lead and thallium salts added in a concentration of 0·04 molecules per cent of the silver halide increase the sensitivity of gold-sensitized *X-ray emulsions* by 50–100%. The addition is preferably made before precipitation. In the presence of vacant silver ion sites in the halide crystals, a complex $[Pb^{++}Ag^{-}_{\square}]$ is produced, which increases the electrical conductivity.(40)

Rhodium has a very powerful action on silver chloride emulsions. It results in a strong reduction in sensitivity accompanied by an important increase in contrast (see silver chloride emulsions).

Cadmium is a retarder of physical ripening. Its action with chloride emulsions results in an increase in contrast. The addition of cadmium salts is made before precipitation.

Copper salts reduce emulsion sensitivity. They are used in some slow process bromide emulsions to increase the contrast by adding before digestion. Copper salts can increase the speed of chloride emulsions when accompanied by organic acids (e.g. citric).(41)

Heavy anions. Certain insoluble silver salts with heavy anions such as tunstate, molybdate, vanadate, have been proposed for increasing emulsion sensitivity. To do this, the corresponding alkali metal salt is added to the solution of alkali halide.

The *thiocyanates*, added before precipitation or during digestion have also been disclosed for increasing emulsion sensitivity.(42)

It is advisable to make reservations as to the efficiency of these products. It can even happen in some cases that there is a complete loss of sensitivity and fog results.

301. Gold sensitizing

Gold increases emulsion sensitivity considerably when added as complex *aurous thiocyanate* (or aurothiocyanate).

In 1925 Kroppf envisaged the possibility of sensitizing an emulsion with gold chloride $AuCl_3$.(43) Then Carroll and Hubbard tried colloidal gold in 1928, Kantelwitz traces of gold salt in the presence of mercuric salts(44) and Schmieschek, basic gold salts.(45)

It was Koslowsky(46) who first had the idea in 1936 of using gold as the aurothiocyanate $NH_4Au(CNS)_2$, inspired by the fact that gold toning is more effective in the presence of an alkali thiocyanate. The process was at first kept secret and used exclusively for Agfa emulsions. Patents were later applied for by many other workers: Keller,(47) Waller, Collins and Dodd,(48) Balsiefen.(49)

According to the generally accepted hypothesis, the aurothiocyanate acts by substituting the silver specks with metallic gold. In fact, *when the emulsion has not been chemically ripened the effect is practically nil.* Faelens(49b) however, has recently shown that silver bromide *without binder* can be immediately sensitized with gold, without a ripening stage. This implies that the decomposition of the aurothiocyanate is catalyzed by the silver bromide itself, and not by the silver in the specks, or more exactly, as Steigmann confirms, by the halide ions.(49c) The experimenters have omitted to specify the size of the crystals used in their tests. Now in practice, it is the large grains which react most favourably to gold sensitizing.

Instead of adding the gold thiocyanate to the emulsion, the latter can be immersed in the solution for a few minutes. In this way the sensitivity and the development rate are increased (James).(50) The gold is deposited autocatalytically; it reaches a thickness of 20–80 mμ after 64 hours immersion. It is resistant to oxidizing agents unlike the silver specks.

Despite its apparent simplicity, gold sensitizing is an operation which is very difficult to carry out conveniently. It is frequently deceptive: for if the simple addition of a suitable amount of a gold salt raises the sensitivity three times, the fog, and even more the instability, increase to such an extent that the emulsion becomes useless after being kept for a few days.

There are two important factors which influence gold sensitization: the *choice of gelatin* and the presence of a *powerful antifoggant*.

Among the most effective antifoggants are the *azaindolizines* (see para. 350).

Gold sensitizing technique. Some workers have shown an increase in sensitivity when using gold chloride or sodium chloroaurate. We have been unable to produce any useful effect from these products. Sodium gold thiosulphate reduces the sensitivity and increases fog. Only the aurothiocyanate has been shown effective.

To prepare ammonium aurothiocyanate add a 1·3 g per litre solution of ammonium thiocyanate to an equal volume of a 2 g per litre solution of gold chloride $AuCl_3$, just before use. For example, 40 mg $AuCl_3$ corresponding to 20 cc of solution, and 20 cc of ammonium thiocyanate solution. Steigmann used

6 cc of 1% $HAuCl_4 . 3H_2O$ in 50 cc of 1% ammonium thiocyanate. The B.I.O.S. report on German industry gives 1·5 cc of solution with 40% Au in 1·5 litre of 1% ammonium thiocyanate, and 6·2 cc of this mixture is used for 50 g silver nitrate.

If the aurothiocyanate is added to a completed emulsion, 30–40 mg $AuCl_3$ is necessary to produce a speed increase of 3X.

If the aurothiocyanate is added before after-ripening, the amount should should be at most one-third of this, as chemical ripening is greatly accelerated with rapid increase in fog.

Gold sensitizing reduces the slope of the main part of the characteristic curve and lengthens the toe. It is mainly effective with the large grains, which are also the most sensitive.

For gold sensitizing to be effective, the parent emulsion must have a very low fog level.

Influence of gelatin on gold sensitizing. The great disadvantage of gold sensitizing is the fog. This originates with the reducing substances present in the gelatin, and particularly the aldehydes. Furthermore, desensitizers in the gelatin prevent aurothiocyanate sensitizing as they form a more stable complex with the gold; these include glutathion, cysteine and the 4-carboxythiazolidines. Traces of metals like copper and tin can also have an inhibiting action from 1 part in 100,000 of dry gelatin.

The choice of gelatin is therefore important. It is, however, very difficult to find gelatins free from reducing substances, for these are not removed with active carbon. In fact, according to work by Landucci and Durante(50b) a certain content of reductones is necessary for effective sensitizing, by enhancing the prior formation of silver specks.

Steigmenn(51) considers that sulphur sensitizers are useless when an emulsion is treated with gold unless the iodide content is less than 4% and the excess bromide during precipitation is small, in which case small quantities of sulphur compounds and retarders are necessary. The same writer classifies gelatins as ultra-inert, inert and gold-sensitive. The ultra-inert gelatins which contain neither sensitizer nor retarder are the most suitable. Gelatins termed inert to gold also give good results. They contain small amounts of sulphur sensitizers and retarders. The 'gold-sensitive' gelatins are those which give fog.

To make the gelatin tests Steigmann preferred a neutral unwashed chloride emulsion ripened in the presence of SO_2 and sensitized with aurothiocyanate.(52) The emulsion is stabilized with 2-mercaptobenzoxazole using 25 parts to 100,000 of dry gelatin.

Effect of *thallium* and *lead* salts: see para. 303 and 371.

Platinum and *palladium*: their salts sensitize, but less effectively than gold.(52b) The study of these elements showed the inhibiting action of gelatin on sensitization by noble metals. Polyvinyl-alcohol is without action.

302. Role of silver iodide

The purpose of adding potassium iodide to the alkali halide is to precipitate a small amount of silver iodide together with the bromide.

The silver iodide itself is not very sensitive to light, but in moderate proportions, up to 6%, it increases, on the contrary, the sensitivity of silver bromide by deforming the crystal lattice, the meshes of the two halides being different. Its presence confers the following characteristics on an emulsion.

(*a*) *Extended under exposure region* therefore a less uniform curve.

(*b*) *Larger grains*. The protection given by gelatin against crystal growth becomes less effective in the presence of a little AgI.

(*c*) The *sensitivity* increases with the AgI content to an optimum value. A fast negative emulsion will contain about 3% iodide whilst a slow emulsion may only contain 0·5%. The optimum concentration varies with the emulsion type and the gelatin.

(*d*) After-ripening cannot be carried on as long with iodide present. With 0·5% AgI digestion is difficult.

(*e*) The tendency to *solarize* increases with the iodide content.

(*f*) *Gold sensitizing* is facilitated.

The presence of silver iodide in an emulsion therefore has both advantages and disadvantages. The advantages are greater sensitivity with extended digestion and better colour sensitivity. The disadvantages are mainly a characteristic curve which is distorted at each end, and coarser grain.

At higher iodide concentrations than those generally used, the latent image is mainly internal, although close to the surface.[53] It is located on the interfaces of the distinct silver bromide and iodide lattices in the same grain.

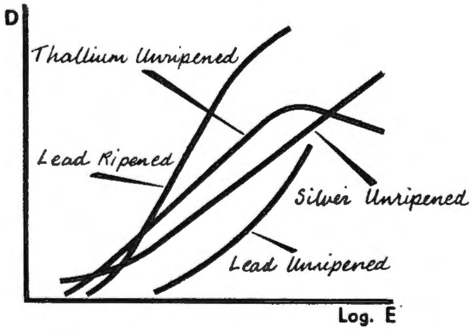

FIG. 48.

303. Lead and thallium emulsions

The introduction of *lead* or *thallium* bromide into an emulsion changes its principal characteristics:

(*a*) The grains become spherical in shape, more so as the proportion of lead or thallium is increased.

(*b*) The sensitivity is reduced, but digestion fog is also lowered and the images are purer.

(*c*) The contrast is increased.

(*d*) The emulsion is more easily solarized.

Emulsions made entirely of lead or thallium halides can be prepared. They have the characteristic curves shown in Fig. 48—very contrasty and readily solarized.

To precipitate lead or thallium bromide, the corresponding nitrates are used as the soluble salts. In other respects the method is the same as for an ordinary emulsion, but the temperature is lower—35°C according to Thom,(54) who studied thallium bromide. The incorporation of thallous bromide in a silver iodide emulsion increases the sensitivity one hundredfold; the maximum is in the green.(55)

Thallium salts, added to ammoniacal, gold sensitized emulsions in quantities from 0·4 to 0·7 mg per g of silver have only a negligible influence.

304. Ultrasonic action

Following the communications of Claus(57) in 1933 affirming the power of ultrasonic vibrations in dispersing silver halides in gelatin, and the memoirs of other workers, the experiments of Protas(58) in 1940, then of Peronnet and Biquard(59) in 1947 had shown that ultrasonics have no specific action on photographic emulsions. The only things which can happen are on one hand, the rupture of certain cyclic links in the gelatin molecule, and on the other, the formation of a latent image by local pressure.(60) More recently, Herold, Jones and Knighton(60b) have, however, successfully used ultrasonic vibrations to increase the sensitivity of emulsions. Their apparatus consisted of a cooled perspex cylinder immersed in oil to transfer the vibration. Under the tank of oil is a *barium titanate* vibrating element. Energy 5W/cm^2 at a frequency of 800,000 c.p.s.

305. Commercial emulsion manufacture

Photographic emulsions are commercially manufactured in 20–250 litre vessels depending on the importance of the undertaking. These tanks are made of stainless steel or enamel. They are generally jacketed for steam heating and fitted with a mechanical stirrer. The enamel ones are of the usual double-wall type in a tipping holder. A more highly developed system which can be heated or cooled at will is fitted with a tight lid enabling work to be done in white light.

The emulsion is either cooled in the precipitation vessel, or is first poured into 20-litre vessels which are placed in vats of cold water. In some works it is put into large flat enamel dishes cooled by water circulating at 2°C.

If the emulsion is in pots it is set by leaving for several hours in a refrigerated room. Neutral emulsions must not be placed in rooms which have had ammoniacal types in them, for there is risk of fog or yellowing.

The set emulsion is shredded in a press by forcing it through a grid with sharp edges.

Washing is carried out with water cooled to 10–12°C by the methods already given in the chapter devoted to this operation. For a 500-litre washing tank, the water flow is generally about 30 litre per minute.

After draining for two hours, the emulsion is remelted either in small lots in stainless steel 20-litre pots or in 300-litre tanks of stainless steel or enamelled iron, heated in the water-bath. Samples are removed every 10–15 minutes for sensitometric tests. The after-ripening temperature must be rigorously controlled, and it is advisable to use a thermostat.

After digestion, the emulsion is cooled rapidly to about 35°C when the finals are added before taking the emulsion to be coated. It can also be kept in a refrigerator until it is used. The final product should be filtered under pressure through a cellulose paste. Some manufacturers merely filter through a cloth bag which retains the large particles and the froth. A storage tank kept at 32°C permits the air bubbles to rise to the surface; it is preferable to use a baffled receptacle which retains the bubbles more effectively and prevents them from being carried to the coating head.

Continuous preparation. Emulsions can be precipitated continuously. A series of pumps introduce carefully controlled quantities of solutions of gelatin + bromide and silver nitrate at constant temperature into a small vessel. After remaining for a short time, the emulsion is circulated through a spiral which is of sufficient length for ripening, then falls into another receptacle where a 50% gelatin solution is added before setting.

Another experimental system was described by Oshima and Ken-Ichi Ariga(61) in which the emulsion is ripened in the precipitation vessel from which it is drawn before adding gelatin. The volume is kept constant at 1000 cc whilst 30 cc per minute of 10% silver nitrate and 10 cc of a solution of 5% gelatin, 23% KBr and 0·9% KI are added, and at the same time 40 cc of emulsion per minute is drawn off, to which is added 10 cc of 53% gelatin.

306. Powdered emulsions

The preparation of powdered photographic emulsions was suggested by Kennet in 1876. They are in fact obtained by desiccation, the product having the appearance of semolina, which keeps indefinitely and can be readily redispersed in water.

The precipitated, washed and remelted emulsion is only partly ripened; it is then broken up through a nickel gauze, the droplets being received in a slightly volatile non-alcoholic liquid. The emulsion (in its proper sense) is then dehydrated at a temperature sufficient to finish the after-ripening. The dry product still contains 15% water.

Slow chloride emulsions are also prepared, which can be manipulated in weak white light, which are used for prints of sheet-metal templates, prints on anodized aluminium or varnished zinc for placards, etc. The aqueous solution is sprayed on, over an isolating varnish, at a pressure of about 3 Kg.

307. Manufacture of silver nitrate

The silver nitrate used for the manufacture of photographic emulsions must be extremely pure and its preparation must be carefully supervised.

The crude 98–99% silver is first dissolved in nitric acid. By electrolysis of the resulting solution, silver with an assay better than 99·9% is obtained. This is redissolved in nitric acid S.G. 1·4. This is boiled until crystallization starts and then poured into receptacles, when 60–70% of the silver nitrate crystallizes overnight. The mother liquors provide a second crop of crystals, frequently of lower purity when the metal has been insufficiently refined. After rinsing in a centrifuge, the crystals are dried, or preferably recrystallized from distilled water.(62)

The silver is dissolved in batteries of double-walled tanks of 309 or 310 steel placed in cascades until the concentration reaches 65%. By evaporation, this is increased to 85%. The nitrous vapours which are evolved are oxidized to nitric acid and are absorbed in water.

In the preparation of silver nitrate, rinsing the crystals with alcohol must be avoided as the latter produces the explosive silver isocyanate.

308. Analysis of sensitive materials

The estimation of the silver and the halides in photographic emulsions is usually made after dissolving the silver halide in a solvent.

(*a*) *Dissolving in N/10 potassium cyanide.* After separation of the metals, the halides are titrated electrometrically in the presence of ammonium nitrate following Clark's method.(64) Wagner and Pelz(65) passed a current of CO_2 then H_2S through the cyanide solution; Ag_2S precipitates leaving in solution the halides, which are titrated potentiometrically. The method of estimation using cyanide is not recommended as it is dangerous and complicated.

(*b*) *Dissolving in sodium thiosulphate* free from halides. Thirty cc of 25% solution for 1 dm^2 of emulsion. The wash waters are added to the hypo solution. Eight cc of 10% Na_2S is then added and the solution brought to the boil; the precipitate of silver sulphide coagulates. After filtering hot and washing the precipitate with hot water, the silver sulphide is decomposed with hot nitric acid which converts it to silver nitrate; distilled water and a ferric alum indicator are then added before titrating with ammonium thiocyanate.(66) The filtrate contains the halides. Sixteen cc of 5N sulphuric acid is added and the solution is left for the SO_2 to be given off. Then 1 cc of N/10 KI is added followed by N/5 permanganate until a bluish colour is produced. The halides are then titrated potentiometrically using N/10 silver nitrate and a silver electrode.(67) The amount of iodide previously added is naturally subtracted from the amount found by titration.

(*c*) *Attack by a caustic alkali* according to the method of Tellez-Plasencia:(68) this produces alkali halides which can be titrated directly, whilst the precipitated silver hydroxide is recovered and converted to nitrate for volumetric or potentiometric estimation.

Estimation of metallic silver. In addition to the usual methods of estimating metallic silver after dissolving in nitric acid, the following can be used:

(*a*) Colorimetric estimation of silver using 2-thio-5-keto-4-carbethoxy-3-dihydropyrimidine, in the presence of a buffer of nitric acid and sodium acetate giving a pH of 2.(69)

(*b*) Colorimetric estimation of silver using insoluble tetramethylthionine mercury iodide which liberates a dye in proportion to the amount of Ag ions.(70)

(*c*) Action of iodine on the silver, and electrometric estimation of the excess iodine with standard sodium arsenite solution. The silver iodide formed is dissolved in potassium iodide and the liberated hydriodic acid is neutralized with sodium bicarbonate. Accurary 0·005 mg to ±1%. The electrode used is a Foulk and Bawden polarized electrode.(71)

(*d*) Formation of radioactive cobalt ferrocyanide on the silver and measurement of the radioactivity with a Geiger counter (Baenziger).(72)

(*d*) Conversion of the silver to the iodide with radioactive iodine I^{131} according to the method of Ballard, Stevens and Zuehlke.(73) To do this, a mixture of potassium ferricyanide and radioactive potassium iodide is used.

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Chapter XIX

NEGATIVE EMULSIONS

309. The preparation of photographic emulsions, and especially negative emulsions, is a critical process whose results depend, as we shall see, on many factors: quality and careful choice of gelatin, purity of the chemicals, preparation equipment, working method, etc.

The reproducibility of an emulsion is not always perfect, especially when it is necessary to use different batches of gelatin. Furthermore, the large-scale application of formulas worked out on an experimental scale, due to the differences in volume brings about variations, so that it is necessary to adjust all the conditions again to produce the same characteristics.

There is, therefore, no exact preparation formula for photographic emulsions, as the results always vary with the worker, his apparatus and the quality of the working materials; some factors, such as the agitation and the temperature of the liquids, can have a great influence if insufficiently well controlled. Above all, it must be remembered that because a gelatin is termed 'photographic' it is not necessarily suitable for an emulsion formula without giving chancy results.

This is why the following emulsion formulas are given purely as illustrations, which can be used as a basis for the preparation of particular emulsions. All the formulas given here have produced excellent results for their originators, but used in a slightly different way, with other gelatins, they may not always give satisfactory results: the different working factors must be adjusted until the desired characteristics are obtained.

In this, and the following chapter, the preparation of the emulsions themselves will be described, whilst in another chapter the *finishing* and *stabilization* of emulsions before coating on their supports will be studied.

310. Neutral emulsions

The greatest danger in the preparation of neutral emulsions is the formation of spontaneously developable aggregates of grains appearing as *black spots* (grit) frequently visible to the naked eye. These spots are reduced in size and number when the following factors are changed during precipitation: dilution of the silver solution, reduction of the proportion of iodide, adjusting the pH to as nearly neutral as possible, raising the temperature, increasing the agitation.

The following formula, in our opinion, is the one which is best from all points of view. The amounts of gelatin and silver nitrate are adjusted to give a suitable viscosity and silver bromide content, two factors which must be borne in mind in the composition of an emulsion for commercial use.

A 70°C	Distilled water	100 cc
	Gelatin	3·5 g
	Potassium bromide	31 g
	Potassium iodide 10%	8 cc
B 65°C	Distilled water	350 cc
	Silver nitrate	37·5 g
C	Dry gelatin	55 g

Pour B into A with stirring, the time being variable between 30 seconds and 5 minutes. Ripen for 60 minutes at 70°C. Add the dry gelatin. Continue ripening for 30 minutes. Cool, set and wash 5 hours. Drain the noodles for 1 hour.

Add 20 g gelatin dissolved in 80 cc water, then 2 cc of 1% magnesium bromide and digest for 2 hours at 55°C. If the noodles have absorbed too much water, add only dry gelatin (2 hours before digestion to allow time for it to swell).

The *gelatin concentration* has the following values at various stages:

Beginning of precipitation	3·2%
End of precipitation	0·75%
End of ripening	13%
During digestion	11%
Silver iodide content	2·1%
Excess of soluble bromide	20%

For more marked ripening, this excess can be increased to 40% using 36 g instead of 31 g.

Amount of silver bromide per litre of emulsion	60 g
Amount of silver per litre of emulsion	34·5 g
Ratio R: gelatin/silver	2·4

Only the starting gelatin should be rich in sensitizers.

Quick precipitation gives higher contrast. Short ripening gives finer grain, balanced by lower sensitivity.

Digestion can be continued until fog starts, without exceeding 0·05. The emulsion is then stabilized with an antifoggant.

If the water in A in this formula is doubled, and that in B reduced, the sensitivity drops; if the iodide is increased the sensitivity may also drop.

Carroll and Hubbard's formula:

A	Distilled water	350 cc
	Ammonium bromide	42·7 g
	Potassium iodide	2·3 g
	Gelatin	20 g

B	Distilled water	450 cc
	Silver nitrate	60 g
C	Dry gelatin	80 g

Pour B into A in 3–9 mins. at 65–70°C. Ripen for 30–60 minutes. Add the gelatin C and continue ripening for 20–30 minutes with stirring. Cool, set, wash and digest at 65°C until fog appears.

Initial gelatin content	5·7%
Gelatin content after precipitation	2·5%
Gelatin content after ripening	12·5%
Gelatin content during digestion	8–10%
Excess of soluble bromide	29%
Silver iodide content	4%
R = gelatin/silver	2·6

Extra-rapid Agfa 'Night film' formula (from F.I.A.T. Final Report No. 355, Aug. 1945. H.M. Stationery Office, London).

A	Distilled water	70 cc
	Potassium bromide	8 g
	Potassium iodide	0·5 g
	Gelatin	1 g
B	Distilled water	90 cc
	Silver nitrate	9 g
C	Dry gelatin	25 g
D	Distilled water	3 cc
	Potassium thiocyanate	0·03 g
	Silver nitrate 1% sol.	sufficient for the precipitate to remain dissolved.

Temperature 65–70°C. Pour half of B into A in one minute, then add the second half in 29 minutes.

Add the gelatin C and ripen for a further 15–20 minutes with stirring. Cool, set and wash. Digest in the presence of D for 60 minutes at 50°C.

311. Double-jet neutral emulsions

To prepare these emulsions, the bromide and silver solutions are added from separate jets into a gelatin solution. The bromide must be adjusted so that it is ahead of the silver by a constant amount. If a drop in the gelatin concentration during precipitation is to be avoided, the colloid is added to the three solutions and a uniform temperature is maintained. Example of formula:

A	Distilled water	400 cc
	Gelatin	12 g
B	Distilled water	300 cc
	Ammonium bromide	61·5 g
	Potassium iodide	3 g
	Gelatin	9 g

C	Distilled water	300 cc
	Gelatin	9 g
	Silver nitrate	90 g
D	Gelatin	60 g
	Temperature 45–70°C.	

Ripen for one hour at 65–70°C, add gelatin D, continue heating for a further 15–20 minutes, cool, set and wash the emulsion. Digest between 55 and 65°C after adding 36 g gelatin.

Concentration of gelatin during precipitation	3%
Concentration of gelatin on setting	9%
Excess soluble bromide	23·5%
Silver iodide content	3·5%
R = gelatin/silver	2·2

The gelatin concentrations and the times can be modified according to the gelatins used.

312. Acid emulsions

Emulsions precipitated in acid solution are generally *slow emulsions*. The acid used is most frequently sulphuric acid, but it is possible to work at a higher pH using citric acid (or other organic acid) or even monosodium citrate.

Two cc of sulphuric acid S.G. 1·18 in solution A of the formula in para. 310 reduces the speed but increases the contrast. The sensitivity increases with the precipitation temperature (70°C) but the optimum gamma is obtained at 55°C. There is an optimum amount of acid beyond which no increase in gamma is obtained.

313. Borax emulsions

Borax emulsions are actually neutral emulsions which are made alkaline to pH 8 during ripening. Steigmann's formula is:

A	Distilled water	110 cc
	Gelatin	4 g
	Ammonium bromide	9·1 g
	Potassium iodide	0·4 g
B	Distilled water	90 cc
	Silver nitrate	7 g
C	Distilled water	20 cc
	Silver nitrate	4 g
D	Distilled water	20 cc
	Silver nitrate	4 g
E	Dry gelatin	24 g
F	Water	15 cc
	Borax	1·5 g

The bromide solution is used at 70°C and the silver solutions at 65–70°C. To achieve stepped precipitation, 20 cc of B is added in 15 seconds, then the remainder of B in 20 minutes with moderate agitation. Ripen for a further 5 minutes then add C in 1 minute. Ripen for 10 minutes. Finally, add D, the gelatin E and the borax solution F. Ripen the whole for 20 minutes maintaining the temperature at 70°C throughout. Set, wash, drain and digest at 65°C in the usual way. During digestion an equal amount of borax can again be added.

Initial gelatin concentration	3·6%
After first precipitation (B)	2%
After second precipitation (C)	1·8%
After third precipitation (D)	1·66%
Concentration for digestion	11·4%
Excess of soluble bromide	6·7%
Silver iodide content	2·7%
R = gelatin/silver	2·9

314. Ammonia emulsions

To prepare ammonia emulsions, a certain amount of ammonia is added to the gelatin-halide solution whereas with ammoniacal emulsions, the silver is converted to the ammonia complex. Ammonia emulsions of high sensitivity can be prepared with suitable gelatins free from sulphur dioxide. Formula example:

A	Distilled water	160 cc
	Gelatin	6 g
	Ammonium bromide	19 g
	Potassium iodide	0·7 g
	Ammonia (S.G. 0·91)	4 cc
B	Distilled water	140 cc
	Silver nitrate	20 g
C	Distilled water	70 cc
	Silver nitrate	10 g
D	Dry gelatin	35 g

Temperature: 42–70°C depending on the retarding power of the gelatin.

Pour B into A in 1–5 minutes. Ripen 10–60 minutes. Add C in 30 seconds then gelatin D and continue heating for at least 15 minutes. Cool, set, wash. Digest at 50°C after adding 9 g of gelatin which is allowed to swell in the noodles.

Gelatin concentrations:

At the beginning of precipitation	3·6%
At the end of first precipitation	2%
At the end of ripening	11%
During digestion	9–10%
Silver iodide content	1·7%
Excess of soluble bromide	11·7%
R = gelatin/silver	2·6

In any formula it is essential to vary only one factor at a time to obtain the optimum required result. Here, besides the temperature, the ripening times, the initial gelatin content and the iodide content, the amount of ammonia can be varied. Some users of this type of formula prefer to precipitate with a gelatin of moderate activity, then add the gelatin rich in sensitizers just before digestion.

A *variation* is to precipitate part of the bromide in neutral solution, then add the ammonia and continue precipitation.

315. Completely ammoniacal emulsions

These emulsions are precipitated using ammoniacal silver nitrate which is simply prepared by adding concentrated ammonia to the silver nitrate solution until the first formed black precipitate of silver hydroxide is just redissolved. The ammoniacal silver nitrate solution is formed of argento-ammonium complexes whose composition varies with time. *The ammoniacal silver nitrate solution ages*: It must therefore be used with the minimum delay if reproducible results are to be obtained. Chibissov and his co-workers have shown that with an old solution, silver nitride is formed in the emulsion;⁽¹⁾ to overcome this disadvantage they disclosed crystalline ammoniacal silver nitrate.⁽²⁾

Formula for fine-grain emulsion:

A 45°C	Distilled water	200 cc
	Potassium bromide	63 g
	Potassium iodide 10%	20 cc
	Active gelatin	25 g
B 35°C	Distilled water	480 cc
	Silver nitrate	75 g
C 45°C	Distilled water	120 cc
	Gelatin (low activity)	65 g

Add B to A in 5 minutes. Ripen 20 minutes at 45°C. Add gelatin C. Wait 10 minutes then cool, set and wash. After draining, swell 40 g of dry gelatin in the noodles and digest for about 60 minutes at 50°C.

Gelatin concentrations:

At the beginning of precipitation	11·3%
End of precipitation	3·6%
End of ripening	11%
During digestion about	10%
Silver iodide concentration	2·7%
Excess soluble bromide	23·5%
R = gelatin/silver	2·3

Amount of silver bromide per litre of emulsion: about 75 g.

It is evident that by reducing the initial quantity of gelatin in this formula, the speed is increased due to larger grains. Furthermore, part of the silver nitrate need not be added until after 30 minutes ripening in order to extend the gradation of the emulsion. In this way ultra-rapid emulsions are obtained with suitable gelatins.

Contrast formula:(3)

A	Distilled water	240 cc
	Gelatin	40 g
	Ammonium bromide	18·4 g
	Potassium iodide	0·6 g
B	Distilled water	50 cc
	Silver nitrate	14 g
	Ammonia	Q.S.
C	Distilled water	30 cc
	Silver nitrate	7 g
	Ammonia	Q.S.
D	Distilled water	30 cc
	Silver nitrate	7 g
	Ammonia	Q.S.

Solution temperatures: A, 45°C; B, C and D, 20°C. Add B to A with moderate agitation. Ripen 5 minutes at 45°C. Then add C, wait 5 minutes and add D. Ripen for a further 20 minutes. The set and washed emulsion is digested for 60–90 minutes at 50°C. The after-ripening must be shorter if the physical ripening is curtailed, that is, with finer grain. For example:

Ripening time	Optimum digestion time	Relative sensitivity	Contrast	Fog
10 mins.	65 mins.	25	3·2	0·01
30 mins.	90 mins.	240	2	0·02

Initial gelatin concentration	17%
Concentration after precipitation	11·4%
Silver iodide content	2·2%
Excess soluble bromide	17·2%

Amount of silver bromide per litre of emulsion: about 56 g.

R = gelatin/silver: 2·3.

Nelson-Kieser formula:

A	Distilled water	360 cc
	Gelatin	40 g
	Ammonium bromide	20 g
	Potassium iodide	0·7 g
	Disodium phosphate	1 g
B	Distilled water	45 cc
	Silver nitrate	14·8 g
	Ammonia	Q.S.
C	Distilled water	45 cc
	Silver nitrate	14·8 g
	Ammonia	Q.S.

Temperature of solution A: 45°C. Add B to A in 30 seconds. Ripen 45 minutes at 45°C. Add C and ripen for a further 15 minutes. Cool, set and wash. Digest at 45–50°C, adding dry gelatin if desired.

Initial gelatin concentration	11%
Gelatin concentration after precipitation	8·5%
Silver iodide content	2·5%
Excess of soluble bromide	21%
R = gelatin/silver	2·8

(after adding 2% of gelatin during digestion).

Start in acid solution. If a small quantity of inorganic or organic acid is added to the bromide solution in an ammoniacal formula the formation of spontaneously developable grains, which may be produced with some gelatins, is prevented. The sensitivity is reduced however. Amount of acid: 2 g citric acid per 100 g silver nitrate.

316. Semi-ammoniacal emulsions

In this type of emulsion, part of the silver is first added as the normal nitrate. After a certain ripening time, the remaining silver is added as the ammoniacal solution, and ripening is continued for the full time. This procedure enables *fairly fast contrasty emulsions* for photomechanical work to be obtained. Example:

A	Distilled water	200 cc
	Potassium bromide	60 g
	Potassium iodide	2 g
	Gelatin	50 g
B	Distilled water	300 cc
	Silver nitrate	25 g
C	Distilled water	260 cc
	Silver nitrate	50 g
	Ammonia	Q.S.
D	Distilled water	120 cc
	Gelatin	50 g

Solution temperatures: A, 60°C; B, 55°C; C, 33°C; D, 45°C. Pour B into A in 2 minutes. Drop the temperature to 45°C in 3 minutes, add the ammoniacal silver nitrate solution C in one minute, then ripen 10 minutes at 45°C. Add gelatin D, stir 5 minutes, set and wash. Add 50 g dry gelatin to the draining noodles, allow to swell for 2 hours, then digest for about 60 minutes at 50°C.

Gelatin concentrations:

Initial	25%
After 1st precipitation	10%
After 2nd precipitation	6%
After ripening	10·7%
During digestion, about	10%

Silver iodide content	2·7%
Excess soluble bromide	17·4%
R = gelatin/silver	3·2

Amount of silver bromide per litre of emulsion: about 55 g.

The temperature of the neutral precipitation stage can be reduced to 45°C if desired, and the ripening time shortened or lengthened, depending on the retarding power of the gelatin used.

Simultaneous precipitation semi-ammoniacal emulsions. The two silver solutions—neutral and ammoniacal—are not added separately as in the preceding formula, but simultaneously. The following is a Steigmann third-ammoniacal formula:

A 65°C	Distilled water	240 cc
	Gelatin	10 g
	Ammonium bromide	18·2 g
	Potassium iodide	0·8 g
	Sodium sulphate anh.	4 g
B	Distilled water	120 cc
	Silver nitrate	20 g
C	Distilled water	100 cc
	Silver nitrate	10 g
	Ammonia	Q.S.
D	Dry gelatin	40 g

The two solutions, B and C are preferably used at 58°C. They are added simultaneously, with moderate agitation, B in 2 minutes and C in 1 minute. After 14 minutes ripening the dry gelatin is added, and heating is continued for 20 minutes before cooling. The washed emulsion is digested at 50–65°C.

The introduction of sodium sulphate into the precipitation solution has, according to the author of the formula, the effect of increasing the contrast greatly. The action of sodium sulphate has only been claimed for this emulsion exclusively.

Gelatin concentrations:

Initial	4·16%
After precipitation	2·17%
After ripening	10·8%
Silver iodide content	2·7%
Excess soluble bromide	8·8%
R = gelatin/silver	2·5

(without adding gelatin for digestion).

317. Emulsion mixtures

The gradation of an emulsion, that is, the exposure latitude, is improved by stepped precipitation. It is increased even more by mixing a slow emulsion with an ultra-fast one. To do this properly, it is essential that the speed and contrast of the slow emulsion are such that the curve joins perfectly onto that of the fast emulsion which it should continue in the high exposure region. As the contrast of the slow emulsion is reduced by mixing, it must be harder than the fast emulsion, the result should be a characteristic curve which is as straight as possible. In the opposite case, the curve has a definite junction point. A perfect mixture is very critical to prepare, for it is also necessary to consider the colour sensitization which can alter the contrasts of the two constituents unequally, and destroy the balance of the curves. The effect of the colour sensitizer must therefore be considered when the characteristics of the parent slow emulsion are established.

These phenomena become more complex when three emulsions of different sensitivity are blended. In principle, extremely long curves can be obtained by combining a large number of emulsions, by integrating, in series, their characteristic properties, the resulting curve then appearing as a more or less uniform chain.

Superimposed emulsions. Many commercial materials are made up of two superimposed emulsions, the first layer next to the base being slower than the rapid outer layer. The joining of the two characteristic curves presents the same difficulties as with blends. Usually the curve has a flat portion.

Note. All the amounts of bromide, iodide and silver nitrate given are assumed to be those of the theoretically dry compounds. In practice, the percentage of water which they contain must be added, and this is determined by drying samples in an oven at 120°C. Commercial gelatin generally contains 15% water; the quantities given can be left as they are.

1. Chibissov K. V., Titov A. A. and Mikailova A. A.: *Doklady Akad. Nauk. U.S.S.R.*, 1950, 453.
2. Sov. Pat. 72,274 (1948).
3. Steigmann.

Chapter XX

SLOW EMULSIONS

318. Slow emulsions, for transparencies and papers, are notable for their fine grain, generally high contrast and absence of fog. Those to be used for transparencies must be rich in silver so that high densities can be readily obtained. Paper emulsions are necessarily weak and used in thin layers, for the image density—and therefore contrast—is doubled by reflection.

Slow emulsions generally have a low iodide concentration and a high gelatin content.

The *choice of gelatin* is of extreme importance, it affects the cleanness, the sensitivity, and above all, the contrast. Gelatins for bromide emulsions are fairly rich in sensitizers and retarders; they generally give solutions of low viscosity. Gelatins for chloride emulsions are inert, but rich in sensitizers; they are also harder.

Only a practical test can show if a gelatin is suitable for a particular formula. This test must not only be made for the determination of sensitometric values, but also the keeping properties.

The properties of a gelatin depend on the nature of the raw materials used in its manufacture. Only the manufacturer can know this: the user is almost always in complete ignorance of the relationship existing between the photographic characteristics of an emulsion and the treatment which the gelatin has received.

Starting with a standard formula, it is possible, however, to prepare emulsions with varying sensitivity and contrast, by bringing into play the different operational factors: concentration of gelatin, precipitation temperature, pH of precipitation, time of ripening, and addition of various substances.

SILVER BROMIDE EMULSIONS

319. Fast neutral diapositive emulsions

We have shown, in the previous chapter, that a neutral negative formula can be used for process work. This formula, suitably modified, will give an excellent, and relatively fast, positive emulsion. Example:

A	Distilled water	100 cc
	Gelatin	10 g
	Potassium bromide	36 g
	Potassium iodide 10%	4 cc

B	Distilled water	350 cc
	Silver nitrate	37·5 g
C	Dry gelatin	50 g

Precipitation temperature: 70°C. Pour B into A in one minute. Add the dry gelatin and continue to heat for 15 minutes, after dropping the temperature to 45°C if only moderate ripening is required. Set, wash and after-ripen for 60 mins. at 55°C after adding 20 g gelatin in 80 cc water and 2 cc of 1% potassium bromide.

To avoid any ripening, the dry gelatin C can be dissolved in 120 cc water. The speed and contrast of the emulsion is dependent on the grain size.

320. Ammoniacal positive emulsions

Good positive emulsions can be obtained by modifying the fine-grain ammoniacal emulsion given in the previous chapter, or the contrast formula. The sensitivity decreases and the gamma increases as the ripening is reduced. A high initial gelatin concentration slows down ripening. In addition, the iodide concentration can be reduced to half. In the contrast formula, the silver nitrate solution can be added rapidly in one stage.

When the physical ripening must be reduced as much as possible, a quantity of sulphuric acid sufficient to neutralize all, or a great part of, the ammonia, must be added immediately after precipitation.

The contrast can be increased if the bromide solution is acidified before precipitation with a little sulphuric or citric acid: for example, 3 cc of concentrated sulphuric acid for 100 g silver nitrate.

The contrast can also be increased by first adding a small proportion of the silver nitrate unconverted (semi-ammoniacal type), for example:

Moderate speed contrasty formula:

A	Distilled water	173 cc
	Gelatin	83 g
	Potassium bromide	46 g
	Potassium iodide	0·7 g
	Sulphuric acid 1 : 6 v/v	0·7 cc
B	Distilled water	240 cc
	Silver nitrate	7 g
C	Distilled water	230 cc
	Silver nitrate	50 g
	Ammonia	Q.S.

Temperatures: A and B, 45°C; C, 35°C. Pour B then C, rapidly into A. Ripening 10 mins. at 45°C. After washing, after-ripen for about 50 mins. at 50°C.

It is very important to after-ripen diapositive emulsions until they have reached their maximum contrast. Sometimes this operation is carried out in the presence of cadmium or copper chloride (in the proportion of 0·3 parts per 1,000 of silver nitrate) which reduces the speed, and increases the contrast slightly. After-ripening in acid solution also reduces speed.

Hard positive emulsions, such as those used in the graphic arts, ciné positives and microfilms are made more and more in chlorobromide types, which will be studied later.

321. Bromide emulsions for high-speed papers

Photographic papers with high speed are used for direct document reproduction. Fast bromide emulsions with high contrast and giving a good black image are needed.

Neutral emulsion:

A	Distilled water	100 cc
	Gelatin	5 g
	Potassium bromide	18 g
	Potassium iodide 10%	4 cc
B	Distilled water	210 cc
	Silver nitrate	18·5 g
C	Distilled water	75 cc
	Gelatin	37·5 g

Solutions at 70°C. Pour B into A quickly. Wait 2 mins. and add the gelatin. Ripen for a further 5 minutes and set. Wash, and after-ripen 50–60 mins. in the presence of 2 cc of 1% potassium bromide. Sensitize to green.

Semi-ammoniacal formula:

A	Distilled water	300 cc
	Potassium bromide	60 g
	Potassium iodide	1·5 g
	Gelatin	160 g
	Sulphuric acid, 10% sol.	2 cc
B	Distilled water	400 cc
	Silver nitrate	10 g
C	Distilled water	600 cc
	Silver nitrate	60 g
	Ammonia	Q.S.

Temperatures: A, 45°C; B and C, 38°C. Pour B into A in one minute, and add C in 30 secs. Ripen 10 mins. at 45°C. Set, wash. After-ripen 45 minutes, after adding 55 g of gelatin and 200 cc water. Stop after-ripening by adding an antifoggant (see emulsion finishing) and green sensitize.

322. Bromide emulsions for printing papers

These emulsion formulas are similar in principle to the preceding ones. Ripening is reduced to a minimum and sufficient 8–10% gelatin is added to the washed product to give a final emulsion containing the equivalent of 20 g silver nitrate per litre. The following proportions can be used as a starting point (ammoniacal type).

A	Distilled water	1000 cc
	Gelatin	230 g
	Potassium bromide	80 g
	Potassium iodide	1·5 g
B	Distilled water	1000 cc
	Silver nitrate	100 cc
	Ammonia	Q.S.

Precipitation temperature: 40°C. Precipitation time 30 secs. to 10 mins. depending on the gradation required; the faster the precipitation, the more vigorous the emulsion. The emulsion is set immediately after precipitation. Ripening can be quickly stopped by adding a dilute acid which neutralizes the ammonia.

After washing, 1000–1800 cc of 9% gelatin is added to the melted emulsion. After-ripening at 50°C increases the sensitivity, and often alters the contrast. The addition of 10–50 mg of cupric chloride during after-ripening gives a reduced speed, often balanced by an increase in contrast. The addition of an acid, sulphuric or citric for example, also reduces the speed.

It is not, however, always necessary to after-ripen a paper positive emulsion. The emulsion can simply be stablized by adding an antifoggant: 3 g of potassium bromide or 1 g of benzotriazole. Changes in the characteristics can nevertheless be produced with citric acid (1 g) and also by a supplementary addition of potassium iodide which iodizes the grain surface.

It goes without saying, that the basic formula can be varied: increase or decrease of the iodide concentration; addition of citric acid to the salts; using part of the silver unconverted, etc. The way in which the emulsion is modified and the magnitude depends mainly on the gelatins used.

323. Agfa Brovira bromide paper emulsions

The F.I.A.T. Final Report No. 355⁽¹⁾ from the investigation teams in Germany gives a number of formulas for Agfa Brovira papers of different gradations, which are reproduced below. The most interesting is the 'extra hard' formula which several firms have tried to reproduce with disappointing results.

The extra hard emulsion has three special features: firstly, it is not the silver nitrate which is poured into the bromide, but the ammoniacal bromide which is poured into the gelatin-silver nitrate solution. Secondly, the contrast is obtained by adding *rhodium chloride* to the silver nitrate, and this is extremely active in very small quantities; it results in a simultaneous reduction of speed. Thirdly, the washed emulsion has a long *after-ripening* in the presence of potassium iodide and citric acid to acquire its characteristics. We would add that for this type of emulsion *special gelatins* are needed which are rich in sensitizers and retarders, gelatins which have been produced by the Cie Rousselot among others.

When such formulas as these are used, an intense *yellowing* is frequently produced due to traces of ammonia in the air and which contaminate the gelatin solution containing silver nitrate. This yellowing is easily avoided by adding to the gelatin 20% of its weight of *citric* or tartaric acid.

More serious is the question of the rhodium chloride. This is extremely unstable in solution. It is better to use the *double chloride of rhodium and ammonium* which is dissolved just before use in 5% sodium chloride. 0·4 mg is sufficient, when added to a litre of an emulsion containing 26 g silver nitrate, to raise the γ to 5. Unfortunately this high contrast is not maintained in the conditions prescribed by the formula. After three months it drops, and the extra hard emulsion becomes an emulsion which is only vigorous. This is undoubtedly due to the instability of the rhodium centres on the silver bromide crystal. This is not the case with silver chloride which, with this metal, forms much more stable compounds.

The sensitivity is proportional to the quantity of ammonia. It increases also, as we know, with the ripening time and temperature with a corresponding decrease in contrast.

For matt emulsions add 11 g starch per litre.

The Brovira emulsions are prepared, *with the exception of the extra hard*, by adding 2 to 1 then 3 to (1+2). The silver nitrate solution 4 is then added and the remainder in the order given. *For the extra hard emulsion*, 4 is first added to 1, following by 3 then 2.

Solution temperatures:

1. Extra hard and special: 45°C; hard, normal: 48°C; soft: 40°C.
4. Extra hard: 45°C; 25°C for the others.

SILVER CHLOROBROMIDE EMULSIONS

324. Methods of preparation

Chlorobromide emulsions are prepared by the action of silver nitrate on a mixture of alkali chloride and bromide in a gelatin solution, and in a *slightly acid medium.*

It takes 58·5 g of sodium chloride NaCl to completely precipitate 170 g of silver nitrate, forming 143·5 g of silver chloride. The equivalent quantity of potassium bromide is 119 g. One mole of sodium chloride can be replaced by one mole of ammonium chloride (53·5 g) or one mole of cadmium chloride (147·1 g).

The sensitivity of a chlorobromide emulsion increases with the proportion of bromide, and with the size of the grains, for the same gelatin and a definite preparation type. In parallel with this, the image colour is less warm as the bromide increases.

Compared with pure bromide emulsions, chlorobromide ones are slow, contrasty and very fine grained. Their sensitivity, however, can be very greatly increased by *colour sensitizing*, as their inherent sensitivity barely reaches the blue. This enables emulsions to be prepared which are, at the

BROVIRA FORMULAS FOR GELATINO BROMIDE PAPER

		Extra hard	Hard	Normal	Special	Soft
1	Gelatin	500 g	500 g	500 g	500 g	4000 g
	Water	20 l	20 l	20 l	25 l	16 l
2	Potassium bromide	750 g	750 g	750 g	750 g	3060 g
	Sodium chloride	—	—	—	100 g	—
	Potassium iodide 10%	100 cc	100 cc	300 cc	100 cc	1250 g
	Ammonia	1000 cc	—	—	200 cc	260 cc
	Water	2·5 cc	—	—	—	25% Am Br = 2 l
3	Sodium chloride 25%	180 cc	180 cc	100 cc	—	—
	Rhodium chloride 1 : 10,000	18 cc	6·5 cc	1–2 cc	—	—
4	Silver nitrate	1 kg	1 kg	1 kg	1 kg	5 kg
	Water	3 l	6 l	6 l	6 l	50 l
	Ammonia	—	1 l	1 l	Add in 10 sec. then AmOH 800 cc	—
	Ammonium nitrate 10%	—	—	—	—	1125 cc
5	Gelatin	2500 g	2500 g	2500 g	2500 g	3750 g
	Water	—	—	—	—	12 l
Ripen		30 mins. at 45°C	30 mins. at 45°C	30 mins. at 45°C	30 mins. at 45°C	—

Brovia Formulas for Gelatino Bromide Paper—continued.

	Then add:	Extra hard	Hard	Normal	Special	Soft
6	Sulphuric acid S.G. 1·18	1200 cc	1500 cc	1570 cc	1575 cc	—
	Citric acid 40%	60 cc	—	—	300 cc	—
	Citric acid 50%	—	250 cc	300 cc	—	—
	Wash the emulsion, remelt and add:					
7	Water	—	—	—	—	60 l
	Gelatin	700 g	1000 g	850 g	1000 g	9000 g
	Potassium iodide 0·65%	300 cc	250 cc	250 cc	250 cc	—
	Potassium bromide 25%	10 cc	10 cc	10 cc	40 cc	—
	Sodium chloride 25%	—	—	25 cc	—	—
	Cupric chloride 1% Cu	—	—	3 cc	—	—
	Ripen	75 mins. at 48°C	55 mins. at 48°C	50–60 mins. at 50°C	60 mins. at 48°C	60 mins. at 75°C
	then add:					
8	Citric acid 50%	40 cc	50 cc	55 cc	50 cc	275 cc
	Before coating add, per litre:					
9	Chrome alum 10%	4 cc	4 cc	4 cc	4 cc	4 cc
	Formalin 30%	7 cc	7 cc	7 cc	7 cc	7cc
	Potassium metabisulphite 10%	2·5 cc	3 cc	2·5 cc	2·5 cc	2·5 cc
	Citric acid 50%	4 cc	4 cc	4 cc	4 cc	4 cc
	Cupric chloride 1%	1 cc	2·5 cc	2·5 cc	—	—
	Saponin 3%	50 cc	50 cc	50 cc	50 cc	50 cc

same time, very fine grained, of high contrast and relatively high sensitivity, and which are used for photomechanical work, microfilms and also for ciné positive films.

Very high contrast chlorobromide emulsions are prepared with *cadmium chloride.* Minute amounts of the double chloride of *rhodium* and ammonium also produce a great increase in contrast. *Potassium iodide* added after precipitation has a slight effect in the same direction. But always, the highest contrast is obtained when the *percentage of chloride* is increased with a *very short ripening* (to the detriment of the sensitivity). Finally, *acidification* of the finished emulsion can also increase the contrast.

Extra fine grain emulsions rich in silver give very warm tone images. They are also the slowest. They are obtained either with a very short or low temperature ripening step or with gelatin containing a high proportion of retarders. The addition of 200 mg/litre of hydrazine hydrochloride has been disclosed by Trivelli and Smith as a means of obtaining the warmest tones. Some chlorobromide emulsions *are not washed.* Although their preparation is apparently simple, in practice it is difficult to obtain adequate sensitivity, and their stability is inferior to washed emulsions. Furthermore, suitable gelatins are less common.

Precipitation methods. In practice there are at least eight different precipitation methods used for preparing chlorobromide emulsions, which can be divided into four groups:

A. *Normal precipitation*
   1. Silver into salts.
   2. Double jet of silver and salts.
   3. Two consecutive precipitations silver into salts.

B. *Reverse precipitation*
   4. Salts into silver.

C. *Part of the chloride precipitated separately at the end*
   5. Normal precipitation, then addition of chloride followed by more silver.
   6. Normal precipitation, then excess silver, precipitated by more chloride (second precipitation reversed).

D. *Separate precipitation of bromide and chloride*
   7. Precipitation of bromide by the silver, then chloride by the silver (two normal precipitations).
   8. Precipitation of bromide by excess silver, then precipitation of the latter by the chloride (second precipitation reversed).

325. Chlorobromide emulsions by normal precipitation (type A)

The gelatin-halide solution is generally acidified with citric, sulphuric or hydrochloric acid. The silver nitrate solution can be neutral or acid (citric or nitric acid). The precipitation temperature varies from 40–70°C.

1. *Wall's formula for warm tones*:

A	Distilled water	500 cc
	Ammonium bromide	20 g
	Sodium chloride	10 g
	Citric acid	50 g
	Gelatin	70 g
B	Distilled water	500 cc
	Silver nitrate	50 g
	Citric acid	50 g

Heat solution A to 70°C and add to it, with stirring, solution B, cold. Ripen for at least 10 minutes. If the emulsion is washed, add, after digestion, 40 g gelatin and 2 g sodium chloride.

1b. *Steigmann's formula*:⁽²⁾

A	Distilled water	450 cc
	Sodium chloride	4·2 g
	Cadmium chloride	1 g
	Potassium bromide	1·35 g
	Gelatin	12 g
	Sulphuric acid 5%	15 cc
B	Distilled water	120 cc
	Silver nitrate	12 g

If the gelatin is poor in retarders, add finally 1–3 cc of 2% egg albumen. More retarders must be present if contrast is required. A soft emulsion must contain very little.

Precipitation temperature: 40°C.

Pour B into A with stirring, then add 42 g gelatin. For a normal emulsion, then add 1 cc albumen solution; 8 cc for a contrasty emulsion. Ripen 15 mins. at 40°C. 7·5% gelatin solution is then added as follows:

Contrasty emulsion	150 g
Normal emulsion	200 g
Soft emulsion	250 g

then the following solutions of 0·1% formolcystine and 1 : 2000 ammonium thiosulphate are added:

	Formol-cystine	Ammonium thiosulphate
Contrasty emulsion	6 cc	6 cc
Normal emulsion	—	3 cc
Soft emulsion	—	—

A second ripening is then given: 20 mins. for a contrasty emulsion, 30 mins. for a normal emulsion and 50 mins. for a soft emulsion. Coat without washing.

Formolcystine is prepared as follows:

Dissolve 1 g of cystine in the minimum of 5% caustic soda at 90°C. Add 0·5 cc formalin and boil for 5 mins. The yellow-brown liquid is made up to 1 litre. It will keep in the dark.

2. *Double-jet emulsion for brown tones:*(3)

A	Distilled water	25 cc
	Gelatin	5 g
	Citric acid	0·5 g
B	Distilled water	15 cc
	Potassium bromide	1·30 g
	Sodium chloride	2·15 g
	Potassium iodide	0·012 g
C	Distilled water	20 cc
	Silver nitrate	5 g
	5% Gelatin sol.	5 g
D	Gelatin	4 g

Temperature of solutions: 45°C.

First add a few drops of the salt solution B to the stirred gelatin solution A, then simultaneously, from two separate jets add B and C in the ratio of 2 cc of B to 5 cc C (each 10 secs. for example). Ripen 10 mins. at 45°C, then cool and set in a refrigerator, cut up and wash for one hour. The shredded emulsion is then melted at 42°C, gelatin D added together with 2 cc phenol solution (see para. 205) and then 0·1 g sodium chloride.

Initial gelatin concentration	20%
Concentration after precipitation	8%
Concentration after re-melting	10–11%

Amount of silver bromide in the chlorobromide: 36%.

Quantity of chlorobromide per litre of emulsion: about 50 g.

2b. *Rapid warm tone double-jet emulsion:*(4)

The gelatin used for precipitation should preferably contain more retarders than the gelatin added later.

A	Distilled water	300 cc
	Sodium chloride	9 g
	Cadmium chloride	0·9 g
	Potassium bromide	4·2 g
	Gelatin	15 g
B	Distilled water	450 cc
	Silver nitrate	24 g

Precipitation temperature: 45°C.

First pour a few cc of A into the mixing crock, then add A and B simultaneously with agitation, taking care that an excess of A is always present. Add 54 g gelatin which dissolves in about 15 mins., the 3 cc of 5% sulphuric acid. Ripen for 1 hour between 70 and 75°C or between 60 and 65°C if 9 cc of 1 : 2000 ammonium thiosulphate has been added:

The above formula should give very high contrast. For contrasty, normal and soft emulsions, use the following proportions:

		Contrasty	Normal	Soft
A	Distilled water	300 cc	300 cc	360 cc
	Sodium chloride	6 g	4·5 g	3 g
	Cadmium chloride	0·3 g	—	—
	Potassium bromide	8·4 g	10·5 g	15 g
	Gelatin	15 g	15 g	24 g
B	Distilled water	450 g	450 g	450 g
	Silver nitrate	24 g	24 g	24 g
	Precipitation temperature	50°C	55°C	55°C
	Dissolve second gelatin at	55°C	60°C	60°C

For the normal emulsion, the second gelatin must contain less retarders and more sensitizers.

For the soft emulsion the amount of retarders must be still less and the sulphuric acid omitted.

3. *Rapid chlorobromide emulsion using two consecutive precipitations:*⁽⁵⁾

A	Distilled water	90 cc
65°C	Sodium chloride	1·5 g
	Cadmium chloride	0·6 g
	Potassium bromide	2·1 g
	Gelatin	9 g
B	Distilled water	60 cc
20°C	Silver nitrate	6 g
C	Distilled water	240 cc
	Sodium chloride	6·3 g
	Potassium bromide	3·51 g
	Sulphuric acid 5%	5–11 cc
D	Distilled water	120 cc
	Silver nitrate	18·9 g

Add B to A in one minute. Ripen 10 mins. at 65°C; add solution C, then D. Continue to ripen for 20 mins. Add 39 g gelatin and ripen again for 30–60 mins. Add 120 cc of 8% gelatin and cool. Coat without washing.

For emulsion choose a gelatin which contains little retarders, but rich in SO_2 or bisulphite, which favour ripening.

Initial gelatin concentration	10%
Concentration after precipitation	1·7%
Concentration for second ripening	9·4%

Quantity of silver chlorobromide per litre of emulsion: about 22 g.

326. Reverse precipitation chlorobromide emulsion (Type B)

4. *'Brovira Braun' extra hard type formula:*

A	Distilled water	150 cc
	Gelatin	10 g
	Citric acid 40%	4 cc

B	Silver nitrate	10 g
	Distilled water	10 cc
	Lead nitrate 1%	10 cc
C	Distilled water	60 cc
	Sodium chloride 25%	20 cc
	Ammonium bromide 25%	11 cc
	Rhodium ammonium chloride 1 : 10,000 in 25% NaCl	0·2 cc
D	Distilled water	180 cc
	Gelatin	40 g
	Potassium iodide 0·65%	2 cc
E	Potassium iodide 0·65%	4 cc

All solutions, except E, at 60°C. The sodium chloride and ammonium bromide solutions contain 25 g in 100 cc water.

Add the silver B to A in 15 secs. with stirring. Wait 30 secs. Add C in 15 secs. Ripen 40 mins. at 60°C. Then pour in the gelatin D and continue ripening for a further 60 mins. Finally add the iodide E, cool and set.

The original emulsion is unwashed. It gives, when developed, a yellow fog. Much better results have been obtained, by the author, with a washed emulsion:

Precipitation temperature	Ripening time mins.	Variable	Gamma	Rel. Speed	Tone
60°C	40+60	—	3·7	17	warm black
60°C	40+ 0	—	6·4	13	warm
45°C	40+ 0	—	8·5	5	very warm
60°C	40+60	Double lead	2·2	25	black
50°C	0+ 0	No rhodium	4·7	14	warm

These figures were obtained on paper. The addition of 1 g per litre semicarbazide hydrochloride or hydrazine sulphate gives warmer tones. Adding 20 mg per litre of gold chloride as the aurothiocyanate doubles the speed. Increasing the proportion of bromide gives a more sensitive emulsion, but the image is colder (owing to the larger grains).

327. Chlorobromide emulsions with part of the chloride precipitated separately later (Type C)

5. *Final chloride precipitated normally.* In this type of emulsion, a mixture of alkali bromide and chloride is precipitated by the silver in acid solution. After a certain ripening time, the remaining chloride is added, then this is precipitated by a second acidified silver nitrate solution. Washing follows, then

after-ripening at 50°C for 30 mins. with the addition of a gelatin solution. Emulsions obtained in this way generally keep badly and have only a slightly warm tone.

6. *Chlorobromide emulsions with second chloride precipitation reversed.* These emulsions give very warm tone images of good quality, but their sensitivity is relatively low, necessitating colour sensitization, and they must be stabilized with antifoggants and also anti-yellowing agents. A typical example for the 'Portriga' type of paper is:

A	Distilled water	750 cc
	Gelatin	62 g
	Potassium bromide	20 g
	Sodium chloride	4 g
	Monosodium citrate	6 g
B	Distilled water	500 cc
	Silver nitrate	50 g
C	Sodium chloride	19·5 g
	Distilled water	125 cc
D	Gelatin	165 g
	Distilled water	600 cc
	Potassium iodide	0·2 g

Precipitation temperature: 40–45°C. The silver solution B is first added to A. After 10 minutes the chloride C is added very quickly. The emulsion is ripened for 30 minutes at 45°C and then the gelatin solution D is added, and ripening is continued for a further 30 minutes. Wash and after-ripen 0–60 minutes at 50°C.

The purpose of the chloride in solution A is to increase contrast. It must therefore be reduced in the case of a softer emulsion. *The monosodium citrate buffers the solution at a moderately low pH to avoid the formation of development centres.* The sensitivity increases with the proportion of bromide whilst the tone becomes colder. The addition of 2·5 g citric acid to the finished emulsion increases the contrast and reduces the sensitivity. Increasing the amount of iodide in solution D increases the sensitivity to the detriment of the warm tone.

6b. *Extra hard unwashed chlorobromide emulsion:*(6)

A	Water (ordinary)	4000 cc
60°C	Gelatin (inert)	400 g
	Sodium chloride	80 g
	Potassium bromide	20 g
	Cadmium chloride	40 g
	Sulphuric acid 10%	100 cc
	Egg albumen 2%	60 cc
	Colour sensitizer 0·5%	120 cc
B	Distilled water	2000 cc
20°C	Silver nitrate	200 g

C	Water (ordinary)	11,000 cc
60°C	Sodium chloride	180 g
	Potassium bromide	40 g
D	Distilled water	3000 cc
20°C	Silver nitrate	400 g
E	Distilled water	3000 cc
21°C	Silver nitrate	200 g
F	Water (ordinary)	3000 cc
50°C	Sodium chloride	100 g
	Gelatin (inert)	400 g
	Cadmium chloride	10 g

Add B to A rapidly. Bring to 60°C and ripen 10 mins. Add C then the silver D in 3 mins. Continue ripening for 20 mins. and add 1350 g of dry inert gelatin; stir for 10 mins., then reduce the temperature to 49°C. Add the silver E then the mixture F and finally 250 cc 2% egg albumen. In the case of a very inert gelatin add 100–200 cc hypo (0·5 g per litre). Add antifoggant and if desired, gelatin solution.

328. Chlorobromide emulsion with separate precipitations of bromide and chloride (Type D)

7. Into a solution of an alkali halide and gelatin, pour, first, a solution of silver nitrate which precipitates the silver bromide. After ripening, add a chloride solution and precipitate with a second silver nitrate solution. Gelatin is then added, and the emulsion is again ripened for a suitable time before being set, washed and digested at 50°C.

The emulsion prepared in this way has relatively coarse grain. It has, however, a high contrast ($\gamma = 3$ for diapositives).

8. *Separate reversed chloride precipitation formula* (Brovira-weich Braun type):

A.	Distilled water	700 cc
60°C	Gelatin	100 g
	Ammonium bromide	30 g
	Citric acid	15 g
B.	Distilled water	1000 cc
60°C	Silver nitrate	100 g
D.	Water	1000 cc
55°C	Sodium chloride	30 g
E.	Water	2000 cc
60°C	Gelatin	400 g

Pour B into A in 10 secs. Stir 20 secs. and add D. Ripen 40 mins. at 60°C. Add E and raise the temperature to 68°C in 10 mins. Stir 25 mins. and cool. Can be washed or unwashed.

SILVER CHLORIDE EMULSIONS

329. Silver chloride emulsion types

Chloride emulsions are used to make 'gaslight' papers for printing amateur negatives. They are available in extra hard grades which enable prints to be made from very thin negatives.

Chloride papers generally give warm black or bluish-black images. The bluish-black tones are readily obtained by adding certain compounds which will be described in the next chapter. Warm black materials are more difficult to obtain commercially as the most effective antifoggants generally favour blue tones, and those which keep the warm tone are less effective stabilizers.

For the image colour to be sufficiently black, relatively coarse grain is necessary which necessitates some ripening. If the grain is very fine the image is definitely warm, and at the same time, the sensitivity is low.

Ivory and chamois chloride papers necessarily have warm tone emulsions.

There are many ways of precipitating chloride emulsions:

(*a*) The simplest is to pour the silver into an acid solution of gelatin and soluble chloride.

(*b*) The soluble chloride is added to the silver solution (reverse precipitation).

(*c*) Some silver is added to a small part of the halide, then the rest of the latter followed by the second silver addition.

(*d*) The silver is added in excess to a part of the chloride (normal precipitation). The rest of the chloride is then added to the excess silver (reverse precipitation).

Reversed precipitation generally results in high *contrast*. Contrast can also be increased by using *cadmium chloride* or a trace of *rhodium ammonium chloride.*

The addition of a small amount of bromide to the soluble chloride reduces the contrast and increases the sensitivity.

Gelatins for chloride emulsions are those with high viscosity, poor in sensitizers but rich in retarders. The presence of SO_2 reduces the contrast. Furthermore, they must not contain hydrolysis products which can form soluble silver complex compounds, and therefore promote the production of *yellow fog*. (See para. 349 F and K.)

Some emulsions are unwashed.

The principal difficulties in the preparation of commercial chloride emulsions are to obtain high contrast and to make them keep. They often need large amounts of stabilizer.

330. Chloride emulsion formulas

Normal precipitation:

A	Distilled water	1600 cc
	Gelatin	200 g
	Sodium chloride	50 g
	Hydrochloric acid	1 cc
B	Distilled water	400 cc
	Silver nitrate	100 g
C	Gelatin	80 g

Precipitation temperature: 60–65°C.

B is poured into A, quickly and with moderate agitation for high contrast, and slowly with vigorous agitation for low contrast. The emulsion is ripened at 65°C for 20–60 mins. It is then set and washed for 3 hours in running water, drained and melted at 40°C; the gelatin C is then added with 1 g sodium chloride.

The above proportions can be altered—the gelatin concentration—the dilution of solution B (which produces a softer emulsion with increased dilution)—and by introducing a little potassium iodide after ripening.

Agfa 'Lupex' type formulas

		Extra hard		Normal		Soft	
1	Gelatin	800	60°C	700	45°C	675	63°C
	Water	15000		30500		20500	
	Hydrolyzed albumen	1500		1500		1500	
	Citric acid	275		—		—	
	Sodium chloride	—		500		500	
	Potassium bromide 25%	—		—		13	
	Sulphuric acid S.G. 1·18	—		100		23	
2	Silver nitrate	1000	55°C	1000	45°C	1000	58°C
	Water	2000		16000		10000	
	Pour 2 *into* 1			*in 20 mins.*		*in 50 mins.*	
	Add						
3	Sodium chloride	565	55°C				
	Water	8500					
	Rhodium chloride	2·5 mg					
	5 N hydrochloric acid	35					
		in 40 mins.					
4	Gelatin	3800	75°C	4000		3675	
	Water	1000		Heat 25 mins.		14000	
	Potassium iodide 0·65%	230		at 60°C		200	
				Add KI sol. 200			
	Ripen	15 mins. at 70°C cool to 60°C		10 mins. at 60°C		55 mins. at 63°C	
	Add:						
5	Potassium iodide 0·65%	400		200		250	
	Ripen	10 mins. at 60°C		10 mins. at 60°C		10 mins. at 63°C	
	Add:						
6	—Mercaptobenzothiazole 1% in alcohol	50		30		50	
	Set, *wash* 2 *hrs.* and add per litre						

Agfa 'Lupex' type formulas—continued

		Extra hard	Normal	Soft
7	Gelatin	2·5	2·5	2·5
	Chrome alum	8	11	11
	Formalin 30%	3	3	3
	Citric acid 50%	1	1	1
	Hydrochloric acid N	1	—	—
	Mercaptobenzothiazole 1%	3	3	3
	Saponin 3%	50	50	50

For matt emulsions: 8–25 g rice starch.

Hydrolyzed albumen: Add 120 g egg albumen to 7 litres water at 35°C. Bring up to 70°C and add 170 cc N/10 sulphuric acid. Heat 3 hours at 90°C and filter through paper. A similar product has been prepared by treating egg albumen with 23° Bé. hydrochloric acid at room temperature.

Practice has shown that hydrolyzed albumen is not indispensable if the gelatin is suitable.

The rhodium chloride is preferably replaced by *rhodium ammonium chloride* $RhCl_6(NH_4)_3 . H_2O$ very freshly dissolved in sodium chloride solution. It is extremely effective in increasing contrast, even in very small amounts. Its presence in the normal emulsion is not necessary as the γ of 4 is adequate.

The emulsions made to the above formulas do not keep well unless a great quantity of antifoggant is included, e.g. benzotriazole. The image colour is therefore bluish.

Reflex copying papers. These papers, which are used for reflex document reproduction, that is exposure to yellow light through the support (the emulsion being in contact with the document) have a very slow orthochromatic emulsion. The emulsion must be very contrasty and have a very small toe to the characteristic curve. The light which passes through the paper the first time to reach the document, is insufficient to produce developable fog. But on the return, after reflection by the document, its effect augments that of the incident light and a developable image results. The extra hard Lupex-type emulsion is very suitable for this type of work, provided that the silver/gelatin+water ratio is increased, and the emulsion is sensitized. The reduction of sensitivity necessary for working in diffuse light is obtained by an increase in the amount of rhodium chloride, and reduced ripening.

331. Chloride emulsions, unwashed, with cadmium (Steigmann)(7)

Contrast formula:

A	Distilled water	420 cc
	Sodium chloride	7·5 g
	Cadmium chloride	0·3 g
	Gelatin	9 g
	Sulphuric acid 10%	15 cc

B	Distilled water	120 cc
	Silver nitrate	15 g

Solution temperature: 60°C.

Pour B rapidly into A, ripen 20 mins., add 54 g of gelatin which dissolves after 15 mins., add 150 cc water at 60°C and again ripen for 30 mins. at 70–80°C. Coat without washing.

Initial gelatin concentration	2·1%
Concentration after precipitation	1·6%
Concentration at second ripening	9%

Amount of silver chloride per litre of emulsion: 18 g.

Normal formula: Work as above replacing only solution A by:

A	Distilled water	415 cc
	Sodium chloride	7·5 g
	Cadmium chloride	0·09 g
	Potassium bromide	0·15 g
	Gelatin	6 g
	Sulphuric acid 10%	15 cc

Soft formula: Reduce greatly the quantity of cadmium chloride or even omit it completely:

A	Distilled water	450 cc
	Sodium chloride	7·5 g
	Cadmium chloride	0·015 g
	Potassium bromide	0·45 g
	Potassium iodide	0·015 g
	Sulphuric acid 10%	15 cc
B	Distilled water	120 cc
	Silver nitrate	15 g

Precipitation temperature: 60°C.

Pour B into A with stirring. Ripen 20 mins., add 54 g of gelatin, 15 mins. after add 180 cc of water and continue with a second ripening for 30 mins. between 70 and 75°C. Coat without washing.

High contrast formula:

A	Distilled water	420 cc
	Cadmium chloride	0·15 g
	Hydrochloric acid 31%	3 cc
	Gelatin	12 g
B	Distilled water	60 cc
	Silver nitrate	3 g
C	Distilled water	30 cc
	Sodium chloride	4·8 g
	Cadmium chloride	0·3 g

D	Distilled water	60 cc
	Silver nitrate	12 g

Precipitation temperature: 60°C.

First pour B into A with stirring. Ripen 10 mins. then, after adding C, pour in D. Again ripen for 10 mins., add 48 g of gelatin and if desired 7·2 cc of a 2% albumen solution. The gelatin is dissolved after 10 mins. After adding 120 cc of water at 60°C the emulsion is ripened a third time for 30 mins. at 70–80°C. It is coated unwashed.

Initial gelatin concentration	2·8%
Concentration after precipitation	2·1%
Concentration for third ripening	8·7%

Quantity of silver chloride per litre of the emulsion: about 17 g.

332. Chloride emulsions with cobalticyanide

According to J. H. Christensen it is possible to increase the contrast of chloride emulsions by incorporating alkali cobalticyanides.(8) Amount: less than 1 g per litre of emulsion.

To prepare the cobalticyanide, dissolve 30 g of cobalt carbonate $CoCO_3$ in acetic acid. Filter, concentrate, then pour into a warm solution of 120 g of potassium cyanide (poison) in 400 cc of water. Then oxidize by bubbling air through. Concentrate and crystallize.

The following formula has been given as an example:

A.	Silver nitrate	100 g
	Distilled water to	300 cc
B.	Ammonium chloride	35 g
	Zinc acetate	8 g
	Acetic acid	0·3 cc
	Distilled water to	300 cc
C.	Gelatin	10 g
	Acetic acid	0·3 cc
	Water to	100 cc

Pour into the gelatin C 13 cc of A and 15 cc of B then continue using double jets, the chloride always being in excess. Time 1–2 mins. Ripen 60–80 mins. at 48°C. Add the cobalticyanide and continue ripening for a further 30 mins. Washing optional.

333. Direct positive emulsions (autopositive)

Papers for development of direct positives have very slow emulsions—as slow as diazo papers. They are used for reflex document copying.

Autopositive emulsions are orthochromatic; printing is by yellow light. They are *artificially fogged* up to the solarization region. They can be fogged by light or by a fogging agent (hydrazine, sulphur compounds, controlled action of an arsenite, etc.).

Although autopositive emulsions can be bromide emulsions(9) they generally use *silver chloride*. Bayer and Cauer(10) recommend the addition of 10% silver bromide and traces of *colloidal silver* for the spontaneous development of the halide grains.

Kendall and Hille(11) have used *photochemical reversal* (para. 214) in the preparation of autopositive emulsions: a *desensitizer* is added to the silver chloride emulsion (0·1 to 2 g per 100 g of AgCl). For example, a chloride emulsion prepared from 100 g of silver nitrate has 17 mg of a desensitizer containing at least one NO_2 group added to it; it is then fogged by exposure to white light until a density of 1·2 is obtained.

Among the desensitizers which can be used are the following:

2-(o-nitrostyryl)-3-ethylbenzothiazolium iodide.
2-(o-p-dinitrostyryl)-3-ethylbenzothiazolium iodide.
2-(o-p-dinitrostyryl) benzthiazole.
2-(p-nitrostyryl)-quinoline methyl-p-toluene sulphonate 3 : 3 dimethyl-2-(p-nitrostytyl)-indolene methiodide.
6-nitro-benzo-1 : 2 : 3-triazole.
5-(o-nitrobenzylidene)-3-ethyl rhodanine.

Another method of obtaining autopositive emulsions, disclosed by Fallesen, Spence and Stauffer(12) is to produce only an *internal latent image* by the action of light. On development in a surface fogging developer only the unexposed grains are developed.

Clayden effect. High intensity illumination of short duration—produces positive images on *silver bromothiocyanate* emulsions containing a halogen acceptor (Registrier Papier L Agfa).

Positive images on silver iodide. In 1839, Lassaigne noted that silver chloride, blackened to light, faded to the latter when treated by potassium iodide. Renwick(12b) made the operation easier by adding sulphite and thiosulphate to the iodide.

Instead of chloride, a bromide lantern plate is fogged to diffuse light for a few seconds, in order to obtain a moderate latent image. Then it is immersed 10 mins. in a bath containing: water 1000 cc, potassium iodide 10 g, sulphite 10 g, thiosulphate 30 g. The plate is washed 30 mins. and dried; it can be kept only a few days. After exposure, it is developed 5 mins. to a positive in water 500 cc, amidol 5 g, sulphite anh. 50 g, to which is added, just before use, 500 cc of a 10% sodium carbonate solution. Fix in 30% hypo at 30–40°C (86–104°F) because silver iodide is not readily soluble cold.

Lüppo-Cramer(12c) succeeded in colour sensitizing these iodized plates, with erythrosin, rhodamine B, and even with phenosofranine and pinakryptol yellow which are known as desensitizers.

The initial sensitivity of the silver bromide does not affect in the sensitivity of the iodized plate.

334. Print-out emulsions (citrate papers)

Print-out emulsions consist of silver chloride to which a halogen acceptor, silver nitrate or citrate, has been added.

Formerly, print-out papers were simply prepared by first impregnating the surface of the paper with *sodium chloride*, then treating this with a solution of *silver nitrate* which left a deposit of silver chloride with an excess of silver;

this was the '*salted paper*' which could not be kept more than three days. A paper with better keeping properties could be made by replacing the sodium chloride by a mixture of sodium chloride and citrate in equal parts. *Chloride albumen paper*, which was used later, also had the disadvantage of not keeping; it was substituted by the gelatino-chloro-citrate paper and with collodio-silver chloride. The following is a formula of a gelatino-citrate type of emulsion:

A	Distilled water	860 cc
	Gelatin	132 g
	Distilled water	330 cc
	Silver nitrate	100 g
	Water	330 cc
B	Sodium chloride	27 g
	Sodium citrate	27 g

Pour A into B with stirring at a temperature of at least 45°C. Three g of salicylic acid dissolved in 12 cc of warm water, 0·4 g of chrome alum and a surface tension reducer are then added.

Alternative formula using Seignette salt (potassium sodium tartrate):

A	Water	500 cc
50°C	Gelatin	115 g
	Water	350 cc
B	Citric acid	20 g
50°C	Ammonium chloride	5 g
	Seignette salt	6 g
C	Distilled water	200 cc
18°C	Silver nitrate	50 g

Pour A into B then C into A+B. Ripen 1 hour at 50°C and add 60 cc alcohol.

Lead nitrate formula. The inclusion of lead nitrate produces more violet images.

A	Water	2200 cc
	Gelatin	215 g
B	Water	150 cc
	Potassium citrate	27 g
C	Distilled water	170 cc
	Silver nitrate	50 g
	Lead nitrate	5 g
D	Water	170 cc
	Citric acid	22 g
	Sodium chloride	5 g

Add in the order B, C, D to A.

Extra-fast formula of Dybvig and Thomson,(12c) for the detection of ionizing particles: citric acid and excess silver nitrate are added to a ripened ammoniacal coarse-grained bromide emulsion. The speed obtained with such emulsions is twenty to a hundred times higher than with ordinary print-out papers.

A 50°C	Water	150 cc
	Potassium bromide	54 g
	Potassium iodide	1 g
	Gelatin	10 g
B	Distilled water	220 cc
	Silver nitrate	64 g
	Ammonia (28%)	59 cc
C	Water	300 cc
	Gelatin	70 g
D	Water	90 cc
	Citric acid	30 g
	Ammonia (28%)	30 cc
E	Distilled water	50 cc
	Silver nitrate	9·6 g

B is poured into A in 20 mins. Gelatin C is added and the emulsion is set and washed. Then D and E are added to the melted emulsion. Higher silver content results in greater speed.

Self-toning citrate papers. Self-toning paper is prepared by incorporating a gold salt in the emulsion—chloride or thiocyanate—corresponding to 2·5 g commercial $AuCl_3$ per 100 g silver nitrate. The gold salt is preferably added to the gelatin before precipitation.

Treatment of citrate papers. After exposure, citrate papers are fixed for 10 mins. in 10% hypo. The image colour is generally an unattractive yellow, which must be toned with gold, or failing that, fixed in a lead toning fixer. Wash 15 mins.

Citrate papers keep badly. The back of the paper sometimes turns yellow. The sheets must be interleaved with *straw paper* which alone seems to guarantee fairly good stability.

Grassman has studied the sensitization of print-out emulsions with pyrimidine and imidazole derivatives.(13)

334b. Other silver salts

A great number of insoluble silver salts can give photosensitive emulsions. The most interesting have been studied by Umano and Nakamura:(13b) these are the silver orthophosphate, pyrophosphate and thiocyanate.

Silver orthophosphate. Solution A: cryst. disodium phosphate 4·8 g and gelatin 1·2 g in 100 cc water. Solution B: silver nitrate 6 g in 60 cc distilled water. Pour A into B in 10 mins. at 40°C., dialyze in distilled water for 60 mins. Add 10·8 g gelatin dissolved in 40 cc water. Coat on glass plates. After-ripening produces fog. Develop in D 72 diluted with 40 volumes water. The images are violet-red. Maximum sensitivity: 480 mμ; limit 561 mμ.

Silver pyrophosphate. Same preparation. Limit of sensitivity, 440 mμ.

Silver thiocyanate. Solution A: potassium thiocyanate 1·8 g and gelatin 1·2 g in 50 cc water. Solution B: silver nitrate 3 g in 100 cc distilled water. Solution C: 10·8 g gelatin in 40 cc water. Limit of sensitivity at 382 mμ with a maximum at 340 mμ.

Silver bromothiocyanate is used in autopositive emulsions, sensitive to Clayden effect (para. 211).

Silver nitride AgN_3. These emulsions have been prepared by R. Zemp.(13c)

COLLODION EMULSIONS

335. General properties

Collodion emulsions consist of dispersions of silver halides—iodide, bromide or chloride—in nitrocellulose. They are notable for their fine grain which confers a high resolving power (AgCl—1000 lines/mm).

Collodion is a solution of nitrocellulose in a mixture of equal parts of alcohol and ether. In the presence of water, and after evaporation, it forms a more or less permeable layer. To prepare an emulsion of a silver salt in collodion, one can either proceed directly, as for gelatin emulsions, or the collodion can first be coated onto glass, and then sensitized by bathing. The formation of the silver precipitate in the colloid is possible because the halides are generally soluble in alcohol.

Celloidin papers are silver collodio-chloride papers, generally made self-toning by incorporating a gold salt. They are still used today, although on a small scale. Coating collodio-chloride emulsions on paper necessitates a special coating machine with horizontal drying and a solvent recovery unit.

336. Wet collodion

Wet collodion was very much used at one time. A paper in 1880 was certain that this was the most practical and cheapest photographic process. It is still used today for the preparation of graticules and in photomechanical work.(14)

The plates are cleaned in dichromate-sulphuric acid solution, rubbed with a pad containing tincture of iodine, dusted with talc and cleaned with a brush. The collodion coated on such plates can be readily removed. If, on the contrary, the coating is to remain on the glass, then the plate is first coated with a thin layer of albumen, made from an egg-white beaten with 20 cc water and made up to 200 cc.

Collodion coating is carried out with a solution such as:

Alcohol (95%)	200 cc
Ether	300 cc
Guncotton	5 g
Ammonium iodide	3 g
Cadmium iodide	3 g
Ammonium bromide	1 g

The salts are ground in a mortar with several 20 cc portions of alcohol, which are added to the guncotton in a large flask. The ether is added. When dissolved, it is left several days to clarify the collodion, which is decanted.

The plates are sensitized in:

Distilled water	1000 cc
Silver nitrate	80 g
Boric acid (optional)	0·2 g

and after draining are exposed wet in a slide protected with blotting paper to absorb the excess silver nitrate. The exposure is very long.

The image can be developed physically, using the excess silver nitrate present in the layer. A solution of 50 g per litre ferrous sulphate acidified with 10 g tartaric (or acetic) acid and containing 30 cc alcohol develops rapidly. The plate is then washed. The image can be physically intensified. Fixing: in hypo.

336b. Eggert and Kleinschrod process

Prepare the following solutions in the order given:

A	Silver nitrate	8 g
	Water at 70°C	3 cc
	Alcohol 99%, tepid	240 cc
	Collodion, 4%	150 cc
B	Zinc bromide, dry	5·6 g
	Alcohol 99%	80 cc
	Collodion 4%	150 cc

Pour A into B slowly, taking one hour. Precipitate everything with distilled water; wash on the filter with distilled water, then with alcohol. Dissolve in 200 cc of an equal part mixture of alcohol and ether containing 0·5 g zinc bromide. Coat on glass plates, and preferably expose and develop before drying. Develop 5 mins. in a glycin developer and fix in hypo.

336c. Dry collodion

Collodion plates gradually lose their permeability when they are dried. This can be overcome by treatment in *tanin* which keeps the collodion porous and is dissolved on development.

The sensitized plates are washed to remove the excess silver nitrate, then immersed in:

Water	100 cc
Tanin	4 g

The drained and dried plates keep well, but they are three to five times slower than wet collodion.

337. Celloidin emulsions

Celloidin emulsions consist of *silver chloride* dispersed in dry collodion. They are *print-out* materials. Here are several preparation formulas:

Formula 1 (Mathet)	A	Alcohol 95%	200 cc	
		Strontium chloride	2 g	
		Lithium chloride	1 g	
		Nitrocellulose	12 g	
		Ether	200 cc	
	B	Distilled water	8 cc	dis-
		Silver nitrate (powdered)	14 g	solve
		Alcohol 90%	50 cc	warm

Pour A into B slowly, and with vigorous agitation. Add 50 cc of ether, 6 cc glycerin and filter.

Formula 2 (Wall)	A	Nitrocellulose	40 g
		Alcohol 95%	900 cc
		Ether	1000 cc
	B	Citric acid	3·4 g
		Lithium chloride	3·4 g
		Strontium chloride	6·8 g
		Alcohol	40 cc
	C	Silver nitrate	15 g
		Water	40 cc
		Glycerin	4 cc
		Alcohol 90%	60 cc
Formula 3 (Trumm)	A	Collodion 4%	500 g
	B	Alcohol	50 cc
		Strontium chloride 10%	3 cc
		Lithium chloride 10%	1 cc
	C	Silver nitrate solution 1 : 1	24 cc
		Alcohol	50 cc
	D	Citric acid 25%	60 cc
		Alcohol	25 cc
	E	Castor oil	1 cc
		Alcohol	25 cc
		Glycerin	2·5 cc

Formula 4	A	Magnesium chloride ($MgCl_2 . 6H_2O$)	1 g
		Alcohol 90%	100 cc
		Ether	100 cc
		Nitrocellulose	3 g

The magnesium chloride is dissolved in the warm alcohol. This is cooled before adding the ether. The mixture is shaken frequently to dissolve the nitrocellulose. The mass does not thicken until it has been left for twelve days. The silver nitrate solution is similarly prepared:

B	Silver nitrate powdered	4 g
	Distilled water, warm	4 cc
	Alcohol 90%	100 cc
	Ether	100 cc
	Nitrocellulose	3 g

Mix the A and B collodions and agitate vigorously; a very fine precipitate of silver chloride is formed and a large excess of silver nitrate remains. The following is added to the emulsion:

C	Water	0·5 cc
	Citric acid	0·5 cc
	Alcohol 90%	4 cc
	Ammonia 20%	1 drop

Formula 5		Lithium chloride anh.	5 g
(Goldberg)	A	Distilled water	20 cc
		Alcohol	70 cc
	B	Silver nitrate	24 g
		Distilled water	30 cc
		Alcohol	60 cc
	C	Citric acid	12 g
		Alcohol	50 cc
		Ether	50 cc

Fourteen cc of each solution is added to three separate 100-cc portions of 2% collodion, and the three collodions thus obtained are then mixed.

Formula 6, for matt paper:

(Trumm)	A	Collodion 4%	500 g
	B	Calcium chloride anh.	1·5 g
		Alcohol	50 cc
		Ether	30 cc
	C	Silver nitrate solution 1 : 1	30 cc
		Alcohol	60 cc
	D	Tartaric acid	0·4 g
		Citric acid	6 g
		Alcohol	95 cc
	E	Glycerin	4 cc
		Water	8 cc
		Ammonia 25%	4 cc
		Alcohol	30 cc

To make the emulsion matt, add 10 cc of an alcoholic 10% solution of dewaxed gum lac.

Gold, as chloride or thiocyanate can be added to all the emulsions given, in the proportion of 1–3 g of chloride per 100 g silver nitrate.

Treatment of celloidin paper. After exposure to daylight or mercury-vapour lamp, until a higher density than required is obtained, the paper is washed for 3 mins., then fixed for 10–15 mins. in 10% hypo. The image colour becomes colder as fixing is prolonged. Wash for one hour, drain and dry. For reddish tones, bathe the exposed paper for 5–10 mins. in 10% sodium chloride. Wash for 1 min. then fix. The tone becomes colder with longer treatment in the saline solution.

338. Polyvinyl alcohol emulsions

Polyvinyl alcohol is the polymer of the hypothetical vinyl alcohol $CH_2 = CH.OH$. It is prepared by saponification of polyvinyl acetate which gives:

$$—CH_2—CH(OH)—CH_2—CH(OH)—CH_2—CH(OH)—CH_2—CH(OH)-$$

Low polymer polyvinyl alcohol is soluble in cold water. Higher polymers are only soluble in warm water; on cooling, they form gels. Polyvinyl alcohol is known in France under the name *Rhodoviol*: type H.S. 100 dissolves cold, H.S. 10 dissolves at 60°C. Sodium carbonate, sodium sulphate, borax (1%), resorcinol, α-naphthol(15) convert the solutions to gels. Other coagulating agents are the polyphenols,(16) the o-hydroxybenzoketones, di-2-hydroxy-3-naphthoylbenzidine, etc.

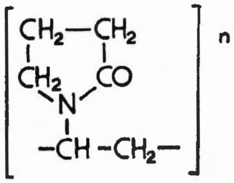
Polyvinyl alcohol can be used to prepare slow or artificially activated emulsions. *It is not miscible with gelatin.* The adsorption of polyvinyl alcohol by silver bromide has been studied by Sheppard, O'Brien and Beyer.(17)

Polyvinyl alcohol has a *retarding action* on ripening which is much greater than that of gelatin.(18)

Polyvinyl acetal can be used as a protective colloid for emulsions. It is prepared by reacting an aldehyde with polyvinyl alcohol.(19) The proportion of hydroxyl groups must be 50–60% for the layer to be sufficiently permeable. Example of preparation: a solution of 100 parts of polyvinyl alcohol in 2000 parts of water is mixed with 50 parts of hydrochloric acid and 25 parts of propionaldehyde. The acetal which separates is washed with water at 60°C. To increase the solubility of the acetal, and enable silver halide to be precipitated, it is recommended that an organic solvent, such as alcohol, acetone or cellosolve, should be added. It is also possible to precipitate the emulsion in another colloid, then add the acetal. Among the dispersion colloids are: the *copolymer of maleic anhydride and vinyl acetate* and water-soluble *ethanolamine-cellulose acetate.* The latter is prepared by reacting p-toluene-sulphonyl chloride on cellulose acetate in the presence of pyridine, then ethanolamine. Precipitation can also be carried out in a solution of *polyacrylamides.*(20)

339. Polyvinylpyrrolidones

N-vinyl-2-pyrrolidone, which is obtained from acetylene with a high pressure reaction, will polymerize to give water-soluble colloids, the *polyvinylpyrrolidones:*(21)



The British Oxygen Co. Ltd. makes polyvinylpyrrolidones with molecular weights from 40,000 to 100,000 which behave like gelatin.(22) In the U.S.A., the Gen. Aniline Corp. produces them at the Calvert city plant.

340. Sensitized cellulose

Cellophane is immersed for five minutes in an M/2 silver nitrate solution, then for 15 minutes in normal potassium bromide. The cellophane is then washed in running water and dried (Eggert and Kleinschrod). G. Sjöstedt has disclosed the following commercial process: the cellulose foil is impregnated successively with M/5 potassium iodide for 2 mins., M/5 to M/2 silver nitrate for 1 min., then M potassium bromide containing M/2 citric acid for 1–15 mins. The contrast increases linearly with the silver nitrate concentration. The sensitivity can be increased by immersing in a solution of ethylenediamine or arginine.(23)

Stachowiak(23b) sensitizes by 30 secs. immersion in a 5·6% iodide solution, then 30 secs. in a 16·9% silver nitrate solution, and finally in a bath containing 19% potassium bromide, and 2·5% nitric acid, at 28–30°C. Resulting gamma 1·2 to 1·5. With 8·5% silver nitrate and a bath containing 24% bromide + 3% nitric acid, and without any iodide, gamma is higher: 2·2.

341. Sensitized cellulose acetate

Kleinschrod and Eggert have sensitized hydrolyzed cellulose acetate in the following way:(24) a solution of 9·8 g of silver nitrate in 20 cc water with 20 cc acetone is poured, in 20 mins. at 45°C into:

Cellulose acetate, strongly hydrolyzed	11 g
Acetone at 70°C	50 cc
Water at 70°C	50 cc
Potassium bromide	7·15 g
Acetone 40%	30 cc

The emulsion is precipitated in distilled water, washed, dried and redissolved in 250 cc 40% acetone before coating. An M.Q. developer is used.

J. Seiberlich(25) has disclosed a method of sensitizing *any permeable support,* by impregnating with an alcoholic solution of silver nitrate, then exposing to the vapour of an organic bromide such as ethyl bromide.

LIPPMANN EMULSIONS

342. General properties

Lippmann emulsions, also called 'grainless emulsions', are formed of crystals of silver bromide which are so fine that they can be seen only with an electron microscope. The diameter of these crystals is between 10 and 50 mμ. Lippman emulsions are used for interference photography for the production of monochromatic filters (see: para. 493).

To obtain such fine-grain emulsions, the use of gelatin with *strong retarding power* is necessary, or artificial retarders can be added. Precipitation must be carried out with *very dilute reagents* and at the lowest possible temperature to avoid ripening. The concentration of silver bromide in the final emulsion is only 8–10 g per litre.

The chloride emulsions are more sensitive than the bromide ones. They are also less transparent. By ripening, the bromide emulsions become more sensitive than the chloride ones by rapid growth of the grains. The addition of *colour sensitizers* prevents the enlargement of the grains; the sensitivity to blue is decreased but that to the green or red is increased. In the presence of a bromine acceptor such as a bisulphite, the increase in sensitivity is accentuated, except when the dye itself is an acceptor, such as Pinaflavol.

Lüppo-Cramer(26) has stated that a grainless emulsion containing 3% iodide is less sensitive than a pure bromide emulsion. The iodide emulsion sensitivity increases on ripening faster than the bromide one, but after 3 hours it passes through a maximum and decreases after 4 hours. The bromide emulsion continues, on the contrary, to become faster.

343. Preparation of Lippmann emulsions

Formula 1 (old type). Mix the two following solutions at a temperature below 40°C:

A	Distilled water	100 cc
	Potassium bromide	1·5 g
	Gelatin	5 g
B	Distilled water	100 cc
	Gelatin	6 g
	Distilled water	15 cc
	Silver nitrate	2 g

A is poured into B with moderate agitation. Colour sensitizers are added and the emulsion is coated onto plates in a very thin layer. As soon as the emulsion is set, the plates are dipped for a few seconds in alcohol, then washed for 30 mins. They are then dried (keeping time: 6 months).

Plates prepared in this way are not sensitive enough to be used as they are. They must be hypersensitized in the following solution for 1 minute:

Distilled water	100 cc
Silver nitrate	0·5 g
Acetic acid	0·5 cc

Drained and dried, they can be used a few hours later. They can be kept for several days. The initial sensitivity is increased fifty times.

Formula 2 (classic type). The method is the same as that for a normal emulsion. The gelatin must contain sensitizers and be very rich in retarders.

A	Distilled water	120 cc
	Gelatin	8 g
	Potassium bromide	1·4 g
	Potassium iodide	0·02 g
B	Distilled water	70 cc
	Gelatin	8 g
	Distilled water	15 cc
	Silver nitrate	2 g
	Ammonia	Q.S.

Temperature: 34°C. Pour A into B very quickly with stirring. Immediately add 10 cc of 10% sulphuric acid whilst cooling. The emulsion is washed and remelted at 50°C.

Formula 3 (chlorobromide type):

A	Gelatin	40 g
	Distilled water	150 cc
	Citric acid 40%	4 cc
B	Silver nitrate	10 g
	Distilled water	10 cc
C	Distilled water	180 cc
	Sodium chloride 25%	18 cc
	Ammonium bromide 25%	16 cc
D	Gelatin	20 g
	Distilled water	70 cc
	Potassium iodide 0·65%	18 cc

Precipitation temperature 36°C. Pour B into A, then, very quickly, C into A+B. Add D molten. Cool immediately. Wash 3 hours. Melt and colour sensitize before coating.

Double-jet formula (Crawford):(27)

A	Gelatin	12 g
	Distilled water	80 cc

B	Potassium bromide	0·281 g
	Distilled water	10 cc
C	Silver nitrate	10 cc
	Distilled water	0·375 g

Temperature: 37°C.

Pour B into C, two drops per sec. Add 3 cc 2% chrome alum and 2 cc of a 0·1% sensitizing dye solution (in alcohol). The emulsion is coated on plates, washed and dried. To have perfectly smooth layers it is recommended to mould the emulsion by pouring it upon the horizontal plate (previously treated with a non-adhesion agent such as chloromethylsilane) then covering with sheet of glass held at a small distance by three pieces of steel wire or any other system. After 30 mins., the covering glass is removed with the emulsion adhering to it.

The *graininess* can be measured by the ratio of the intensities of blue light/red light diffused by the emulsion layer (3·3 to 3·7 with a 2,900°K lamp and Ilford filters violet 621 and red 608).

Resolving power: 5,000 lines/mm.

More bromide in the formula gives coarser grains.

Bromination of colloidal silver.(28) A dry gelatin layer containing colloidal silver, treated in a solution of cupric bromide, washed and dried, is sensitized in silver nitrate solution.

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1. London. H.M. Stationery Office, 1945.
2. *IX Int. Cong. Phot.*, Paris 1935.
3. Author's formula.
4. Steigmann.
5. Steigmann.
6. Steigmann A.: *Brit. Jl. Phot.*, 1946, 140; *Sci. et Ind. Phot.*, 1946, 138.
7. *IX Int. Cong. Phot.*, Paris 1935.
8 F.P. 971,858 (1950).
9. Nishimura, Furuya and Kono: *Jl. Soc. Sci. Phot. Japan*, 1951, 17–27; *Sci. et Ind. Phot.*, 1952, 262, give the following emulsion: A = water 150, gelatin 10, potassium bromide 8·8, potassium iodide 0·65, potassium chloride 0·4; B = water 35, silver nitrate 15, ammonia Q.S.; C = water 125, potassium bromide 8, gelatin 20.
10. F.P. 993,337.
11. Kodak-Pathé: F.P. 989,400 (1951).
12. Kodak-Pathé: F.P. 983,013; 1,001,730; 1,001,739.
12b. Renwick: *Brit. Jl. Phot.*, 1920, Nos. 3142 and 3143.
12c. Lüppo-Cramer: *VI Congrès Int. de Photogr.*, 1925.
12d. Dybvig H. T. and Thomson T. R.: *Phot. Eng.*, April 1954, 127–132. The image can be intensified by heating, the citrate acting as a physical developer; or by post-illumination to long wavelength radiation (Becquerel effect).
13. Grassman H.: *Zeits. Wiss. Phot.*, March 1951, 233–252.
13b. Umano S. and Nakamura N.: *Jl. Soc. Sci. Phot. Japan*, May 1954, 59–65.
13c. Zemp R.: *Thèse*, Zurich and *Zeits. Naturforsch*, 1953, 389–395.
14. Chassang C.: *La technique moderne du procédé au collodion humide*. Paris, Gauthier-Villars Ed. 1936.
15. Kodak-Pathé: F.P. 961,819 and U.S.P. 2,311,058.

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20. Kodak-Pathé: F.P. 1,055,759.
21. Reppe W.: monograph of 72 pp. *Verlag. Chemie*, G.m.b.H. Weinheim/Bergstr., 1954.
22. *Ind. Chem.*, March 1953, 122.
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23b. Stachowiack: Bild und Ton, Oct. 1955, 271–273.
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25. G.P. 660,164 (1934).
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Crawford B. H.: *Jl. Sc. Instrum.*, Sept. 1954, 333-335.
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Chapter XXI

STABILIZING AND FINISHING PHOTOGRAPHIC EMULSIONS

BROMIDE AND SILVER ION CONCENTRATION

344. Law of mass action

Consider a reversible equation of the type

$$A_2 + B_2 \rightleftharpoons 2AB$$

For each temperature there is a fixed state of equilibrium. If (A_2), (B_2) and (AB) represent the molecular concentrations of the reactants in equilibrium we have the relation $(A_2) \times (B_2)/(AB)_2 = K_{AB}$.

K_{AB} is the *dissociation constant* of the compound AB. Its reciprocal is the constant of formation.

When an electrolyte is dissolved in water it dissociates into its mobile constituents, or *ions*. For example, with silver nitrate:

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

The metallic cation Ag^+ and the acid anion NO_3^- are in equilibrium with the non-dissociated salt.

In the case of a very sparingly soluble salt such as silver bromide, the dissociation is very slight. We have nevertheless the ionic reaction

$$AgBr \rightleftharpoons Ag^+ + Br^-$$

and by applying the law of mass action to the ions we have

$$\frac{(Ag^+) \times (Br^-)}{(AgBr)} = K_{AgBr}$$

But the solution is saturated with AgBr which is present in great excess. The concentration (AgBr) therefore remains practically constant. This results in the relation

$$(Ag^+) \times (Br^-) = Ct$$

where Ct, which has a constant value, is the product of the concentrations of the ions Ag^+ and Br^-, and is called the *solubility product*.

345. Variations in the concentration of silver and bromide ions

Let us now consider an emulsion containing pure silver bromide: this is partially dissociated into its ions. The addition of an excess of Br^- ions as potassium bromide brings about a reduction in the concentration of Ag^+ ions, as the solubility product remains constant. Conversely an excess of Ag^+ ions as silver nitrate diminishes the concentration of Br^- ions.

At temperature t, the concentration of silver ions has a fixed value represented by the ordinate ma of the curve in Fig. 49, and equal to Ct. By assuming that the bromide is completely dissociated at very great dilutions, and representing the number of added KBr molecules by b, (b–x) gram-ions of new Br^- are formed, x being the number of molecules of AgBr re-precipitated. We have, therefore, $[(Ag^+)-x]\ [(Br^-)+b-x] = Ct$. By replacing (Ag^+) and (Br^-) by $\sqrt{Ct}$ we have $x^2-(b+2\sqrt{Ct})x+b\sqrt{Ct} = 0$, a simple quadratic equation.

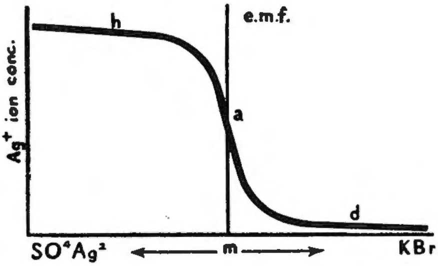


FIG. 49.

Referring again to Fig. 49, the reduction in the concentration of Ag^+ ions by adding bromide is represented by the portion ad of the curve. The addition of silver sulphate, on the contrary, reduces the concentration of Br^- ions, (Ag^+) increases along the part ah.

The silver ion concentration is shown by variations in the e.m.f. of the system.

346. Measurement of the silver ion concentration

The silver ion concentration of an emulsion is measured by immersing a silver electrode in the liquid mass, and measuring the potential compared with a reference electrode.

First, the *potential difference* is determined between a *silver electrode* in a solution of known silver ion concentration and a standard hydrogen electrode (para. 34), at a fixed temperature. As the potential of the hydrogen electrode is, by definition, zero, the potential ϵ_0 of the known solution is:

$$\epsilon_0 = \epsilon_N + \frac{RT}{F} \log (A_0^+) \text{ where } \frac{RT}{F} = \frac{\epsilon_0 - \epsilon_N}{\log (A_0^+)}$$

By repeating the operation with the test emulsion:

$$\epsilon_0 = \epsilon_N + \frac{RT}{F}\log(A^+) \text{ or } \epsilon = \epsilon_N + \frac{\epsilon_0 - \epsilon_N}{\log(A_0^+)}\log(A^+)$$

and as

$$\epsilon_N = 0{\cdot}80, \log(A^+) = \frac{\epsilon - 0{\cdot}80}{\epsilon_0 - 0{\cdot}80}\log(A_0^+)$$

If, instead of using a hydrogen electrode, a *bridge*⁽¹⁾ is made between the emulsion on one side and the known silver solution on the other, with two silver electrodes, the relation

$$e = \epsilon_0 - \epsilon = \frac{RT}{F}\log\frac{(A_0^+)}{(A^+)}$$

is obtained where e is the measured e.m.f., ϵ_0 the potential of the known solution and ϵ the potential of the unknown solution, in this case, the emulsion (para. 34).

In practice, the known solution is a suspension of silver bromide containing an excess of either silver ions (using silver sulphate) or bromide ions (using potassium bromide). The e.m.f.'s are measured by the usual electrometric methods.

The curve in Fig. 50 shows the amounts of bromide and silver sulphate which must be added to give different Ag^+ concentrations in 175 cc of emulsion containing 0·04 gram-mols. of silver bromide (7·52 g); it is seen that the neutral point is at about $\log(Ag^+) = -6{\cdot}5$, but as the emulsion already contains soluble bromide, an excess of the silver salt must be added.

The number of equivalents of KBr or $\frac{1}{2}(Ag_2SO_4)$ which must be added to 1000 mols. AgBr, to give a given Ag^+ concentration (and therefore a corresponding Br^- concentration), are as follows:

	(Ag^+)	Gm-equivalents per 1000 AgBr	
Low concentrations			
	$0{\cdot}65 \times 10^{-9}$	15	KBr
	$0{\cdot}7 \times 10^{-9}$	12·25	,,
	$0{\cdot}77 \times 10^{-9}$	11·25	,,
	$0{\cdot}9 \times 10^{-9}$	5·25	,,
	1×10^{-9}	3·5	,,
↓	$0{\cdot}7 \times 10^{-8}$	0·35	,,
Neutral point			
↑	1×10^{-8}	0·25	$\frac{1}{2}(Ag_2SO_4)$
	1×10^{-7}	1·5	,,
	1×10^{-6}	3·5	,,
	1×10^{-5}	6·75	,,
High concentrations			

Schleussner's method. The reference solution is an M/1000 solution of silver bromide obtained by adding 20 cc of M/10 potassium bromide to 10 cc of M/10 silver nitrate + 970 cc distilled water, which is kept in the dark. Two spirals of silver wire protected by glass tubes are used as the electrodes. One is used for comparison whilst the other is dipped in the emulsion.

The electrodes are connected to a sensitive millivoltmeter, the measurements being made in red light. When both electrodes are immersed in the reference solution, the potential must be zero; if not the electrodes are cleaned, first in 10% caustic (10 mins.) then in 1% cyanide (5 mins.) and finally in dilute nitric acid until bubbles are produced, before washing in distilled water. A table shows the relation between the e.m.f. in mV, the concentration of bromide in 0·0001 g/mol/litre. Temperature corrections are also included.

$$\epsilon = k \log (C_1/C_2) \text{ where } k = 0{\cdot}1985\,(273 + t)^\circ\text{C}$$

and C_1 and C_2 are the bromide ion concentrations (*Phot. Ind.*, Feb. 1941, 115).

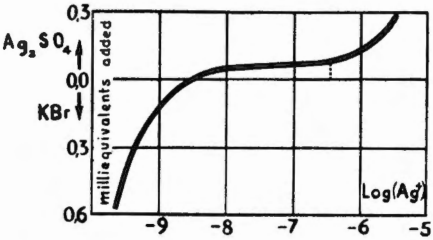


FIG. 50.

EMULSION STABILIZING

347. Effect of silver ion concentration

The *sensitivity* of a photographic emulsion increases with the *concentration of silver ions*: there is an increase of redox potential, that is, an increase of oxidizing power. We have also seen (para. 35) that this potential varies with the pH (degree of acidity or alkalinity of the medium).

Together with the sensitivity, the *fogging tendency* of the emulsion increases: the Ag^+ and Br^- ions of the silver bromide crystals give, in the presence of traces of moisture, silver hydroxide $Ag^+/(OH)^-$ and hydrobromic acid Br^-/H^+. The silver hydroxide is also reduced by gelatin, or other reducing agents, to metallic silver according to the reaction:

$$\underset{\substack{\text{Silver}\\\text{Hydroxide}}}{Ag^+/(OH)^-} + \underset{\text{Hydrogen}}{(H^+ + e^-)} \rightarrow \underset{\text{Silver}}{Ag} + \underset{\text{Water}}{H^+/(OH)^-}$$

When the specks of silver form a sufficiently large group, they make up centres of spontaneous development which produce fog. The dry emulsion when left, continues, in short, the after-ripening at a slower rate, which can, however, become appreciable when the silver ion concentration exceeds a certain value.

To retard this formation of age fog and to improve *keeping* it is necessary to maintain the Ag^+ concentration within well-defined limits. This is achieved by adding a certain amount of Br^- ions as potassium bromide, whose effect, as we saw in the preceding paragraph, is to reduce the Ag^+ concentration below the fog region. In all cases careful measurements must be made.

If an excess of Br^- is added to reduce the concentration of Ag^+ and ensure long stability, the sensitivity is also reduced. Sensitivity and stability are two opposing factors and a compromise must be reached.

Slow emulsions are more easily stabilized than fast ones; this is explained by the fact that large quantities of soluble bromide may be added without inconvenience. Thus bromide papers will keep well for three or four years whilst negative materials deteriorate much more quickly.

A shelf life of 6–12 months can only be assured for a negative emulsion if the Ag^+ concentration does not exceed $0{\cdot}5 \times 10^{-8}$, which corresponds to an addition of 2·5 KBr per 1000 AgBr. This Ag^+ concentration must not fall below $0{\cdot}8 \times 10^{-9}$ (10 KBr per 1000 AgBr) or the sensitivity will drop considerably.

The potassium bromide can be advantageously replaced by *magnesium bromide* with which both the bromide and magnesium ions are effective. Two to 4 cc of a 1% solution can be added, before after-ripening, to a litre of negative emulsion.

The nature of the emulsion influences the stability greatly: the degree of degradation and activity of the *gelatin* are the main factors. Furthermore, *ammoniacal emulsions* are less stable than neutral ones. Ammoniacal emulsions after-ripened at low temperatures are more stable than those digested at a high temperature.

The most important external influences which must be considered are *temperature* and *humidity*: they can bring about rapid changes in sensitive layers, by favouring the mechanism given above.

The *loss of sensitivity* on storage of photographic layers appears to be due to an oxidation reaction, especially by atmospheric oxygen. On the contrary, the *increase of superficial fog* is inhibited by oxygen.(2) In both cases the changes are accelerated by humidity and temperature. *Internal fog* is attributed to thermal agitation in the interior of the crystal.

To study the keeping properties of dry emulsions they are artificially aged by being left in an *oven* at 40–50°C. The results obtained are not absolutely identical with those of natural ageing, but very useful information is obtained.

Desiccated films. To ensure good keeping, a sensitive layer must be carefully dried. The desiccants which are generally used are calcium chloride, preferably absorbed on active carbon, and silica gel. Anhydrous calcium sulphate, activated alumina, crumpled paper, cotton, rice and tea leaves are also desiccants but less effective.

Before unrolling desiccated films, they must be rehumidified by leaving for 48 hours in a room at a suitable relative humidity. Unless this precaution is taken, static discharge sparks are liable to occur on unrolling, which affect the film.

348. Low temperature storage

Sensitive materials, particularly high-speed and colour ones, can be satisfactorily stored at low temperatures. Even for short-term storage it is inadvisable to exceed 25°C (77°F). It is recommended that films be kept at 15°C (59°F) if stored for 6 months and at 10°C (50°F) for 12 months.

A *very low temperature* of about −15°C (5°F) ensures even greater stability, provided that the films are put into *sealed containers*. For use in tropical conditions solid carbon dioxide (−70°C) can be used advantageously.

The wrappings of refrigerated films must not be removed before warming up to normal temperature or condensation of atmospheric water may occur on the material.

After manufacture, films are conditioned in an atmosphere of 40–60% R.H., and the water content of the emulsion does not exceed 15%. Refrigeration and hermetic sealing does not result in internal frosting unless the water content reaches 34%.⁽³⁾

349. Organic antifoggants

A large number of organic compounds have strong antifogging properties. Some of them stabilize emulsions much more effectively than the bromides. When added to chloride emulsions the antifoggants produce bluish colours, with the exception of certain mercapto derivatives.

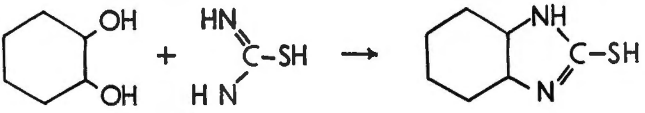
As a general rule, the solubility of the silver salt of an antifoggant must be lower than that of silver bromide,⁽⁴⁾ which results in a reduction of the Ag^+ concentration around the crystal.

A. *Cyclic amines.* Diphenylamine $C_6H_5—NH—C_6H_5$ (in a concentration of 1 mol. per 100 mols. AgBr) and certain benzidine derivatives having at least two NH_2 groups.⁽⁵⁾

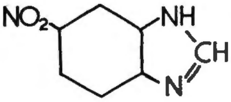
B. *Iminazoles.* The best known of these compounds is 6-nitrobenziminazole.⁽⁶⁾ It occurs as pink needles M.Pt. 207°C. It gives a nitrate which is used in practice (M.Pt. 215–225°C with decomposition). Solubility in 50% alcohol: 0·5%; in 10% caustic soda: 1%. Concentration: 10–30 mg per litre of emulsion.

The benziminazoles are prepared from the o-phenylenediamines and the iminoethers.⁽⁷⁾ p-nitrobenziminazole can be prepared merely by boiling nitro-o-phenylenediamine with formic acid.

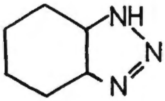
Mercaptobenziminazole is a very active stabilizer⁽⁸⁾ and an antioxidant. It is prepared by condensing thiourea with pyrocatechin.



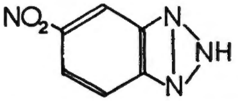
However, 2-thio-4-methyl-5-acetyliminazole is better.



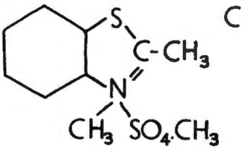
p-nitrobenziminazole



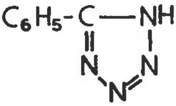
benzotriazole



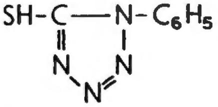
p-nitro-*pseudo* azimidobenzene



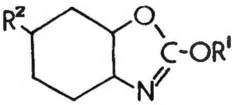
2-methylbenzthiazole methyl sulphate



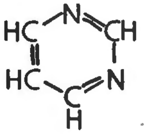
5-phenyltetrazole



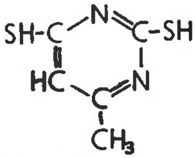
1-phenyl-5-mercaptotetrazole



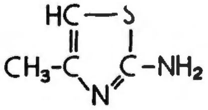
oxybenzoxazole



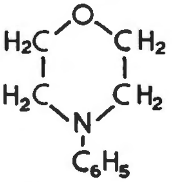
pyrimidine



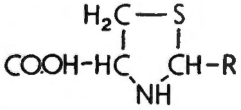
4-methyl-2:6-dimercaptopyrimidine



2-amino-4-methylthiazol



phenyl-morpholine



4-carboxythiazolidine

The thioiminazoles reduce the sensitivity considerably, with the exception of 3-allyl-2-dimethyl-2-thiohydantoine.

C. *Triazoles.* The benzotriazoles are widely used in the manufacture of photographic emulsions, as well as for development antifoggants. Ordinary *benzotriazole* is in the form of white needles melting at 93–97°C. One g of the pure compound will dissolve completely in 100 cc water or 100 cc absolute alcohol. It is better to use it in aqueous alcohol. Concentration: 10–20 mg per litre of emulsion.

Benzotriazole is estimated argentometrically in caustic solution. Bromide and iodide are detected, according to the A.S.A. standard, by adding to 5 cc of 1% aqueous solution: 1 cc of concentrated sulphuric acid then 5 cc of a solution of 1·5% ceric sulphate and 1·5% sulphuric acid. When the mixture is shaken with 1 cc chloroform, the latter must not be coloured.

5-methylbenzotriazole is a white crystalline powder melting at 80–84°C. *p-nitro-ψ-azimidobenzene* is a benzotriazole.

The benzotriazoles are prepared by the action of nitrous acid on the ortho-diamines (see Noelting, *Ber.*, **20**, 3001).

D. *Tetrazoles.* The tetrazoles, to which attention was drawn by Steigmann, have a 5-atom nucleus. The phenyltetrazole derivatives having an active mercapto or imino group are effective stabilizers for neutral emulsions.

Murobushi, Ichifugi and Ashikawa⁽⁹⁾ have given the following, used at a concentration of 10^{-4} mol. per molecule of silver nitrate.

1-phenyl-5-mercaptotetrazole (strong ripening retarder).
5-phenyltetrazole.
5-(m-nitrophenyl)-tetrazole.

E. *Thiazoles.* The derivatives of *2-methylbenzthiazole* are antifoggants, including the methiodide (or ethyl-p-toluenesulphonate) of 2-methylbenzthiazole added in a concentration of 20–80 mg per litre of emulsion.⁽¹⁰⁾

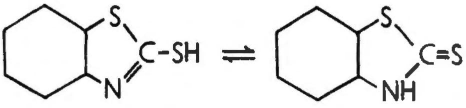
Suzuki and Toriu⁽¹¹⁾ have studied *2-amino-4-methylthiazole* and *2-diethylamino-4-methylthiazole.*

Kashida, Yokota and Hai⁽¹²⁾ have prepared a *2-aminothiazole-5′ : 4′ : 5 : 6-quinoline* which stabilizes neutral and ammoniacal emulsions. To prepare this substance, dissolve 4·6 g of 6-aminoquinoline in 61 g of glacial acetic acid cooled in ice and salt. Add 18 g of potassium thiocyanate dissolved in 90 g acetic acid, then, drop by drop, 5·4 g bromine dissolved in 45 g of acetic acid. After 12 hours, the solution is concentrated in vacuo, water is added and the solution neutralized with sodium carbonate. The product is recrystallized from methanol (Yield 4·8 g).

Kashida⁽¹²ᵇ⁾ has also disclosed *2-thio-4-methyl* and *2-thione-3-benzyl-4-methylthiazole* and *2-benzylidenehydrazino-4-oxathiazoles.*

F. *Mercaptobenzthiazoles.* Mercaptobenzthiazole is sometimes used as an antifoggant, especially in silver chloride black tone emulsions at a concentration of 20–30 mg per litre of emulsion, and in bromide emulsions, before washing, using 1–3 g per kg of dry gelatin. It is, however, a weak antifoggant and it is better to use 2-methylmercaptobenzthiazole. Against *yellow fog,* 200 mg of mercapto derivative is necessary per kg of gelatin.

Mercaptobenzthiazole exists in two tautomeric forms:



The N-ethyl and N-benzyl derivatives have a better stabilizing action than the simple compounds.⁽¹³⁾ The benzyl derivative is slightly soluble and gives bluish toned images with silver chloride.

For the preparation of mercaptobenzthiazole, see the patents listed.⁽¹⁴⁾

G. *Oxazoles.* The oxazoles are considered superior to the corresponding thiazoles as stabilizers as they reduce the emulsion sensitivity less. They are used at a concentration of 20–30 mg per litre.

Mariani and Martinelli have, in a recent paper,⁽¹⁵⁾ disclosed *2-hydroxybenzoxazole* and *2-hydroxy-6-nitrobenzoxazole* as very efficient stabilizers.

The mercaptobenzoxazoles correspond to the mercaptobenzthiazoles. With them, chloride emulsions retain their black tone. Concentration: 20–30 mg per litre.

The antifogging properties of the thiazoles and the oxazoles is again found in indoline derivatives such as 1-methyl-dimethylindoline dimethylsulphate.

H. *Thiosemicarbazides.* Thiosemicarbazide with the formula NH_2—CS——NH—NH_2, prepared from hydrazine sulphate and potassium thiocyanate, is an antifoggant. The *aldehyde-semicarbazones* are, however, more active.(16)

I. *Pyrimidines.* Pyrimidine derivatives are strongly adsorbed onto the surface of the grains, which to some extent explains their strong antifogging action. Kikuch and Sakaguchi(17) have measured the normal free energy to form the silver salt, and the solubility product of fifty-five pyrimidine derivatives.

Pyrimidine has a 6-atom nucleus having two nitrogen atoms in the 1 : 3 (meta) positions. Koseki and Fukawa(18) have prepared and studied the photographic properties of thirty-three derivatives.

The best antifoggants are the following:

2-mercapto-4-methylpyrimidine.
2-mercapto-4-methyl-6-hydroxypyrimidine.
2-mercapto-5-methyl-6-hydroxypyrimidine.
2-mercapto-3-allyl-4-methyl-6-hydroxypyrimidine.
2-mercapto-4 : 6-diaminopyrimidine.
2 : 6-dihydroxy-4 : 5-diaminopyrimidine.
4-methyl-2 : 6-dimercaptopyrimidine.

The amount of any of these compounds which is required is at least 3–6 mg per litre of bromide emulsion. Kendall had already disclosed the *2-mercapto-4-hydroxy* and *2-amino-4-hydroxypyrimidines.*(19)

The halogenated hydroxypyrimidines have been claimed by Knott,(20) for example the *5-chloro-* or *bromo-2 : 6-dihydroxypyrimidine.* Amount: 10–20 mg per litre of emulsion. *Thioderivatives* of 2 : 6-dihydroxypyrimidine were disdisclosed by Sheppard and Vanselow.(21)

J. *Thiazolidines.* The 4-carboxythiazolidines which are, as we know, contrast modifiers (para. 270) can, depending on the example, be fog producers or antifoggants. The derivatives of *penicillin* are thiazolidines:(22) the penicilloic, penicillic and penaldic acids and penilolaldehyde. They are all retarders of chemical ripening. Penicillamine is a fogging agent. Tajima and Kawaguchi(23) have prepared 2-styryl-4-carboxythiazolidines which are weak sensitizers or desensitizers with maximum activity in acid medium.

K. *Iodonium derivatives* have been disclosed by Steigmann.(24) They are primarily very effective *anti-yellowing agents*. The *Antiflavog* of 'Felix Sager and Dr Grossler' (Heidelburg, Germany) is diphenyliodonium nitrate and is used in amounts from 100–200 mg per litre of chloride emulsion. To prepare it(25) dichlorophenyliodide $C_6H_5ICl_2$ is converted to iodosobenzene, C_6H_5IO, then to iodoxybenzene $C_6H_5IO_2$. This, treated with silver oxide, then with sodium nitrate, gives diphenyliodonium nitrate. By combining the latter with benzotriazole in the presence of ammonia, an addition compound, *Antipanog*, is formed which is an anti-yellowing agent and an antifoggant, used at a concentration of 40–150 mg per litre of emulsion.

Kashida has recommended, as a particularly active antifoggant, *4-(2′ : 4′-diiodophenoxy) quinaldinic acid.*(12b)

L. *Thiobarbituric acids.* The thiobarbituric acids, related to the pyrimidines, have an antifogging action in a concentration of 10^{-5} to 10^{-6} compared with the amount of $AgNO_3$. Among the most active we would mention phenyl-thiobarbituric acid, 2-hydroxylidine-thiobarbituric acid and 3-methoxy-4-hydroxybenzylidine-thiobarbituric acid.(26)

M. *Benzene-sulphinic acids.* The benzene-sulphinic acids are prepared by treating benzene with aluminium chloride, first in a current of hydrogen chloride, then a current of sulphur dioxide at a temperature below 10°C. At a concentration of 3–5 g per litre they have an antifoggant action with some emulsions. *They are used as antioxidants in photographic emulsions.*

N. *Alkaloids.* Especially the hydrochlorides of *quinine* and *quinidine* at a concentration of 1 mol. per 100 AgBr. Sheppard and Vanselow have disclosed morpholine derivatives such as *phenyl-morpholine.* Concentration: 20–400 mg per litre. Other very effective antifoggants are *2′-aminothiazole-5 : 6 : 5′ 6′-hydrocinchonidine* and its derivatives. 2-picolic acid is also active.

O. *Thioanilides* such as thioacetanilide.(27) These compounds are strong desensitizers.

P. *Saccharin and pyrazoline derivatives.*(28)

Q. *Brominated fatty acids* and *acetylene dicarboxylic acids* as their soluble salts.

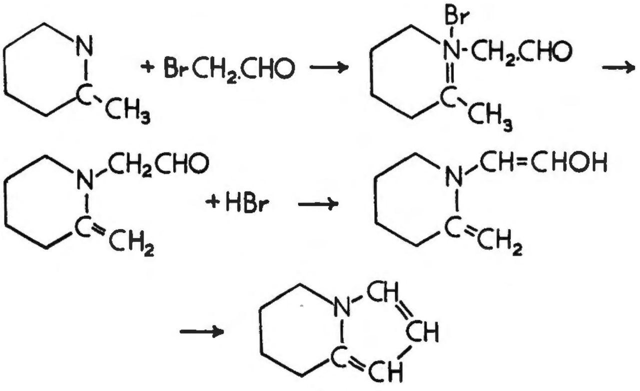
R. *Protein degradation products*: cysteine(29) and histidine(30) hydrochlorides.

S. *Allylaminothiodiazole hydrosulphide* and *2 : 6-dimercapto-4-keto-3 : 5-diphenylpenthiophene.*(31)

350. Indolizines

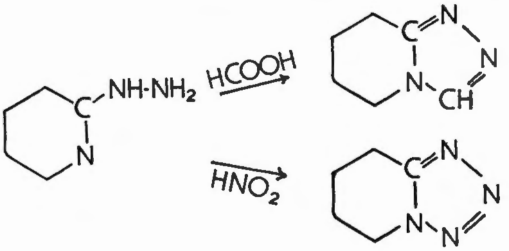
The most remarkable of all the photographic emulsion stabilizers are the *aza-indolizines* discovered in 1935 by Birr.(32) They were kept secret for many years, and enable gold sensitizers to be used which, as we know, produce considerable storage fog.

Indolizine is produced by reacting picoline (or methylpyridine) with bromacetaldehyde, following the scheme of Tschitschibabin:



Indolizine

An *azaindolizine* is obtained when the starting compound is α-hydrazinopyridine. It is reacted with nitrous or formic acid (Markwald and Rudzik):(33)



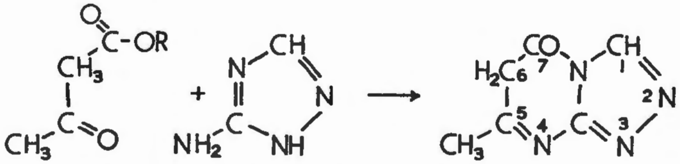
2:3-diazaindolizine

1:2:3-triazaindolizine

α-hydrazinopyridine

With formic acid, a diazaindolizine is produced, and with nitrous acid, a triazaindolizine.

It is possible to obtain more complex derivatives by the action of an aminotriazole on an acetoacetic ester, by Bulow and Mitarbeiter's method:(34)



acetoacetic ester 3-amino-1:2:4-triazole 5-methyl-7-oxy-2:3:4-triazaindolizine (enol form)

5-methyl-7-oxy-2 : 3 : 4-triazaindolizine is a powerful stabilizer. It is used in 1% aqueous solution.

There is also *4-hydroxy-5-ethyl-6-methyl-2 : 3 : 7-triazaindolizine.*(34b)

With a tetrazole, a 1 : 2 : 3 : 4-tetrazaindolizine is formed. The indolizines can, however, have very varied constitutions and it is easy to see that the number of these derivatives is very great.

In general, a 3-amino-1 : 2 : 4-triazole is condensed with ethyl ethoxymalonate to produce a *6-carbethoxy-5-hydroxy-2 : 3 : 4-triazaindolizine.* Cat and Van Dormael(35) reacted other amines of cyclammonium bases such as 2-aminobenziminazole, 4-phenyl-2-aminoiminazole, 4 : 5-diphenyl-2-aminoiminazole, etc. with acetoacetic esters, malonic nitriles, and cyanacetic esters. These esters have two reactive groups such as keto, nitrile, aldehyde or ester, in the β position.

Birr and Walther(36) have recently shown that the 1 : 3 : 4-triazaindolizines are formed in fact with the nitrogen atoms in the 2 : 3 : 4-positions; position 1 being that which immediately follows the middle nitrogen adjacent to the two nuclei.

351. Use of antifoggants

Antifoggants are either added to the emulsion or to the developer. Added to the emulsion, they confer stability, therefore long storage life. The *concen-*

tration used in this case is in the order of 20 mg per litre of negative emulsion, although this amount can vary widely according to the type of emulsion, the degree of after-ripening, the purity of the gelatin and the nature of the antifoggant. It can be as high as 300 mg per litre with chloride emulsions containing 20 g silver nitrate per litre. The optimum amount can only be found empirically.

The simplest *method of use* is to add the antifoggant (in aqueous, alcoholic or aqueous-alcoholic solution) *after digestion* at the same time as the other 'finals'. It is also possible, and frequently advantageous, to add a small amount before digestion in place of the bromide, to slow down chemical ripening and prevent the production of a high fog level. In some chloride emulsion formulas, it is even added before washing, but this does not dispense with a final addition.

The *actual effectiveness* of an antifoggant can only be shown by experiments with the coated and dried emulsion kept over long periods at normal temperatures. A rough idea of its action can be obtained by *prolonged digestion* for several hours, then by an *oven test* on the dry emulsion (10–60 hours at 40°C (104°F) in a dry atmosphere). No absolute value should be given to the results obtained, as *time and temperature do not have equivalent effects.*

Bluish tones are generally produced by the addition of antifoggants to chloride emulsions. The antifoggants include nitrobenziminazole, benzotriazole, methylbenzthiazole, quinine hydrochloride and ethylbromacetate. If the bluish tones are undesirable, certain mercapto derivatives can be used to avoid the effect.

Addition to the developer. The antifoggant can be added to the developer in a concentration of about 200 mg per litre. Too great an amount can bring about a reduction of sensitivity. The addition of benzotriazole to developers for chloride emulsions can produce bluish tones.

EMULSION FINISHING

352. Finals

Before an after-ripened emulsion is coated on its support, certain compounds must be added to it to produce certain photographic characteristics, to ensure good storage and to facilitate coating. These are:

1. *Water* to adjust the coating weight.
2. An *antifoggant*—necessary.
3. A *pH buffer*—optional: citric acid, mono- or disodium citrate, etc. Sheppard[(36b)] disclosed diethylbarbituric, malic, malonic, diethylsuccinic acids, etc. as buffers.
4. A *sensitizing dye*—optional: for colour sensitizing.
6. A *removable filter dye*—optional—such as tartrazine, using 30 cc of a 2% solution per litre of emulsion, to limit light penetration; or a permanent pink dye for warm tone papers.
6. An *antioxidant*—optional—such as sodium benzene-sulphinate or pyrocatechin (colour emulsions).

7. An *antiseptic*—optional.
8. A *matting agent*—optional.
9. A *hardener*—necessary.
10. A *wetting agent*—necessary.
11. *Alcohol* to reduce viscosity—optional.
12. A *plasticiser*—optional—1 : 1000 glycerin.
13. *In the case of chloride emulsions, a contrast stabilizer.* Developed chloride images lose contrast when dried hot. This phenomenon is due to the aggregation of silver particles with an increase in reflecting power.

Traces of various compounds can be used to prevent this loss of contrast: mercaptans, compounds with imino groups (in basic medium), potassium iodide, selenosulphate, selenites, tellurites, mercuric nitrate, chloroauric acid, chloroplatinic acid, etc. (See Schwartz: *Ind. Eng. Chem.*, Anal. Ed., 1940, 369.)

353. Antiseptics

The antiseptics suitable for use in emulsions are *phenol*, *thymol*, *methyl p-hydroxy-benzoate* and *p-chloro-m-cresol.*

Methyl p-hydroxybenzoate (Solbrol, Nipagine T) can be used at a concentration of 0·2–1% of the weight of dry emulsion. It is first dissolved in alcohol.

When *phenol* is added to emulsions made with some poor gelatins, in quantities greatly in excess of those required for antiseptic purposes, it serves as an excellent antifoggant: 4 g of phenol in 8 cc alcohol and 10 cc water for a litre of emulsion containing 60 g AgBr.

There are many other strong antiseptics but their action towards photographic emulsions is not well known.

Sodium orthophenylphenate: four times as active as thymol or methyl p-hydroxybenzoate.

Sodium pentachlorophenate (Xylophene, Santobrite).

p-chlorometaxylenol.⁽³⁷⁾ One part to 1000 dry gelatin. Soluble in water to 0·5%.

Cationic surface active agents such as lauryl-dimethylbenzyl-ammonium (Zephiran) can be used as antiseptics even at 1 : 20,000. These compounds appear to arrest the growth of bacteria rather than kill them.

354. Matting agents

Matt emulsions are obtained by simply adding *starch* prepared as follows:

Rice starch	100 g
Cold water	150 cc

Make into a paste, add 180 cc water at 55°C then filter.

The amount for 1 litre of emulsion is 40 cc. Reduce to one-half or one-third for semi-matt materials. Films are generally only made matt on the back.

Matt surfaces are also obtained by precipitating ethyl cellulose or cellulose acetate in the emulsion.⁽³⁸⁾

Colloidal silica is replacing starch. Kaolin gives rough surfaces.

355. Hardeners

The gelatin of negative emulsions is hardened with *chrome alum*. The amount of chrome alum is 1% of the weight of gelatin. It is used as a freshly made 5% solution which is added slowly with sitrring to avoid any coagulation. In paper emulsions, from 1·6–2% of the weight of gelatin is used.

Compounds of *zirconium* and other tetravalent metals of group 4 of the periodic table have been disclosed for replacing chrome alum.(39)

For hardening the gelatin of paper emulsions, *formalin* or formaldehyde is widely used as well as chrome alum (which has the advantage of increasing the viscosity. The addition of enough formalin completely hardens the gelatin, *but after a period of at least 15 days*, enabling it to be glazed with no risk of melting. If too little formalin is used the gelatin melts and sticks to the plate or the blanket; if too much is used, the paper, as it ages, leaves unglazed spots on glazing. The amount which is necessary depends on the nature of the gelatin and on its initial physical state.

Commercial solutions, said to be 40%, have a density of 1·090 at 15°C. They contain 360–380 g H.CHO per litre. To avoid polymerization to paraformaldehyde, 10–15% methanol is frequently added.(40) Dilute solutions polymerize less readily. Formalin is estimated colorimetrically using Schiff's fuchsine reagent.(41)

Concentration of formalin for paper emulsions: 16–24 cc of solution diluted with four parts of water for 100 g gelatin, that is, 3·2–4·8 cc of concentrated 40% solution to 100 g gelatin. If the initial concentration is 30% the calculation must be adjusted.

Many organic hardeners have been proposed to replace formalin which has the *disadvantage of accelerating emulsion fog* to the detriment of good keeping, and it also has a choking odour.

Glyoxal, the dialdehyde of glycol, CHO—CHO, is sometimes used.(42) Its commercial 30% solution contains polymers, 5% glyoxylic acid, 2% acetic acid, 0·03% formalin and 0·18% of inorganic matter. D = 1·25, pH = 3·5–4·5. Glyoxal has no odour. From the photographic viewpoint, it can produce *fog* in rapid negative emulsions and a *loss of contrast* in paper emulsions. Amount for positive bromide emulsions: 8 cc of 30% concentrated solution for 100 g gelatin, in addition to chrome alum.

Dihydroxymethylurea (Finish EN—Sandoz; Ureol AC—Ciba) at a concentration of 4 g per 100 g gelatin hardens but reduces contrast.

The *dihydroxyketones* at a concentration of 0·5–5 g per 100 g gelatin,(43) including fructose and p-hydroxybenzoylcarbinol. Also halogenated ketones: dichloroacetone.

White(44) has disclosed the use of halogenated derivatives of the *aldehyde acids* such as dibromo-butenaloic acid, at a concentration of 0·5–5 g per 100 g gelatin. It is also called mucobromic acid COOH—CBr = CBr—CHO, and is obtained by Simonis' method.(45) If the pH of the emulsion is above 7, use the corresponding sodium salt.

Variations in the melting point during storage can be prevented, according to Sheppard and Houck(46) by adding a *hardening accelerator*, such as resorcinol, phloroglucinol, cresol, thymol, etc. Concentration: 0·2% of the weight of gelatin.

Hydroxyaldehydes up to the pentoses, such as arabinose.(47)

Aminoaldehydes(48) like piperidinoacetaldehyde hydrochloride or diethyaminoacetaldehyde at a concentration of at least 0·5 g per 100 g gelatin.

The condensation products of the *dialkylamines* with formalin are also gelatin hardeners.(49)

Worwell and Kaye have put forward the hypothesis that the hardener combines (at the isoelectric point) with the amino groups of the lysine derivatives. In acid solution attachment is via the glutamic acid groups.(50)

356. Wetting agents

Gelatin is a compound which is made hydrophilic by its —CO . NH— and amino groups; it is made hydrophobic by its $—CH_2—$ groups. A gelatin layer, coated and dried has its hydrophobic groups outermost. This prevents wetting with water, although organic solvents readily make contact. This is the reason why a *photographic emulsion coated onto a gelatin treated base cannot stick perfectly without the use of a wetting agent.*

Surface tension. The wetting agents, also called surface active agents, have the property of lowering the surface tension of liquids.

This tension is the force, in dynes per cm necessary to break the contact between a platinum ring touching the liquid (Lecomte Du Nouy tensiometer). It can also be measured by the Wilhelmy method which is to partially immerse a sheet in the gelatin solution or emulsion. Surface tension supports the sheet. It is enough, to balance the resulting couple, to find the force exerted on the sheet by the liquid. The Dognon-Abribat tensiometer is suitable for this measurement. Perfect wetting of the sheet is assured by making the surface matt. The emulsion temperature must be kept constant with a thermostat.

A surface-active agent is a compound in which one part of the molecule is hydrophilic and the other is lipophilic. The hydrophilic part is made up of a polyalcohol, a sulphate or a sulphone group, the lipophilic group is a hydrocarbon chain. If, for example, the lipophilic chain of an oleic compound is always oriented *out of* the water (weak hydrophilic force) the attachment of polyethylene oxide chains makes this substance hydrophilic and literally draws the oleic chain *into* the water.

The surface-active agents are divided into three groups:

(*a*) *Anionic wetting agents*: that is, when only the anion is active, for example, the sulphonated, sulphated or carboxylated fatty alcohols. The salt-forming groups are, respectively, $—SO_3Na$, $—OSO_3Na$ or —CO . ONa.

(*b*) *Cationic wetting agents* or ammonium quaternary salts in which the fatty radical is positively charged. Example, hexadecyltrimethylammonium bromide:

$$[R—N \equiv (CH_3)_3]^+Br^-$$

(*c*) *Non-ionic wetting agents.* These are the saponins, the hydroxyethyl fatty substances (Peregal O, Cemulsols) and phenolic side chain compounds.

Only the anionic and cationic compounds are used in practice as emulsion additives for coating. The cationic compounds are used in development to reduce the induction period.

An important condition of the use of a wetting agent is its *chemical inertness towards the emulsion.* Sensitometric and storage tests must precede its experimental use. Fog can be produced by impurities in the product.

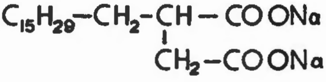
Saponin is the most widely used wetting agent for emulsion coating although it has only moderate surface active power.(50b) It is a natural product of uncertain chemical constitution, and its activity varies with its source, which must be carefully controlled. The sources are still quillaya bark, horse-chestnuts and soapwort root. Saponin is used in a concentration of 5–10 cc of a 5% solution per litre of emulsion.

Alkyl sulphates with the general formula $R.CH_2—O.SO_3.Na$ are improperly called sulphonated fatty alcohols. The fatty portion contains 8–15 carbon atoms. The most common are sodium *capryl-*, *undecenyl-*, and *lauryl sulphates* $CH_3—(CH_2)_{10}—CH_2—O—SO_3Na$. *Teepol* is a mixture of secondary alkyl sulphates of caprylic to stearic alcohols at a concentration of 21%.

All of these compounds must be in the pure state, otherwise storage fog will be produced.

The surface tension of water is reduced from 70 to 45 dynes by adding 20 mg of the dry product per litre.

The *succinic sulpho-esters* are very active, especially those from 1-methyl-4-ethyl-hexanol.(51) They are obtained by reacting ethyl maleate with sodium bisulphite. Another interesting succinic derivative is sodium pentadecylene-succinate with the formula



$$C_{15}H_{29}-CH_2-\underset{\substack{|\\ CH_2-COONa}}{CH}-COONa$$

Condensation products of succinic anhydride with tertiary amines including a group which can react with carboxyl bases has also been disclosed(52) for example, tetradecylene succinic anhydride and diethylethanolamine.

Two other surface active agents suitable for use in emulsions are:

Nekal BX—sodium isobutylnaphthalene-sulphonate.

Igepal C—condensation product of a dodecylphenol with ethylene oxide. Concentration 8 cc of 4% solution per litre.

Superimposed emulsions. Better adhesion between superimposed emulsion layers is achieved if the two wetting agents are of different types, e.g. a succinic derivative and Nekal BX, Saponin and Igepal, Igepal and Nekal, etc.

357. Antifrothing agents

Wetting agents have the disadvantage that they encourage frothing, which is a great nuisance during coating. It is often necessary to stand the finished emulsion before running into the coating trough. The addition of certain alcohols can rapidly disperse froth: *butyl*, *amyl*, *benzyl alcohols* or better, *2-ethylhexyl alcohol* (2-ethylhexanol of the Carbide and Carbon Chemical Co.) and *3 : 5 : 5-trimethylhexyl alcohol* (Nonanol—I.C.I.).

These compounds are also, like the amyl alcohols, energetic surface active agents. They can therefore bring about a pronounced reduction in surface tension if too high a concentration is used and if another layer is coated on top this operation would be made more difficult. The amyl alcohols have a very choking smell.

Another variety of anti-frothing compounds includes glycerin and glycol esters such as *glyceryl monolaurate* or *propylene glycol monolaurate.*

358. Viscosity of emulsions

It is important to know the viscosity of emulsions as it controls the thickness of the layer. It depends on the *gelatin concentration*, the natural *viscosity of the gelatin* and the *amount of hardener* added (especially chrome alum). It can be reduced by adding water or alcohol.

The viscosity of an emulsion increases with the *time* which the emulsion is *left* in the coating machine, due to the progressive hardening action of the hardeners. It is important to bear this in mind.

The viscosity drops as the temperature rises but this reduction is not proportional. The viscosity drops violently around the setting point but as the temperature increases the variation becomes of less and less importance. If the emulsion sets at 27°C (81°F) the drop in viscosity is almost insignificant around 40°C (104°F). It is, on the contrary, very definite between 32 and 36°C (90–97°F). The progress of this phenomenon can be respresented by a hyperbolic curve.

According to Bogomolov, the setting temperature is given by $t_{gel} = 22{\cdot}8 + 0{\cdot}13\eta_{39}$ where η_{39} is the viscosity in centipoises at 39°C. The viscosity is related to the temperature t by the relation $\eta = B\sqrt{t - t_{gel}}$ where B is a characteristic constant of the emulsion. Shor(53) has shown that the curves $\log \eta = f(t)$ are in fact formed of two straight lines which cut at about 35°C. If the viscosity at 40° is known, then:

$$\text{at } t < 35^\circ\text{C}: \eta_t = \eta_{40} \times 10 \exp(0{\cdot}40 - 0{\cdot}1t) \text{ with } \frac{d\eta}{dt} = -0{\cdot}025\,\eta$$

$$\text{at } t > 35^\circ\text{C}: \eta_t = \eta_{40} \times 10 \exp(0{\cdot}75 - 0{\cdot}02t) \text{ with } \frac{d\eta}{dt} = -0{\cdot}05\,\eta$$

Viscosity measurement. The viscosity is due to internal resistance which opposes the flow of a liquid, that is, a displacement of its molecules relative to each other. It is therefore a negative force. The unit is the *poise*; it is the opposite of a force of 1 dyne.

If the rate of flow of an emulsion or a simple solution of gelatin down a capillary tube maintained at constant temperature by circulating warm water is measured, the *coefficient of viscosity* is given by the formula $\pi r^4 pT/8lV$ where V is the volume which flows out, T the time to flow, p the flow pressure, r the radius of the tube and l its length. The *specific viscosity* is given by comparison with that of water which is fixed at 100. To do this, viscometers similar to the Baumé one is used. The French A.F.N.O.R. apparatus consists of a cylinder of thick brass whose conical base is drilled with a calibrated hole. The cylinder is first plunged into hot water at the same temperature as the emulsion, drained and filled to the brim with emulsion whilst the hole is stopped up. An outer rim enables the apparatus to be filled to the brim. The emulsion is allowed to run out and the time in seconds is noted whilst a small thermometer is put into the liquid to determine its exact temperature. The opening in the instrument is chosen to give a flow time in the order of 90 seconds.

A more rapid method of measuring the viscosity, is to rotate a cylinder in the liquid and measure the opposing force. This is the principle of the Couette-Sheppard apparatus. Another very convenient instrument is the *Brookfield Synchro-Lectric Viscometer* (made by Brookfield Engineering Laboratories at Sloughton, Mass., U.S.A.) which is made up of a small electric motor having a cylindrical rotor attached: the speed of the motor is reduced more as the opposition due to the viscosity is greater. The scale is graduated in centipoises.

High-frequency impulse viscometer. This apparatus, based on the principle of magnetostriction, includes a generator of high-frequency current which elongates (about 0·5 μ) a thin sheet. When this is plunged into a liquid the oscillations are damped and their average amplitude decreases with increasing viscosity. The measurement is therefore very rapid and is carried out with the minimum inconvenience, for all that has to be done is to immerse a stem in the liquid to be measured, and read off the viscosity on a dial. The simplicity of this method is only equalled by the complexity of the apparatus required: in addition to the generator, an amplifier and an integrating circuit. The high-frequency impulse viscometer was perfected by Rich and Roth (Hartford, Conn., U.S.A.) and the Bendix Aviation Corp. (Cincinnati, Ohio, U.S.A.).

359. Emulsion coating

The emulsion is coated onto paper or film either by *dipping*, or with a *roller*. In the dipping process the base passes under an ebonite roller into a trough of emulsion, removing a certain amount. In the second process, it is an auxiliary roller which dips in the reservoir, and by turning deposits emulsion on the base. The roller does not touch the support. Its diameter and speed of rotation determines the amount of emulsion carried up. The triangular space formed between the roller and the support is filled with emulsion; it is the 'bead' which must be kept full.

Roller coating is more difficult to perform correctly than dip coating; if the roller diameter, its speed of rotation, the speed at which the base is moving, the emulsion viscosity and surface tension are not correctly adjusted, parallel line marks in the direction of travel will result.

Many other coating systems have been tried: doctoring with a *knife* kept a short distance away or with a *'blade' of compressed air*, scraping with a rotating shaft around which is wound a spiral of very fine wire, spraying with a spray gun, etc.

During the whole coating operation, the emulsion must be kept at *constant temperature*; this is fixed between 32 and 38°C (90–97°F) depending on the emulsion viscosity and the required setting speed. The emulsion viscosity must be higher when the dipping method is used. It is, however, difficult to maintain the temperature constant throughout the length of the trough, so an excess of liquid is fed into the trough so that it overflows. Furthermore, care must be taken that the cold air from the setting chamber does not flow down into the emulsion trough.

The thickness of the coating is fixed by the viscosity of the emulsion at a given temperature and by the machine speed. The more viscous the emulsion and the higher the machine speed, the thicker the coating.

The layer evens out by running back vertically. After receiving the liquid emulsion, the film (or paper) is drawn up vertically for a height of 3–6 feet.

Setting. The films are cooled in a chamber fed with cold air at 15°C. The temperature must be neither too low nor too high, for setting can only take place after a fixed period of time. Papers are set either in a long chamber or by passing them over a metallic drum cooled internally.

Supercoating. The set emulsion receives, preferably by dipping, a thin surface protective gelatin layer. This very critical operation is termed supercoating. The gelatin solution is made up of:

Water	800 cc
Inert gelatin	22 g
Alcohol	200 cc
5% alum	0·8 cc
5% Saponin	5 cc

Too high a percentage of alcohol brings about the formation of coagulation streaks.

For the best supercoating, the temperature of the coated paper or film must be balanced with that of the gelatin solution. If the emulsion is too cold, the layer does not adhere (streaks) and if it is too warm there is a risk of remelting it. The temperature of the supercoating solution is kept at about 27°C. After supercoating the emulsion is again cooled.

Thick bromide paper for postcards, which is dry-glazed, is not generally supercoated.

Coating speed: 18–45 feet per minute depending on the type of machine and the length and efficiency of the drying chamber. Most frequently it is about 18 feet. Some document papers, which do not need a uniform coating, are coated at high speed.

Transport of the base. The base is driven at the end of the coating machine with a felt blanket fitted with a suction system. Irregular running on one side or the other leads to the formation of creases and stops the machine.

Width of the base. The three standard widths of paper and film are 43, 48 and 54 inches but there are many other smaller widths.

Plate coating. Emulsion is coated on plates with a weir having the shape of a tray. This tray is fitted, on the side where the liquid is introduced, with an inclined plate which is hinged and ends with a sheet of celluloid. The celluloid rests very lightly on the glass plates moving by underneath it, and the emulsion flows down it. The glass plates positioned by guides of variable width, are moved by rollers, one group of which is cooled with water. The amount of emulsion coated is determined by the flow from the tube which carries the liquid.

Another form of weir is made up by a roller dipped into a dish which feeds an inclined plate via a scraper.

360. Emulsion drying

After coating with emulsion, photographic films and papers are dried for several hours in drying chambers 80–100 yards long. The support is arranged in festoons 6–12 feet high supported by sticks 15 in. apart. The sticks are supported by two chains which advance slowly. Thus the festoons starting from one end of the drying chamber are dry by the time they reach the other end and can then be rolled up.

The sticks have the disadvantage that they leave marks. They can be replaced by hollow cylinders.

The drying chamber can be in a straight line or horse-shoe shaped. The air temperature is at a maximum in the middle. For the first quarter is must be 25–30°C (77–86°F); in the second and third quarters 30–40°C (86–104°F) and 20–25°C (68–77°F) in the remainder. Drying which is too fierce crinkles the edges of the paper and makes its manipulation and reeling very difficult, and this is why the relative humidity must be constantly controlled. Good drying depends above all on careful distribution of the air: the air led out of one section and readmitted in another, saturated with moisture, can obviously have no useful effect.

The air brought into the drying chamber should be filtered, preferably over ferrous hydroxide then over paper, then washed with water at 10–15°C (50–59°F) before being reheated. In some works the air is merely passed through an oiled filter. For correct drying, more than 100,000 cubic feet of air per hour must be used for each machine.

Machine with rapid drying (Agfa) for thin layers. These machines are used for the manufacture of multilayer colour films. The film after receiving the emulsion by dipping, is immediately dried with air at 35°C *without intermediate setting*. The path of the film consists of a vertical run of 6·5 feet, then a horizontal one of 46 feet. A large 16 ft. drum enables the film to be brought back. Speed: 10–13 feet. Drying time: 10 minutes. Thickness of dry layer: 10 μ.

The same operation with a normal machine requires a drying chamber 160 feet long at a speed of 26 feet per minute and uses 40,000 cubic feet of air per hour at 35°C and 30% R.H.

Continuous running machine. The coated film is set in a vertical chamber, then passes into a drying room through which it moves continuously in a zig-zag guided by upper and lower rollers. The upper rollers guide the film by its two non-coated edges whilst the lower rollers with lateral flanges keep it vertical and compensate for stretching and shrinkage. The drying chamber is divided into sections through which the temperature increases then decreases. The rollers are mounted on ball bearings. A viscometer is permanently installed in the emulsion trough.

Photoelectric control of the liquid emulsion layer. The thickness of the layer of liquid coated on the film can be immediately measured with a system of a light source, a filter which only transmits infra-red, a photo-cell and a galvanometer (with a scale or a recorder).

The thickness is checked in this way at several points across the width of the band. With a lateral sweep using a mobile infra-red source, the thickness can be measured everywhere.

Shrinkage. An emulsion test coated on a thin film of oxidized aluminium is dried. The shrinkage of the dry emulsion is measured by the contraction of the metal foil. It is stated that the shrinkage passes through a maximum at the isoelectric point. The shrinkage corresponds to the crinkling of film or paper bands in the coating machines.

Difficulties of emulsion coating. Coating is a very critical operation and it is rare that it can be carried out without incident owing to the fact that it is necessary to work in almost complete darkness. A coating of a constant thickness, without bubbles, streaks or dust, is very difficult to obtain. The problem becomes still more complex when it is necessary to superimpose several layers for colour work.

1. *Concentration bridge.* A chain of two silver nitrate solutions of different concentrations, and in which two silver electrodes Ag^1 and Ag^2 are immersed, following the plan $Ag^1 \mid (AgNO_3)^1 \parallel (AgNO_3)^2 \mid Ag^2$. If $(AgNO_3)^2$ is more concentrated than $(AgNO_3)^1$, and if Ag^1 is joined to Ag^2 by a metallic conductor the electrochemical system produced has an e.m.f. which will tend to circulate the current from Ag^2 towards Ag^1, the more concentrated solution(2) loses ions to the corresponding electrode—$Ag^+ + e^- = Ag$. The electrons necessary for this movement come via the conductor, in the opposite direction to the arbitrary current, from the electrode Ag^1 in the weaker solution; here, it is the metal which tends to dissolve in the solution to form ions, $-Ag = Ag^+ + e^-$. The Ag^+ ion enriches the solution(1) whilst the electron e^-, travelling to Ag^2 discharges the ions in solution.(2) The observed e.m.f. is composed of two terms ϵ_1 and ϵ_2 corresponding to the potential differences which occur between each electrode and the solution in which it is immersed.
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ULTRA-VIOLET PHOTOGRAPHY

GENERAL CHARACTERISTICS OF THE ULTRA-VIOLET SPECTRUM

The existence of ultra-violet radiations, forecast by Herschel in 1800, was established by Ritter, Inglefield and Wollaston immediately after the discovery of the infra-red.

At about 415 mμ the violet darkens considerably and at 396 mμ colour becomes greyish and hardly visible. In practice the ultra-violet spectrum extends from 400 to 13 mμ.

361. Ultra-violet sources

Natural sources. The ultra-violet region of the solar and stellar spectra is limited by the atmosphere in which we live. The short wavelength ultra-violet produces ozone when it reacts with oxygen and oxone absorbs these radiations strongly. Ten miles above the earth is a layer containing sufficient ozone to absorb all the ultra-violet below 290 mμ. The transmitted solar radiations contain only 5% of ultra-violet rays.

Artificial sources. A study of black body radiation shows that the emission of ultra-violet rays increases with the temperature: the *arc lamp* is much richer in these radiations than the incandescent lamp whose emission is negligible. The limit of the arc spectrum, which is more extensive than the sun after absorption, is a little beyond 300 mμ. The strongest emission band is at about 290 mμ. It can be accentuated by incorporating *metallic salts* in the arc carbons.

The light given by the oxy-hydrogen flame on chalk or magnesia gives no radiations beyond 300 mμ and the intensity drops sharply beyond about 350 mμ.

Heated metals, necessarily at a fairly low temperature, emit little ultra-violet.

Magnesium light is much richer: its limit of emission is at 280 mμ.

Metallic vapours give lines of much shorter wavelength: iron at 237 mμ, zinc at 202 mμ and aluminium at 185 mμ. It is the same with *spark spectra.* Sparks formed in water are used as sources in spectro-photometric measurements. An iron rod covered with Eder's alloy (Cd Fe Pb) gives an almost continuous spectrum from 481 to 231 mμ together with many lines as far as 202 mμ.

By discharge in rarefied hydrogen, 103 mμ can be reached. The mercury-vapour lamp is very rich in ultra-violet lines up to 200 mμ, the spectrum has about forty strong lines, one of the most intense of which is at 365 mμ.

Beyond this limit, the quartz bulb absorbs the majority of the radiations. The emissive power of the mercury lamp is increased by operating under pressure: up to 40 atm. in air and more than 100 atm. if the lamp is water cooled.

A high-voltage discharge through an acetylene flame gives a continuous spectrum which extends considerably further into the ultra-violet than that of the usual light sources.

362. Absorption

The absorption of the ultra-violet by various substances varies greatly. The following are transparent to the near ultra-violet (300–400 mμ): mica, celluloid, Canada Balsam, glycerin, acetone, etc.

Transparent to the middle ultra-violet (200–300 mμ): fused quartz, rock salt, fluorite, alum, gypsum, sugar, water, alcohol, liquid ammonia.

The absorption limit obviously depends on the thickness.

Window-glass transmits to 310 mμ. Its transmission curve varies with the time of exposure to light.

Ordinary glass	$n = 1{\cdot}51$	transmits down to 295 mμ.
Light flint	$n = 1{\cdot}57$	transmits down to 305 mμ.
Dense flint	$n = 1{\cdot}69$	transmits down to 335 mμ.

Helioglass transmits down to 280 mμ.

Crystal quartz is more transparent than fuzed quartz. Its transmission limit is 185 mμ.

The middle ultra-violet is readily absorbed by the air as far as 200 mμ.

The radiations below 305 mμ are detrimental to living cells. As to the eye, the cornea is opaque to rays below 295 mμ and the crystalline lens to those below 350 mμ.

Ultra-violet transmitting filters. Glass coloured with *nickel oxide* is transparent to ultra-violet and opaque to the visible spectrum. Similarly with the following glasses (309 to 400 mμ with a maximum at 360 mμ)

Corning Ultra Violet 586
Chance No. 14
Schott U.G.1, U.G.2, U.G.4.

Also used are:

Silvered quartz (transmission to 320 mμ).
Wratten 18A (gelatin filter).
Solution of p-nitrosodimethylaniline (200–370 mμ). (See para. 469.)

Absorbing filters. In para. 466 the composition of many ultra-violet absorbing filters will be given. To these add the following solution:

Cerium ammonium nitrate 1 : 1000 acidified with sulphuric acid: transmits radiations above 375 mμ. Ten times as concentrated, it only transmits above 460 mμ.

363. Spectrographs

Prism spectrographs are used exclusively for the study of the ultra-violet down to 125 mμ. Below 125 mμ they are replaced by metal grating instruments.

Flint prisms are used for spectra between 400 and 360 mμ.

Quartz is used between 400 and 180 mμ.

To reach 125 mμ fluorite (CuF_2) prisms must be used and work carried out in a vacuum.

Schott Uviol prisms can be used down to 253 mμ.

With quartz, a special prism must be used because of the birefringence and rotatory power. Two 30° half prisms, one from a laevorotatory and the other from a dextrorotatory crystal are used, cut in such a way that the refraction pattern is perpendicular to the optical axis, and stuck together with a trace of water or glycerin (Cornu prism). The use of the apparatus requires great care due to the invisible radiation. When the collimating lens is achromatic (quartz-fluorite) the collimator is adjusted with radiation which is easy to standardize. The sensitive layer is placed obliquely to the axis of the convergent lens and takes the shape of a caustic curve. The apparatus is then adjusted approximately using a fluorescent screen, for example, uranium glass or a gelatin layer 0·15 mm thick containing 1 : 1000 aesculine and 2·5 : 1000 uranine. Successive negatives are made to standardize. The Fery apparatus has no lenses, but a curved face prism, and gives a spectrum from 670 to 215 mμ with a length of 21 cm.

ULTRA-VIOLET SENSITIVE LAYERS

364. The maximum absolute sensitivity of silver bromide is at about 350 mμ in the ultra-violet. The sensitivity then decreases rapidly to 300 mμ because of absorption by the gelatin, and at 240 mμ is practically nil.

We shall see in the fourth part of this work that the sensitization by dyes is possible only if there is a certain gap between the spectral absorptions of the emulsion and the dye. As the photographic emulsion absorbs the majority of the ultra-violet, the absorption maximum of the dye must be displaced towards the longer wavelengths; this is the case with the simple oxacyanines which sensitize silver chloride but not silver bromide. It can therefore be understood that there can be no sensitizing substances for the ultra-violet, at least in the limits of spectral sensitivity, by a process similar to that of colour sensitization.

There are actually two principal methods of preparing ultra-violet sensitive emulsions, with many variations:

The Schumann method.
The fluorescent layer method.

365. Schumann method

The method invented by Schumann in 1894 is to prepare a fine-grain emulsion containing only a small proportion of gelatin. The absorption of radiations by the colloid is in this way reduced to a minimum. With ordinary emulsions only the surface layer is affected.

The preparation method is as follows:

A suspension of silver bromide is made in very dilute gelatin. After some time the liquid, coated on plates, deposits the silver bromide which takes down with it a very small amount of gelatin; the excess liquid is removed leaving a very thin layer of silver bromide with a small amount of colloid.

Hopfield and Appleyard process. The emulsion is coated upon gelatin-coated plates. Unexposed commercial plates, fixed in hypo and alum, washed for 8–10 hours in running water then in distilled water before drying in a dust-free place are used.

Each plate is placed on a piece of plate-glass 1 cm smaller each way than the plate, resting on a perfectly level glass table and each supported by two perfectly cylindrical glass rods 8 mm diameter. A sheet of thin paper the size of the plate glass can be placed between the latter and the plate.

Using a pipette, a layer of molten emulsion 2–3 mm thick is poured onto each plate and allowed to remain for three hours. To remove the excess liquid, one edge of the plate can be run along a vertical glass tube whilst the other edge is slightly raised. Care must be taken not to disturb the layer deposited on the plate. This is then dried in a horizontal position.

The emulsion is prepared as follows:

In the waterbath at 60°C is:

Distilled water	100 cc
Gelatin	7·5 g
Potassium bromide	15 g

into which is slowly poured (in red light):

Distilled water	100 cc
Silver nitrate	18·75 g

with constant agitation. The vessel containing the emulsion is corked and kept at 50°C for 30 mins. for ripening.

After decanting, the emulsion is set, noodled and washed for three hours at 10–12°C. After draining and remelting, the emulsion is ready for coating.

More rapid, but softer plates are obtained by ripening for a much longer time—at 60°C. The sensitivity is increased fifteen times, the fog not becoming important until after three days.

These plates enable wavelengths down to 50 mμ to be recorded. They keep for a maximum of two months.

Instead of using a support covered only with gelatin, plates which have not been fixed can be used. In this way a very extended spectral sensitivity can be obtained.

If films are used, they must be kept flat during preparation.

There are now new plates commercially available—*Eastman Kodak SWR*—having a very low gelatin content, and which are very sensitive (as fast as fluorescent layer plates). These plates have been studied by Schoen and Hodge (*J.O.S.A.*, 1950, 23–28).

Duclaux and Jeantet Process. Commercial plates are placed horizontally in the bottom of a dish of dilute sulphuric acid (100 cc of acid S.G. 1·84 per litre). After four hours immersion at an average temperature of 25°C (a little higher at the beginning, a little lower at the end) they are carefully removed and immersed in a dish of water through which running water passes so slowly that the liquid is not disturbed. After 30 mins. the plates are dried; as the remaining emulsion layer is very thin, drying takes only a few minutes.

This layer, poor in gelatin, is very fragile and must be covered with a thin layer of collodion before development. By immersing the plate in water before the collodion is dry, it is possible to develop the plate normally.

The plates giving the best results are fine-grain cold tone lantern plates. At $\lambda = 184$ they are ten times more sensitive than ordinary Schumann plates and two hundred times more sensitive than before the acid treatment.

366. Superficial fluorescent layer method

This method, also due to Duclaux and Jeantet, consists in applying to the surface of an ordinary plate, a very thin layer of a fluorescent substance which, excited by ultra-violet radiations, emits radiations of longer wavelengths in the blue-violet which expose the emulsion.

The selected substances must have a blue or violet fluorescence, and must be soluble in a solvent which does not swell gelatin. Good results have been obtained with a solution of *aesculine* in glycerin. It is, however, better to apply a few drops of *machine oil* using a wad of cotton. The fluorescence is due to the presence of hydrocarbons such as phenanthrene, anthracene, etc.

Before development the plate is washed with ether, then with alcohol. Other solvents can be used.

Fluorescent layers which are thinner and more effective are obtained by using a solution of the oil in a volatile solvent—alcohol or petrol.

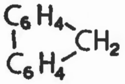
The sensitivity of ordinary or orthochromatic plates treated in this way is double that of the sulphuric acid treated ones. With a water-prism spectrograph, sixty iron lines between 199·5 mμ and 187·6 mμ can be recorded with an exposure of a fraction of a second. Three minutes exposure enables 151 lines to be recorded in the same spectral interval.

Lyman was, in this way, able to photograph the ultra-violet down to 58 mμ.

Many other substances have been suggested to replace machine oil:

Vaseline oil in petroleum ether (Beach).
Clear paraffin oil (Nujol type).
Salicylic acid in alcohol (1%) (Thovert).
Fluorene—2·5% in ethyl acetate.

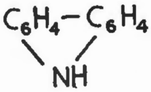
Before use, 4% of a saturated alcoholic solution of bleached shellac can be added. Fluorene, with the structure



is a compound with a violet fluorescence. It melts at 113°C. It is found in coal-tar fractions taken off between 270° and 300°C. B.Pt. 295°C. Fluorene can be replaced by the following:

2% *Carbazol.*
2% *Ethyl carbazol.*
2% *Naphthylamine sulphonic acids.*

Carbazol or dibenzopyrrole has the formula



M.Pt. 238°C, B.Pt. 351°C, contained in crude anthracene from which it can be extracted as the potassium salt by fusion with potash: N-ethyl carbazol melts at 68°C.

Among the naphthylamine sulphonic acids are: 1-naphthylamine-4-sulphonic acid. Obtained by treating 1-naphthylamine with an excess of sulphuric acid at 130°C.

2-naphthylamine-1-sulphonic acid.
2-naphthylamine-6-sulphonic acid.
2-naphthylamine-6 : 8-disulphonic acid (4%).

We would also add 2-naphthol-6 : 8-disulphonic acid—4%. It is best to use these compounds in a slightly alkaline solution.

Dihydrocollidine carboxylic ester in a volatile solvent. It is removed with acetone.

Eastman 103a—0 plates are provided with a resinous fluorescent layer 10 μ thick. The maximum fluorescence is at 315 mμ. After exposure, the layer is removed with *hexane*. No information is given on reciprocity failure between 15 secs. and 7 mins., nor on the intermittency effect.⁽¹⁾

367. Actinometric paper

Apart from the silver salt emulsions, there is a host of organic and inorganic compounds which are sensitive to ultra-violet rays. These compounds are discussed in the chapters concerned with inorganic photosensitive systems and with the photochemical formation and destruction of organic compounds. They have only a limited application in the practical recording of the ultraviolet. We would mention, however, an *actinometric paper* sensitive to the far ultra-violet based on the formation of a *triphenylmethane* dyestuff which has previously been converted to the *cyanide* compound. Light liberates —CN groups. The following formula is a variation of that of J. Lifschitz (1919) by Chalkley (*J.O.S.A.*, 1952, 387).

Filter paper is impregnated with:

4 : 4′ : 4″-triaminotriphenylacetonitrile	0·1 g
Acetonitrile	10 cc
Toluene	10 cc
Crystolite	1 g
Toluene (warm)	10 cc
β-(p-tert. butylphenoxy)-ethyl alcohol	5·8 g
Toluene to	80 cc

(Crystolite is a Rohm and Haas methacrylate.)

The white paper becomes pink in sunlight. It is sensitive between 230 and 326 mμ.

When the dyestuff contains hydrophilic groups, the solvent may be water. The preparations of such substances: ethyl green, xylene blue VS and xylene blue AS cyanides have been described (*J.A.C.S.*, 1955, 1848).

APPLICATIONS

368. The scientific applications of ultra-violet photography are numerous: spectrography and spectral analysis, metallurgy, biology, botany, astronomy, etc.

When a subject is photographed through a filter of a solution of *p-nitrosodimethylaniline* (transmission 370–200 mμ) or a solution of *cobalt sulphate* or *Hofmann violet* (380–300 mμ) it is stated that on the image, the shadows disappear.

The differences of reflection or transmission of ultra-violet by different substances enables interesting photographic effects to be obtained.

White zinc oxide appears absolutely black.

Polished silver also appears black.

White flowers 'phlox' which absorb ultra-violet give an almost black image.

Photography of the full moon with ultra-violet shows a black deposit around the Aristarchus crater which is not found in ordinary photographs.

Photomicrography in ultra-violet light enables evidence to be obtained of the structure of objects whose details cannot otherwise be seen.

The resolving power of a microscope objective, that is, the property of showing fine detail, varies with the aperture and the wavelength. If δ is the smallest distance between two points which can be seen and separated, we have the relation

$$\delta = \frac{\lambda}{2b}$$

where b is the objective aperture given by the formula $b = n \sin \alpha$, n being the refractive index of the medium in which the objective is working and α is the angle between the optical axis and the extreme ray passing through the objective.

To increase the resolving power the aperture can be made very large, or the shortest possible wavelength can be used. As there is a limit to the aperture, the second solution must be adopted. Ultra-violet light is used, as near monochromatic as possible.

The objective is of fused quartz and is corrected for spherical aberration. The slides are of quartz. The immersion liquid must be transparent to the radiation used—e.g. water+glycerin. With the naked eye, a fluorescent image is used.

The light source may be a mercury lamp whose light is filtered as has been shown already, or a spark in air or better, in water. Instead of filtering, the radiations can be separated with a special spectrograph.

In addition to a characteristic differentiation of the object details by their opacity differences, there is therefore an increase in the resolving power of the apparatus. But there is also an increase in the resolving power of the emulsion due to the limitation of penetration of the rays into the layer when there is less diffusion. Between 436 and 365 mμ there is a difference in resolving power of 1·5 to 2.(2) The measurements can be made with a resolving power meter like Burmistrov's(3) with an achromatic quartz-fluorite objective, a wet collodion graticule on quartz and a filtered mercury arc. The applications of the process are in fact very numerous in all branches of science and industry especially in anatomy, biology, botany, textiles and metallography.

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1. Lee and Weissler: *J.O.S.A.*, 1953, 512.
2. Breïdo: *Zh. tekhn. Fiziki*, 1952, 508–514.
3. *Sci. Ind. Phot.*, **8(2)**, 204.

Chapter XXIII

X-RAY AND CHARGED PARTICLE PHOTOGRAPHY

ACTION OF X-RAYS ON PHOTOGRAPHIC EMULSIONS

369. X-ray sources

X-rays are produced by bombardment of an *anticathode* in a *vacuum* with a high-speed *electron* stream.

A practical X-ray source consists of a bulb which is evacuated to a high vacuum, inside which are heated a tungsten *filament* to emit electrons, kept at a negative potential (cathode), a *positive electrode* (anode), and between the two, a metallic obstacle or *anticathode*. The speed of the electrons emitted by the filament is higher as the voltage between the latter and the anode is increased.

The electrons directed towards the anode are intercepted by the anticathode. They strike the metallic atoms of the latter violently, and the resulting disturbance produces an emission of *electromagnetic waves* called X-rays. *Positive particles* of matter are simultaneously produced, and are directed towards the cathode.

X-rays are of the same nature as light waves, but have a much higher frequency. Their wavelengths vary from 12 Å for 'soft' rays, to 0·05 Å for the 'hard' rays. Beyond this are the γ rays of radium with a wavelength 100 times smaller.

The nature of the X-ray beam emitted by a tube is dependent on the *metal of the anticathode*: each *electronic shell* of an atom (see para. 840) produces an identical emission of characteristic λ (indicated by the letters K, L, M, etc.). In other words, each element, due to its differently constituted electron system has its particular *X-ray spectrum*. The rays are therefore divided according to the *atomic number* of the element, the square root of the frequency being a function of these atomic numbers, of the form: $\nu = A(\pi - B)^2$.

To obtain the X-ray *spectral images*, that is, to analyse them, *diffraction gratings* with very fine spacing made of *natural crystals* are used.

370. Photographic action of X-rays

X-rays, which are much more energetic than light rays, have a powerful action on photographic layers *when absorbed by them.*(1)

If ϕ indicates the ratio $\frac{\text{liberated Ag}}{\text{quanta absorbed}}$, the following yields are obtained:⁽²⁾

λ (Å)	4,356	4,047	3,658	1·54	1·09	0·63	0·24
ϕ	0·96	0·92	0·93	148	210	363	920
	violet		ultra-violet	Hard X-rays			

A single X-ray quantum will make a silver bromide grain developable. It follows that *sensitivity specks* do not take part in latent image formation, and that desensitizers (towards visible radiations) are inactive relative to very short wavelengths.

The radiation is more effective as the wavelength is shorter: thus a quantum of 0·06 Å makes 10 silver bromide grains developable, whilst a 1·3 Å quantum will only put one grain in this state.⁽³⁾ 10^8 quanta per cm^2 of 1·3 Å radiations are needed to produce a density of 1·5.

The *reciprocity law* is directly applicable to X-rays, because of the independence of these radiations towards the centres of attraction of the sensitive crystals. It is the same with the *intermittency effect* whose influence is nil.

Unlike visible radiation, the effect of X-rays on a photographic layer is to first produce an *internal latent image* before producing an *external* (*surface*) *latent image*. The characteristic curve is only a straight line at high densities.

The X-ray latent image can be destroyed by low intensity visible radiation: this phenomenon is known as the *Villard effect*.

Influence of wavelength. The minimum wavelength of the radiation diminishes, as we know, as the voltage applied to the tube is increased.

E.M.F. (kV)	0·08	1	12	120	220
λ (Å)	140	12	1	0·1	0·05

This is given by the formula $\lambda_0 = 12{,}340/E_{kV}$.

Now, silver bromide has two absorption minima, at 0·48 and 0·92 Å due to the K discontinuities of silver and bromine. Because of this it is necessary to work at $\lambda = < 0{\cdot}48$ to avoid fluctuations due to wavelength. Radiations with λ greater than 0·48 are arrested by silver foil.

X-rays are selectively absorbed by the radiographed object and any variation in λ affects the contrast of the dense parts of the image. The clear areas, on the other hand, are affected by penumbra variations.

The emission spectrum of the tube has a continuous background, with bands characteristic of the anticathode metal, generally copper (E = 26–40kV) or tungsten (200–250 kV). The intensity of the spectrum is proportional to the atomic number Z of the metal and to the square of the voltage.

X-rays are stopped by lead. On the contrary, they readily pass through the metals with low atomic numbers, particularly beryllium, which at a thickness of 0·5mm transmits 56% of 2·5 Å radiation; aluminium only transmits 27% for a thickness of 0·025 mm.

Part of the radiation absorbed by an obstacle is re-emitted as *secondary radiation*, of longer wavelength, which is generally undesirable. The secondary radiation of an aluminium filter is, however, less troublesome; it is readily absorbed by black paper.

Granularity increases as the wavelength decreases, but below 0·12 Å the variations are small.(4) At high powers there is a diffusion effect of photo-electrons around the initial grain.

X-ray sensitometry. A rotating lead disc is used with cut-out sectors, giving, for example, 5 exposure times per revolution, the shortest being 1/10th sec. The test plate is positioned 30–50 cm from the exit opening of the tube. The results obtained are not always comparable as the coefficient of efficiency of the emitting tube varies with the time (overheating, release of occluded gas etc.) Furthermore, there is no simple relationship between the ionisation energy and the effective photographic energy due to variations in the spectral composition, the energy of a quantum being inversely proportional to the wavelength.

A common criterion of sensitivity is often given by the abscissa value corresponding to a density of 0·05 above fog.

With a 200 kV tube, the emission is filtered by a steel plate 19 mm thick. Distance from exit: 90 cm. Exposures from 5 seconds to 20 minutes.

Contrast. This depends on the tube voltage and on the development time. The contrast decreases with the voltage and naturally increases with the development time. To reduce contrast, expose more and develop less.

Metallic screens. These are thin metal foils stuck to card. They are used in industrial radiography. The most common metal is lead with 6% antimony, but gold, platinum and bismuth are also effective. Their action is due to emission of electrons. There must be perfect contact between screen and film. Intensification: 3. Application to microanalysis.

Antidiffusion grids. A grid of thin layers of lead absorbs the diffused rays (as well as a fraction of the direct rays), and in this way increases contrast. Antidiffusion grids are used in medical radiography at high voltages (150 kV) to reduce the exposure time to a third.(6)

371. X-ray sensitive layers

It has already been stated that the quantum efficiency of the photochemical action of X-rays on silver gelatinobromide is very high, always on condition that these rays are *absorbed* by the sensitive crystals. Now the majority of the rays pass through the photographic layer and produce no effect. *Only a small fraction of the incident radiation is absorbed* (1%) to lead to the formation of development centres. This is explained by the fact that the image is formed in the interior of the grains.

The absorption yield can be increased by using an *emulsion very rich in silver bromide* and coating a *thick layer* of it. As the thickness of the layer prevents convenient development and fixation, it is preferable to coat the base on *both sides* with a normal thickness.

The resulting improvement is not great. To increase the action of the X-rays, the following expedient is used: each emulsion layer is supercoated with a *fluorescent layer.*⁽⁷⁾ Excitation of this layer results in the emission of visible light—blue or violet—which affects the silver salt normally.

The fluorescent substance can be placed *under* the emulsion layer in the form of a finely divided white pigment, as with Kryptoscreen radiographic paper.

The intensifying screen *reduces the image sharpness,* but considerably *increases the sensitivity.*

Emulsion preparation. Radiographic emulsions must be sufficiently contrasty, completely fog-free and made of hardened gelatin. They must be developable in urgent cases, at any temperature. The silver content of a double coated radiographic emulsion without screen can reach 3·6 g per sq. ft. A sensitive layer for screen radiography contains up to 1·2 g of silver per sq. ft. An ordinary negative film contains only 0·65 g of silver.

Radiographic emulsions have a high iodide content. They have little gelatin. The grain is quite coarse and has a maximum of 3 μ. The thickness of each coating is about 25–30 μ; it is reduced by half for emulsions used with a screen (that is, relatively insensitive to X-rays but very sensitive to ordinary light).

Some photographic emulsions studied by Sauvenier⁽⁸⁾ gave the following characteristics by exposure to X-rays:

The contrast drops with precipitation time up to 25 seconds then increases to 2 minutes precipitation. The differences are small if ripening is curtailed.

The contrast drops with the ripening time (50%).

The sensitivity increases with the precipitation time and with the ripening time (with exceptions).

Digestion (chemical ripening) time generally has little effect on X-ray emulsions. Only the weak surface image, which can form, is intensified by high voltage radiation.⁽⁹⁾

Emulsions precipitated in the presence of 0·04 mol. per cent (relative to AgBr) of a *lead* salt are 50–100% more sensitive to X-rays. This phenomenon, noted by Schwartz in 1926 for thallium, was verified for lead by Mueller in 1935.⁽¹⁰⁾ An excess of lead results in desensitisation.

Gold thiocyanate as potassium aurothiocyanate increases the sensitivity of X-ray emulsions. This sensitivity is further increased by incorporating a lead halide during precipitation. The increase is 5X for 1·07 Å radiation and 10X for 0·011 Å.

Lead ions assist the formation of vacant silver ion sites⁽¹¹⁾ and of the complex system ($Pb^{++}\ Ag^{-}_{\square}$) which serves as an internal trap, whilst the aurous ion adsorbed on the surface serves as a surface trap.

'*Screenless*' *formula* (after F.I.A.T. Final Report, No. 355).⁽¹²⁾

A T: 45–50°C	Water	300 cc
	Potassium bromide	100 g
	Gelatin	12 g
B T: 27°C	Water	500 cc
	Silver nitrate	100 g
	Ammonia	Q.S.

C	Gelatin	25 g
D	Gelatin	30 g

Pour half of A into B in one minute. After 15 minutes, add the remainder of B in 15 minutes. Add C. After the gelatin has dissolved, cool, set, wash and digest at 50 °C.

For coating: with D add glyoxal, chrome alum and saponin.

'*Screen*' formula

A 50°C	Water	480 cc
	Potassium bromide	150 g
	Potassium iodide	1·5 g
	Gelatin	30 g
B 27°C	Water	900 cc
	Silver nitrate	150 g
	Ammonia 25%	Q.S.
C	Gelatin	150 g
D	Gelatin	120 g

Pour 400 cc of B into A in one minute. Ripen 7 minutes at 50°C and add the remainder of B in 7 minutes, ripen for 15 minutes more and add C. After the gelatin has melted, cool, set, wash and melt at 52°C. Add D and digest for 60–90 minutes.

To perfect a radiographic emulsion, the various factors which can modify the characteristics must be varied successively: choice of gelatin, AgBr/gelatin ratio, iodide content, precipitation rate, ripening time. Washing can be replaced by sodium sulphate precipitation.

The slow, relatively fine-grained 'screenless' emulsions are generally more contrasty than the fast coarse-grain ones. The characteristic curves of the slow emulsions have a toe extending to D 1·7 instead of 1·1 for the fast emulsions. The characteristics of an X-ray emulsion depend not only on the nature of the emulsion, but on its thickness, that is, the amount of silver per unit surface area. Rapid films are rich in silver. A dental X-ray film must be adequately exposed in one second at 55 kV and 8 mA.

The properties of emulsions for use with fluorescent screens are similar to those for ordinary photography.

Development. A developer for X-ray films must be very active, but with a high bromide content to give high contrast without fog. Examples:

	Typical formula	Ilford ID–19
Water to	1000 cc	1000 cc
Metol	5 g	2·25 g
Sodium sulphite anh.	60 g	72·5 g
Hydroquinone	7·5 g	8·75 g
Sodium carbonate anh.	42 g	50 g
Potassium bromide	4·5 g	4 g

An increase in hydroquinone at the expense of the metol gives high contrast but lower sensitivity.

With ID 19, the development times at various temperatures are 16° C (61° F): 6–8 minutes. 20° C (68° F): 4–5 minutes. 24°C (75° F): $2\frac{3}{4}$ to $3\frac{1}{2}$ minutes. For dental films the time is 5–8 minutes at 20° C and 4–10 minutes depending on type for industrial films.

372. Fluorescent intensifying screens

Fluorescent screens permit a considerable reduction in exposure. They improve contrast but reduce resolving power. This becomes lower as intensification is greater.

Fluorescent screens are usually used in pairs: a thin front layer and a thicker rear one. There are three main types: calcium tungstate screens, zinc sulphide screens and lead and barium sulphate screens.

Grain size has very little effect on image sharpness, for the grains are divided into clumps, and it is the size and topography of these clumps which determines the sharpness. Their size varies from 20 to 100 μ.⁽¹³⁾

Calcium tungstate $CaWO_4$ screens exist in various types depending on the size of the crystals (2–20 μ) and the layer thickness. The brightness of a tungstate screen increases with the energy of the radiation, that is at short wavelengths. In fact, the losses are very great below 80 kV.⁽¹⁴⁾

Zinc sulphide screens. Zinc sulphide, in 10–15 μ crystals, is activated by traces of silver or cadmium sulphide. Traces of nickel prevent fluorescence. The crystals are large as grinding reduces their fluorescent power. The zinc sulphide screens are brighter than the tungstate ones when $\lambda \leqslant 0{\cdot}11$ Å which corresponds to a voltage lower than 70 kV.⁽¹⁵⁾ Their efficiency, unlike the tungstate screens, does not vary with the penetrating power. They are known by the name 'Fluorazure'.

Lead and barium sulphate screens of Renwick and Tasker. The substance is precipitated in the active state. Optimum content 5 or 20% $PbSO_4$. The grains are about 1 μ. These screens are mainly used for industrial radiography, and for high-voltage medical work. Dampness can result in parasitic fluorescence.

Emission wavelengths. Tungstate, 350–560 mμ; zinc sulphide, 390–550 mμ; lead sulphate, 300–450 mμ.

Intensifying factor. Tungstate, 10–30 at 40–90 kV; zinc sulphide, 40 at 40–90 kV. At 200 kV the intensifying factor for tungstate screens passes to 400.

Contrast. Without screen, 2·1; tungstate, 3·1; sulphide, 3·2; sulphate, 2·7.

The second (rear) screen always has double the amount of fluorescent substance of the front screen.

Other intensifying screens: with zinc, or zinc + beryllium silicate, borate or germanate.

373. Copies of radiographs

Radiographs have a large density range, often greater than 3, which cannot be reproduced by photographic papers which at best only give a density of 1·8 (chloride papers).

To retain local contrast whilst reducing the general contrast, it is necessary to utilize masks. Yule⁽¹⁷⁾ has disclosed the use of *unsharp masks* for this purpose.

The working method is as follows:⁽¹⁸⁾

(*a*) First print a mask of the clear areas on process film and under-develop it so that the original densities of 0·1 and 0·7 are reproduced by densities of 0·7 and 0·1. By registering the original with this mask, a uniform density of 0·8 should be obtained.

(*b*) The highlight mask obtained in this way is mounted 12 mm from the original using a piece of plate glass, and registering the two. The image faces of the two films are outermost, and with the original against opal glass, place an unexposed film against the mask. Expose and develop moderately to produce the unsharp mask.

(*c*) Print a negative of the original + unsharp mask onto film.

(*d*) Print a positive of the negative (*c*) on paper.

Copies of medical radiographs by solarization on X-ray film with a single layer with a supplementary exposure (30–60 seconds in ordinary light) and development in the presence of an antifoggant.(19

374. Applications

Medical radiography by very penetrating X-rays. The voltage used for medical radiography is generally between 40 and 90 kV. More penetrating radiation emitted at 150 kV enables the dose received to be reduced as well as the exposure time, at the same time as ensuring better quality images.

Radiocinematography without a screen can be carried out at 10 f.p.s. With a fluorescent screen 50 f.p.s. can be reached easily.

Polychromatic transposition. Donovan(21) has proposed making three radiographic negatives using three radiations of different penetrating power, obtained respectively at 45 kV for soft tissues, 90 kV for bones and an intermediate voltage. Each negative is differently colour developed: magenta, cyan and yellow. By superimposing the three, a colour transposition of the radiograph is obtained which can differentiate certain particular elements.

A transposition in only two colours can also be used.

Industrial radiography. Radiography of thick steel objects requires high voltage generators—200 to 2,000 kV. An antimony-lead screen (6% Sb) must be used to absorb the less penetrating radiation. The thickness of this screen varies from 2·5 to 5% of the thickness of the steel object.

For industrial radiography with a 22 MeV Betatron see Miller and Steeley.(22)

Radiomicrography is primarily used for biological work. The microradiographic technique, conceived in 1913 by Gaby was perfected by Dauvillier, Lamarque, then Barclay. It needs point opening generator tubes. Mitchell(23) used a tube for diffraction taking 5–10 mA at 5–20 kV with a glucinium opening. A molybdenum anticathode enabled a very narrow waveband to be obtained. The sensitive layer is a Lippman plate twice coated, at 40 cm from the exit. Another apparatus described by Legrand and Salmon(24) uses K α radiation from chromium of λ 2·28 Å. In this case the sensitive plate is 5 cm from the tube exit. Exposure time: one minute. A small exit with a 1 mm^2 focal patch is made by Machlett, but Ely(25) has disclosed a system with a rotating anode giving a focal patch of only 0·3 mm^2. We would finally mention a 4-mirror X-ray microscope made by Kirkpatrick and Pattee, based on the reflecting power of glass and metals for X-rays at a narrow angle of incidence: this system enables abberations to be reduced, and reaches a high separating power.(26)

375. Gamma radiography

Gamma rays, emitted by radium, affect photographic films in the same way as X-rays. The resulting images, however, lack sharpness, contrast is often low and exposures are too long. The radium is mounted in a copper capsule 4 mm thick. The sensitive material is placed between the lead foils which serve as intensifying screens. The rear screen is 0·75 mm thick, whilst the thickness of the front one depends on the thickness of the steel to be photographed:(27) for 12·7 mm steel the screen is 0·75 mm and for 76 mm of steel, 0·45 mm.

Radon is more effective than radium. Radon is an inert gas resulting from the disintegration of radium. It emits high intensity γ rays. Their lower penetration increases contrast. On fine grain emulsions it is possible to obtain images of better quality than those from 200 kV X-rays.(28)

Use of radioactive isotopes can advantageously replace radium and even X-rays for radiography. The principal ones are *lanthanum 140*, *cobalt 60*, *tantalum 182*, *iridium 192*, *cesium 137 and thalium 170*. Application in industrial radiography: lanthanum,(29) tantalum, cobalt(30) and cesium(31) for steel; iridium for light alloys.(32) The emission of thalium is comparable in action with 80 kV X-rays.(33)

The life of these elements is often short. Their half-life periods are: iridium 74 days, tantalum 97 days, thalium 129 days, cobalt 5·3 years, cesium 37 years (radium 1,580 years).

376. Contamination of emulsion packages by atmospheric radioactive substances

Some accidental fogging of X-rays film has been due to the radioactivity of the card used for packing. The latter appears to have been made radioactive by contamination of the water or straw used in its manufacture by atomic experiments.

The contamination can take place over great distances, as it has been possible to detect radioactive matter (emitting electrons or β-particles) in the atmosphere of the Paris area, and particularly in rain water.(34)

To detect and measure the radioactivity of cardboard it is necessary to work with about a dozen kilos. The ash is taken up in hydrochloric acid at 70° C: the radioactive matter is present in the filtrate. It is precipitated with barium sulphate.(35) The elements of the radium and uranium group emitting β-particles can be identified in this way: one of them is only emitted by their disintegration products.

This emission of β-particles produces black spots on radiographic emulsions. Production of α-particles also occurs, which can affect nuclear emulsions.

PHOTOGRAPHIC ACTION OF ELECTRONS

377. General observations

Electrons affect photographic materials. According to their energy (which depends on the speed with which they are directed) their action approaches either that of visible light or of X-rays.

An electron transfers its energy to silver bromide more easily as its energy is reduced. The ratio between the number of grains developed and the average number of electrons received, is a function of this energy expressed in keV.⁽³⁶⁾ An emulsion will therefore be less sensitive to high energy electrons (emitted at very high voltage). The result of this is that ionization is greatest towards the end of the trajectory of each electron, and that the grains at the beginning of the path acquire only a sub-image.⁽³⁷⁾ However, even though it loses only a fraction of its energy (about 25 keV) an electron can make several grains in its path developable although a quantum of light can only liberate a single electron.

The highly penetrating electrons diffuse laterally which reduces the resolving power (2 μ at 10 kV and 17 μ at 50 kV).

When emitted at a very low voltage, 5 V for example, electrons have no effective action on gelatin emulsions, they will affect silver bromide free from protective colloid. Meier has recorded them on Schumann plates (used for ultra-violet photography). Above 50 V gelatin plates begin to be affected.

At low voltages the photographic action of electrons follows the sensitometric laws of visible light. Below several kilovolts the results obtained are similar to those given by X-rays. Some electron microscopes work at 220–300 kV but from 20 kV the impact produces a flourescent emission. In this case a filter of aluminium foil 1 μ thick is used 15 cm from the sensitive surface, placed inside a Faraday cylinder. A thin aluminium deposit, or even cellophane, can also be used as intensifying screens at high velocities (factor 1·5).

The images produced by electrons can be made visible immediately with *fluorescent* screens. This occurs on oscilloscope and radar screens. It is often convenient to photograph these fluorescent screens. The best screens for photographic reproduction are zinc sulphide ones (blue fluorescence) and zinc and cadmium sulphide (yellow-green fluorescence) activated by silver. For the shortest exposures the wavelength of the emission maximum of the screen should correspond to the sensitivity maximum of the emulsion.

Kopp and Mollenstedt's electron micrographic technique⁽³⁹⁾ uses an intermediate fluorescent screen. This consists of a layer of zinc oxide obtained by vacuum evaporation.

378. Electron emulsions

Emulsions for electron work should be *rich in silver bromide.* For this, Von Ardenne disclosed Schumann type UV plates, others used process plates. The *sensitivity* increases as the grain becomes coarser, for to become developable, the large grains need less ionization than small ones. On the other hand, the resolving power drops with layer thickness, so it is necessary to limit this, even though a thick layer records the trajectories more completely.

The *contrast* should not be too high except for slightly absorbent samples, otherwise very hard images are obtained.

Koseki, Karigome and Tajima studied the behaviour of a neutral iodobromide emulsion.⁽⁴⁰⁾ They found an increase in sensitivity with chemical ripening. The contrast increases with the silver concentration at high voltages (40 kV) whilst it drops at low voltages (20 kV) at the same time as sensitivity.

The specific sensitivity of the grains towards electrons emitted below 80 kV was increased by Berriman by *colour sensitizing*, although there is no direct relationship between optical sensitization and the action of electrons: the effect is undoubtedly due to a modification of the surface condition of the grains. The increase in sensitivity enables the grain size to be reduced to 0·2 μ (NT 2a plates). Development 30–40 minutes in D 19 developer.

379. Autoradiography

Autoradiography is the recording of the electron rays from a histological section impregnated with a differentially absorbed radioactive isotope. This technique was used in 1924 by Lacassagne and Lattès. In 1947, Pelc had the idea of *stripping the dry emulsion* from its support and applying it to the specimen after damping with water. Such an emulsion must be rich in silver, and have very fine grain, but must be coated in a thin layer of 4–12 μ on an underlying gelatin layer of 10 μ, which is attached to the glass with a hydrophobic substratum. The section is placed on a microscope slide coated with hardened gelatin, then the whole is immersed in water. A small strip of emulsion is floated face down over the specimen and slide. After 3 minutes the latter is raised and together with the film is drained and dried.(41)

For standardization, emulsions for autoradiography are 'exposed' to gelatin coated plates containing a radioactive element (iodine 131, phosphorus 32 or sulphur 35) acting as a source of radiation. The resolving power is determined using grids activated with iodine 131, obtained by iodizing a photographic image.(42) The power of the action of these plates is expressed in microcuries.(43)

Development: in a low-alkali developer to avoid diffusion of the dyes in the specimen. In addition it is necessary to check that these dyes do not desensitize the emulsion.

The number of electrons emitted by the radioactive isotope, whatever it is, determines the density, which should be at least about 0·5.

Ageno(44) has suggested placing a fluorescent film between the emulsion and the radioactive specimen to amplify the effect: the fluorescent substance may be tetraphenylbutadiene (D × 2), zinc sulphide (D × 3) or calcium tungstate (D × 6).

A uranium intensified photographic image can give a copy after several months contact with a sensitive layer. Rosenblum obtained a better result in only 30 minutes by incorporating traces of plutonium nitrate in the intensifier.(45)

CHARGED PARTICLES

380. Photographic action of charged particles

The photographic emulsion is sensitive to the action of charged particles: light ions such as electrons, protons, deuterons, tritons, helions (α-rays), or heavy, like the fission products or uranium in addition to the neutrons and mesons.

Very diverse sources can be used: protons from a cyclotron, α-rays from polonium, neutrons emitted by paraffin surrounding glucinium and radium.

The charged particles act on photographic emulsions by ionization: the energy absorbed by the silver bromide is proportional to the ionizing power. Particles with a single charge have the least ionizing power.

The energy of the ionizing particles is denoted in millions of electron-volts, whilst that of the visible photons by only 2 to 3 electron-volts. The probability P that a silver bromide grain will become developable is given by the equation(46)

$$P = c\{1 - \exp[-b\,(dE/dR)^{1/2}]\}$$

in which E is the energy in MeV, R the length of the track in μ, and b and c are parameters. These last are the same for various particles but change with the emulsion.

When a particle strikes a sensitive layer it activates the movements of the constituent atoms, particularly C, N and O (perhaps producing transitory substructures). In imparting some of its energy to the emulsion, the particle liberates a certain number of electrons whose velocity is a function of its own, and which act on the silver bromide crystals. Some electrons are raised to the conduction band due to the collisions produced in the crystals. The primary effect of the charged particle lasts less than 10^{-13} seconds.

381. Nuclear emulsions

Emulsions for the recording of charged particles, called nuclear emulsions, have a very high concentration of silver bromide (80%), fine grain (0·1 to 0·5 μ), and are coated in very thick layers—50, 100, 200, 400, 700, 1,200 and even 2,000 microns.

Ordinary emulsions, such as diapositive ones, are but slightly sensitive to moderate energy protons, but they can be used, should the occasion arise, for the study of high energy protons and for mesons.

To prepare a nuclear emulsion, concentrated reagents must be used which are poured simultaneously, and very slowly into a gelatin solution which dilutes the liquid streams sufficiently for the grain to be very fine. Furthermore, to avoid any ripening, no excess of soluble bromide is added, and precipitation is carried out at a relatively low temperature in the presence of an inactive gelatin.

Many writers have worked out nuclear emulsion formulas. The preparation of the principle ones is given below, but it should not be forgotten that a formula which will succeed for one person can give deceptive results to another. The nature of the gelatin, the personal stirring and a host of other uncontrollable factors intervene.

Demer's formulas. The first 'double-jet' formula gives a concentrated emulsion with a grain size of 1 μ. Prepare:

Gelatin 6%	75 cc
Silver nitrate 60%	30 cc
Potassium bromide 42% (equivalent solution).	30·5 cc

The nitrate and bromide solutions are poured slowly and simultaneously into the gelatin solutions, with vigorous agitation, over a period of 30 minutes at 40°C. The bromide solution should be 0·5 to 1 cc ahead of the nitrate solution. The emulsion is then set, washed, remelted and coated. It is insensitive to ordinary light. Twenty-five cc of the water in the gelatin solution can be replaced by 25 cc alcohol after the gelatin has been dissolved.

To improve reproducibility Demers used equipment in which the nitrate and bromide were introduced by two syringes, or, preferably, two stainless steel pumps for nylon extrusion.⁽⁴⁷⁾ The piston determining the flow of bromide can be adjusted with a rack and pinion.

Formula 2:

A. Solution containing 600 g $AgNO_3$ per 1,000 cc.
B. Solution containing 420 g KBr per 1,000 cc.
C. Solution of 15 g gelatin in 167 cc water with 83 cc alcohol. Temperature: 40–50°C.

After adding 1·3 cc of B to C, add 100 cc of A and 100 cc of B simultaneously in 3 minutes. The initial stirring speed of 240 r.p.m. is increased to 550 r.p.m. Set at 0–2°C, wash for one hour at this temperature, and melt for coating. Sensitize before use by bathing in 6% triethanolamine for one minute, or better, add 12·5 cc triethanolamine to 1,000 cc emulsion.

Formula 3. Prepare the following solutions:⁽⁴⁸⁾

A. 600 g $AgNO_3$ per litre (D = 1·482).
B. 420 g KBr per litre (D = 1·228).
C. 225 g gelatin in 1,500 cc water, and add 500 cc 90% alcohol.

Precipitation temperature: 48°C.

One cc of bromide solution is first added to the gelatin solution. A pump must add 1,911 cc of A and another, simultaneously, 1,950 cc B. The excess of B is kept constant at 2%. The flow, first slow, is speeded up and the jets drop below the liquid level. If drops of A and B reach the stirrer, a spontaneously developable precipitate of silver bromide is formed.

The emulsion is cooled in water at 12–15°C, then set in a refrigerator at 0–5°C, shredded and washed for 2–4 hours below 5°C. Before coating, digest at 50°C and add precisely 40·5 cc triethanolamine. Finally 1·5 g thymol dissolved in 300 cc alcohol.

Thick emulsion layers must be dried very slowly to avoid cracking (2 days for 300 μ).

Grain diameter 0·08 μ. After development, 0·1 to 0·2 μ in the weak tracks and up to 0·4 μ in the dense ones.

Halg and Jenny formulas:⁽⁴⁹⁾

A	Distilled water	70 cc
	Gelatin	6·5 g
B	Distilled water	23 cc
	Potassium bromide	14 g
	Cadmium chloride cryst. 10%	5 cc
	Potassium iodide 10%	2 cc
C	Distilled water	30 cc
	Silver nitrate	18 g

Temperature 50°C.

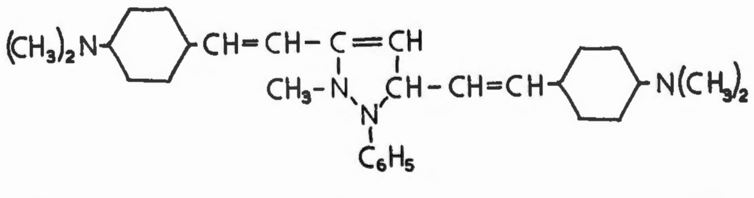
Pour B and C simultaneously into A taking 28 minutes for B and 27 minutes for C with constant stirring. Ripen 45 minutes at 50°C. Set, wash 16 hours then digest at 35°C. Make up to 150 cc and add 9 cc of the solution: distilled water 78 cc, chrome alum 2 g, 96% alcohol 60 cc, 10% potassium bromide 0·75 cc, glycerin 42 cc. Also add 5 cc of 0·2% wetting agent and finally a sensitizing dye like acridine orange (1 cc of 0·2% solution). Coat 15–30 cc of emulsion per 9 × 12 cm plate. Dry at 34°C. Layer thickness: 50–100 μ.

Alternative formula(50) for better recording of α-particles. Select a gelatin rich in retarders and sensitizers.

A	Distilled water	60 cc
	Gelatin	3·6 g
	Nitrobenziminazole 0·2%	1 cc
B	Distilled water	30 cc
	Potassium bromide	14·8 g
	Potassium iodide	0·6 g
	Cadmium bromide (hydrated)	0·7 g
C	Distilled water	30 cc
	Silver nitrate	20 g

Temperature: 37°C.

Add three drops of B to A, then simultaneously B and C at the rate of two drops per second, dropping to one drop every three seconds. Total time 30 minutes. Agitation is increased towards the end. Add 6 cc of 0·91 ammonia, wait 5 minutes (which trebles the speed), then neutralize with 4·5 g citric acid. Add 1 g gelatin, allow 12 minutes to dissolve, then set. Wash 15 hours. Melt at 28°C, make up to 200 cc and add 2% alum, 2 cc; glycerin diluted with 2 volumes water 6 cc and 5 cc of a 0·04% alcoholic solution of the 'Ciba' sensitizing dye with the formula



For a 400 μ coating, 50 cc of emulsion is used on a 5 × 8 cm plate. Set one hour. Dry two days. AgBr concentration: 84%. Grain diameter: 0·5 μ.

Markocki formula:(51)

A 60°C	Distilled water	100 cc
	Gelatin	8 g
B 20°C	Distilled water to	50 cc
	Potassium bromide	19 g
	Potassium iodide	0·4 g
	Cadmium nitrate cryst.	1 g
C 20°C	Distilled water	50 cc
	Silver nitrate	22·5 g

Add 5 cc of B to A, then 5 cc C, and continue alternately. Ripen 50 minutes at 60°C, set, wash 8 hours, melt and add: distilled water 5 cc, alcohol 5 cc, 2% alum 2 cc, 1% potassium bromide 1 cc.

A comparative study of the various formulas has been made by Cüer and Simon.(52)

Sensitizers. Some dyes sensitize nuclear emulsions. These are: erythrosin, eosine, rose Bengal, methyl violet, acridine orange and more complex ones of the type given above. Sensitization to protons by Pinakryptol yellow has been contested by several workers.

Triethanolamine increases sensitivity slightly. Diphenylamine has a similar action, particularly towards α-particles. Such sensitizers generally contain NH_2 or OH groups. Jenny has tried many compounds including dehydrothiotoluidine-sulphonic acid and pyrrol derivatives. The auxochromic groups which cede electrons are the most effective.

Weak latent images from protons can be latensified by immersing for 1–5 minutes in 0·01% hydrogen peroxide (Demers).

Borate emulsions. The boron nucleus is readily disintegrated by a slow neutron with the emission of an α-particle (whose track in an emulsion is 7 μ). Impregnation of an emulsion with a borate therefore sensitizes to neutrons. Lithium borate is preferably used. This is prepared(53) by neutralizing 225 g boric acid dissolved in 700 cc water with 51 g of lithium carbonate. The carbon dioxide is expelled by boiling. The solution is filtered and made up to a litre giving a 15% solution. It contains 39 mg of boron and 10 mg lithium per cc. 3% glycerin and 0·004% of a wetting agent are added, and 8 cc of solution per dm^2 is applied to the emulsion. After standing for 16 hours in a damp atmosphere the plates are drained and dried.

Commercial nuclear plates are generally for one or several particle types. They differ between themselves by the emulsion type, the grain size, the sensitivity or the thickness. They may be impregnated with various salts: borates, glucinium, bismuth, or uranyl salts.

The most sensitive plates are used to record proton and meson tracks, those with medium sensitivity for α-particles, which are readily distinguished from the finer proton tracks. The slow plates enable the heavy fission particles to be studied.

Each emulsion has a safety limit for the registration of various particles. For example, for the NT2a plate these limits are:(54) electrons 50 kV, protons 100 MeV, deutons 200 MeV, $\alpha > 400$ MeV, mesons 10 MeV.

Emulsions without support. Nuclear emulsions 150–300 μ thick can be supplied without supports, enabling a large number to be stacked for recording cosmic rays.(55) For example, 50–600 μ layers separated by silk paper were exposed to these radiations at an altitude of 10,000 M.(56) Registration marks are made with X-rays. Then each layer is applied to a subbed plate after immersion in glycerin and water. To avoid frilling the substratum can be made up of a first layer of sodium silicate (3% solution) which is dried, followed by 5% alum-hardened gelatin, which is not dried before the damp emulsion is applied.

382. Development of nuclear emulsions

Exposed nuclear emulsions must be developed as soon as possible because of *latent image regression.* The fading is greatly increased by heat: 5 hours at 50° C will destroy the image. It is even more pronounced as the grain is finer, when the plate is old and when the particles have a low velocity. Acid pH and moisture favour fading.(58)

The latent image regression is due to recombination of the silver nuclei, which are internal, with bromine after ejection of electrons. This electron ejection is partly due to aerial oxidation in the presence of moisture, and partly to thermal agitation.(59)

Fading of tracks is avoided at low temperatures, by keeping in an atmosphere of nitrogen or by impregnation, before exposure, with sodium nitrate, (5 minutes in a 10% solution).(60)

The first developers used for nuclear emulsions were M.Q. ones, with a high sulphite content to develop the internal image: metol 2 g, anhydrous sulphite 75 g, hydroquinone 8 g, anhydrous sodium carbonate 85 g, potassium bromide 5 g, water to 1000 cc or D.19 containing 2, 100, 9, 50 and 5 g of the same compounds.

The use of very thick layers requires a considerable modification of the development technique, started by Dilworth, Occhialini and Payne, by immersing the plate in cold developer, and allowing the temperature to rise slowly.(60b)

Amidol development	(61)	(62)
Water to	1000 cc	1000 cc
Sodium sulphite anh.	18 g	7·5 g
Amidol	4·5 g	3 g
Sodium bisulphite lye	—	14 cc
Boric acid	35 g	—
Potassium bromide	0·8 g	—

The exposed plate is immersed in distilled water at 5°C for 2 hours, then for 2 hours in the developer at 5°C with frequent agitation.(63) It is then drained and warmed up to 21–33°C. After a suitable time, which may be up to 50 minutes, the temperature is again reduced to 5°C in 10 minutes. The plate is immersed in a stop bath of 0·5% acetic acid, fixed in 40% hypo containing 0·7% ammonium chloride and washed at 5°C. A little colloidal silver may be formed. This is removed with 0·08% ferricyanide followed by rapid fixing. A final clearing bath of 3% ammonium acetate, 1% citric acid and 1% thiourea followed by washing is also recommended together with impregnation with a plasticizer such as hexylene glycol, carbowax or Ansco Flexoglass.(64) The sequence of operations for a 600 μ layer in bath 61 can be summed up as follows: impregnation with water at 5°C—150 minutes, impregnation with developer at 5°C—150 minutes, 'dry' development at 23°C—180 minutes, cooling to 9°C—5 minutes, stop bath—150 minutes, fixing at 5°C—75 minutes, washing at 5°C—30 hours, clearing at 5°C—24 hours, plasticizing at 5°C—1 hour, drying at 21°C—5 days.

Metol developers. Some workers prefer metol developers to amidol ones, for example: (A) water to 1000 cc, metol 3 g, anhydrous sulphite 12·5 g; (B) water to 1000 cc, anhydrous sodium carbonate 50 g, bicarbonate 50 g.

Mix equal volumes of A and B, cool to 2°C and immerse the plate for 1–10 hours according to thickness. Re-heat to 21°C in 10 minutes and keep at this temperature for 30 minutes or more.

Metol can be used with borax;(65) (A) water to 1000 cc, metol 3 g, anhydrous sulphite 12·5 g; (B) water to 1000 cc, borax 40 g. Mix equal parts of A and B. For a 200 μ layer immerse the plate in the developer $< 5°C$ for 120–150 minutes. Allow it to warm to 19°C in 15 minutes, then immerse in another portion of developer at 19° C, and leave for 60 minutes. Rinse and place in a 0·5% acetic acid stop bath for 75 minutes at 19° C. Rinse and fix in a hardening fixer for 26 hours, then in 3 non-hardening baths for 26, 36 and 40 hours respectively. Wash 72 hours.

Caustic developers. Demers disclosed the use of D8 (para 63) diluted with an equal volume of water,(66) then a chlorhydroquinone developer. Water to 1000 cc, anhydrous sulphite 30 g, pure chlorhydroquinone 45 g, caustic potash 32·5 g and potassium bromide 8 g. Just before use dilute with 6 parts of water. Development time 7½ hours at 0·2° C for an emulsion 300 μ thick. Stop 15 minutes, fix 2–5 hours.

Fixing of nuclear emulsions is generally carried out in 40% hypo. It is extremely slow: 3 weeks for a 1,200 μ layer.(67) Slow rocking of the fixing dish reduces the time to half. By using a sintered glass support, the fixer can have access to both sides of the emulsion (Occhialini and Rechenmann).

Ammonium thiosulphate at 5° can only be used for layers less than 600 μ as it reduces the developed image.

To reduce distortion it is best to replace the fixer progressively with sodium sulphate, which is then diluted.

Background fog, which often appears on the plates can be eliminated by Libermann and Barschall's method: the unexposed plate is immersed in a developer for a longer time than normal, washed, then treated in 0·5% sulphuric acid and 0·07% permanganate for 30 minutes. The plate is then washed, cleared in 10% bisulphite, re-washed and dried. It can then be used to record the fission of uranium 235, for example, by exposure to neutrons.

Another method is to apply the Herschel effect(67b) using a 500 watt infra-red lamp with a Wratten 88 filter.

Parasite tracks due to cosmic rays. These can be removed by a method disclosed by Weiner and Yagoda, and used by Albouy, in which the plates are placed in a damp atmosphere for several hours.(68) Mitilsch, Matiasek and Karlik(69) have stated that the action of the water is actually due to the chlorine which it contains: with water containing 12 mg chlorine per litre, removal is achieved in its vapour after 5 hours at 60° C.

383. Measurement and differentiation of nuclear tracks

Each particle results in the appearance, in the developed emulsion, of a track made of a certain number of grains, the number being greater as the particle velocity is lower. By dividing each track into sections of a few μ, the silver grains can be counted. If the grains cannot be enumerated then all sections of the trace separated by a break are counted, and similarly, when the emulsion is thick, only the breaks are seen. Sometimes the aggregated grains can be separated by swelling the gelatin.(70)

An accurate microscope enables measurements to be made $\pm 1\,\mu$, on condition that humidity variations in the ambient air are avoided, for between 55% and 80% the thickness can increase 25%.(71) Mechanical instruments have been invented for the examination of the plates;(72) some of them include a photomultiplier tube.(73) In this way, after measuring the number, the course and the diffusion, the velocity, mass and charge of the particles can be evaluated.(74)

Differentiation. The latent tracks of particles with different ionizing power are more or less readily developed, enabling them to be separated by varying the pH of the developer. Stevens(75) used a bisulphite-amidol solution with a mixture of two buffer solutions of di- and tri-sodium phosphate and sulphite. The most alkaline developer only develops the tracks of the least ionizing particles, whereas the most acid solution only develops the fission tracks. A plate impregnated with 2% chromic acid before exposure, dried and impregnated with thorium acetate, gives, under the action of neutrons, only the fission tracks, by preventing the formation of proton tracks.

The proton tracks are finer than the α-particle tracks: a plate impregnated with thorium nitrate and kept wet for 50 minutes gives, after washing and development, a large number of α-tracks which are chemically intensified (Powel, Occhialini, Livesey and Chilton).

Uranyl ions prevent neutron tracks from forming, which enables plates to be bombarded by these particles in the presence of a uranyl salt, or a uranate in dilute acetic solution.

With 1–4% of uranyl ions, the proton paths disappear and those of X-rays are weakened (broken). The tracks of fission particles are still quite sharp.

Oxidizing agents like chromic acid, by dissolving the surface and subsurface image, remove α-particle tracks.

Finally, the penetrating power of each group of particles can be measured by interposition of aluminium foil in steps.

Cosmic rays are made up of a mixture of γ-rays, mesons, electrons, positrons and protons of high energy, which act on the emulsion by liberating electrons. In 24 hours a surface 1 cm² is traversed by about 840 cosmic particles at sea level.(76) An X-ray emulsion has its fog increased by 0·05 in a year. A nuclear plate exposed for several days on a mountain top leaves tracks longer than 10 mm and stars with 12–15 points. Impregnated with borate, it is suitable for the recording of slow mesions, which themselves bring about the disintegration of atomic nuclei. Electron plates are readily affected by cosmic rays. The very high energy particles disintegrate the silver and bromine nuclei in the emulsion, producing patterns.(77)

Blackening laws. Kinoshito has established the following relation for α-particles and a single layer material:

$$D = D_m(1 - e^{-CN})$$

where N is the number of α-particles per unit area of the plate during time t, and C is a probability constant.

In the case of thick emulsions, C decreases at high densities, and in some cases, increases to a maximum value, then decreases. Sheppard, Wilkins, Wightman and Wolfe have suggested the two equations:

$$D = 1{\cdot}57D_M(1 - e^{G/G_M}) \text{ and } G = G_M(1 - e^{-kN/G_M})$$

where G is the number of accessible grains in the emulsion and k the average number of grains per track.

Special techniques. Some studies require the immersion of the emitting substance in the emulsion. The support generally consists of wires(78) or capillary tubes(79) buried in the sensitive layer.

Russell effect. Metals with a bare surface can affect photographic layers in the absence of light. This can take place at short distances even through paper, cellophane or aluminium. It is practically nil in vacuo or in hydrogen,(80) more intense in oxygen. Zinc, magnesium and cadmium are the most active metals (24 hours at 0·1 mm). Aluminium, nickel, tin, antimony, chromium, and magnesium take several days. Copper, tin and mercury—almost inactive—give active alloys.

The photographic action of metals has been attributed to radiation emitted by the metal under the influence of cosmic rays, with the formation of hydrogen peroxide whose effect is added to that of the radiation. Another explanation attributes the generation of particles to the oxidation of the metal only. A third theory proposes that the photographic effect is solely due to the hydrogen peroxide formed during the oxidation of the metal,(81) with no radiation intervention. The last explanation seems the most likely.

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Chapter XXIV

PHOTOSENSITIVE SYSTEMS AND SPECIAL TECHNIQUES

384. Photosensitive systems

The salts of silver are not the only ones which are light sensitive. Those of various other metals, have, in various degrees, the ability to react under the action of luminous energy, the phenomenon generally taking place by a redox effect.

We have already mentioned the preparation of photographic emulsions using salts of *lead* and *thallium*. The *mercury complexes* comprise another interesting group. Lead, thallium and the mercury complexes form insoluble halides and organic salts: their systems are analogous to those of silver halide emulsions.

The salts of *iron* and *cobalt* on the other hand form soluble photosensitive systems, even in the absence of protective colloid. Their sensitivity is effective when they are in the complex state.

There are two other categories of photochemical reaction which we shall study in later chapters: these are the insolubilization of dichromated colloids and the photochemical destruction of dyes.

The photosensitive systems apart from the silver salts, the dichromated colloids and the dyes have not at the moment a great practical importance; however, their theoretical study is not without a certain interest.

INSOLUBLE SYSTEMS

385. The best known insoluble systems are the silver halide emulsions. Note first that these can be obtained in the absence of any protective colloid:⁽¹⁾ *pure silver bromide* plates can be obtained by sedimentation on a layer of rubber; in this way phenomena which would be masked by gelatin can be studied (para 285). We know also that *daguerreotypes* were plates of polished silver which were treated with the vapour of iodine, bromine, or chlorine: the silver halide formed on the surface of the plate was, after exposure, able to attract mercury vapour in all the exposed areas (amalgam formation).

The action of light on the halogenized plates can be demonstrated by immersing two such plates (chlorine treated for example) in an electrolyte and joining them with a conducting wire: a current passes through the wire when one plate is illuminated, leaving the other in darkness.

386. Mercury salts

Many mercury salts show a definite photosensitivity:⁽²⁾

Mercurous nitrate, $HgNO_3 . H_2O$, which is only soluble in acid solutions (nitric) is converted to a basic salt after three minutes exposure to diffuse light. The image cannot be seen; it must be developed in a solution of ferrous sulphate and tartaric acid which only reduces the basic salt to metallic mercury. The residual mercurous nitrate is stabilized by conversion to mercurous chloride with an alkali chloride solution.

Basic mercurous tartrate is also very sensitive. It can give an image developable in ferrous tartrate as above, or a print-out image. The image is stabilized by substituting platinum for the mercury, by treating with a solution of platinic chloride in tartaric acid.

Masic mercurous tartrate is prepared by saturating a solution of tartaric acid with mercurous carbonate.

Basic mercurous oxalate which is formed when mercurous carbonate is boiled in a solution of a neutral acetate, gives, like the tartrate, both direct and developable images. A mercurous oxalate paper requires, for development, an exposure of about fifteen minutes. Ferrous tartrate is used for development and sodium chloride for fixing. The image can also be developed physically by heating at 100° C: this phenomenon is reversible, the image returning to its original state after a few days.(2b)

Mercury-ammonium oxalate. This is the most interesting compound of the series. Mercuric chloride, treated with excess sodium carbonate gives a precipitate of mercuric carbonate. This is washed and heated with a solution of ammonium oxalate; by double decomposition this gives mercury ammonium oxalate.

Mercury ammonium oxalate(3) can be dispersed in gelatin as an 'emulsion'. Several seconds exposure in sunlight and development in alkaline sulphite gives black mercury images. Hypo fixes slowly in concentrated solution, or thiocyanate can be used.

387. Insoluble lead salts

Besides the lead halides which have already been described, many salts have been claimed by various experimenters for the preparation of sensitive materials:

Sheppard and Vanselow(4) disclosed organic salts such as the *oxalate*, *malonate*, *succinate* or *thioacetate* dispersed in gelatin.

Lead arsenite despersed in gelatin can be developed by heat.(5) Lead oxides and sodium arsenite ground together in a mortar give a mixture which darkens rapidly in light.

Lead xanthogenate gives a latent image which is developable with ferrous sulphate after treating with silver nitrate (Philips).

Gelatino-lead nitride emulsions have been studied by Moskovitch (*Phot. Abst.*, Dec. 1940, 215). They are less sensitive than gelatino-silver nitride ones.

Other metals used. Zinc and *cadmium sulphides* for printing out, in presence of moisture (*Zeits. Phys. Chemie.*, Jan. 1956, 146–159).

387b. Phosphotungstic acids

Simple and mixed tungstic acids, and most particularly silicotungstic and phosphotungstic acids are reducible by light. A study of these compounds by L. Chalkley (*J.O.S.A.*, 1954, 699–702) has shown that the *phosphotungstic* acid of the No. 12 series of Keggin (*Proc. Roy. Soc.*, 1934, 144, 75), colourless and water soluble, changes to *phosphotungstous* acid, water and spirit soluble. The reaction favoured by organic substances:

$$H_3\,PW_{12}\,O_{40} \rightarrow H_4\,PW_{12}\,O_{40}$$

Phosphotungstous acid, which forms the image can reduce iron, silver or gold salts (silver and gold precipitate). Treated by amines, the two acids become insoluble but keep their original colours. Phosphotungstic acid can be combined to the leuco-derivatives of triphenylmethane basic dyestuffs, to give insoluble and colourless salts. These salts, when exposed to radiations less than 440 $m\mu$, give the corresponding black phosphotungstites which are altered by air into coloured phosphotungstates. The remaining leucobase must be removed with benzene.

388. Endothermic compounds

Certain endothermic compounds (that is compounds whose formation involves the absorption of heat and which are therefore unstable) can decompose violently, in a *very explosive way* under the influence of an intense exposure. These photosensitive endothermic compounds have been studied principally by Eggert, Arens and Berchtold;(6b) the principal ones are: nitrogen iodide, silver nitride, the mercury nitrides, lead nitride, silver oxalate, silver acetylide, silver imide Ag_2NH.

Nitrogen iodide can be prepared on paper. It needs an exposure of 18 watt/second (300 watt/second for silver nitride) to give a positive image. This is stabilized in a solution of silver nitrate. Nitrogen iodide is only sensitive to visible radiations.

SOLUBLE SYSTEMS

389. The most common soluble photosensitive salts are those of *iron, cobalt, manganese, uranium, lead* and, of course, *silver*.

Soluble *lead acetate* gives homogenoeus layers which are sensitized with thioacetamide, a compound which readily parts with sulphur. Staib and Hickman added hexaminocobalt chloride and stabilized with acetic acid.(6) The ammonia from the hexamine is liberated by light, and accelerates the reaction of the lead with the thioacetamide.

Lead acetate only, in gelatin, gives a brown image on exposure to light; this can be intensified with silver nitrate.

Silver nitrate darkens in light.(7) Its decomposition is accelerated by organic compounds capable of accepting the group $(NO_3)^-$, or which reduce it (glucose, tartaric acid etc.). If the reducer is too vigorous there is the risk that the paper will darken without exposure.

The following mixture can be used:

Silver nitrate	8 g
Citric acid	16 g
Distilled water	100 cc

By exposure to sunlight, brown-violet or red-brown images are obtained which can be washed and preferably fixed in dilute hypo.

Although the darkening of silver nitrate was known since its discovery by the Arabs in the eighth century, it was not attributed to light until the beginning of the eighteenth century.

390. Iron salts

The ferric salts, especially the chloride, are sensitive to the action of light.

Ferric chloride is reduced to ferrous chloride and chlorine. The reaction is reversible and stops at a state of equilibrium

$$2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2$$

if the chlorine formed is not taken by a halogen acceptor.

Ferric chloride dissolved in a mixture of alcohol and ether is reduced by blue and ultra-violet radiations. The same thing happens with cupric chloride. We have already seen, at the beginning of this book, a similar reaction with mercuric chloride, which is also seen with mercuric iodide in hypo solution.

391. Iron organic complexes

With organic polybasic acids *iron* forms complexes of the formula $(Fe^y A_n{}^a)^x$ in which y is the valency of iron, a the valency of the organic acid and x that of the resulting *complex ion*: the relation $x = an - y$ must apply, n being the number of molecules of acid. For example:

With bivalent oxalic acid COOH—COOH and trivalent ferric iron, the *ferri-oxalate ion* is obtained $[Fe^{+++}(C_2O_4)^{--}{}_3]^{---}$, which is negative and trivalent, the three negative valencies being the difference between the three positive valencies of iron and the six negative valencies of oxalic acid. The ferrous ion Fe^{++} gives the *ferro-oxalate ion* $[Fe^{++}(C_2O_4)_2{}^{--}]^{--}$ in the same way. These groupings have already been considered in connexion with ferrous oxalate developers and the change from the ferrous to the ferric state by oxidation and *vice versa* (para 33b).

The ferrous ion Fe^{++} on oxidation passes to valency 3 by losing an electron to give Fe^{+++}. On the contrary, by gaining an electron the ferric ion Fe^{+++} passes to valency 2 giving Fe^{++} which automatically brings about a re-arrangement in the complex structure.

It will be recalled that in the *complex ions* the simple metallic ion (such as Fe^{+++}) is disguised although it takes part in oxidation-reduction reactions: the ordinary analytical reactions do not indicate its presence without previous decomposition (which may be easy or difficult): thus the ferri-oxalate ion has not the characteristics of iron.

However, each complex ion dissociates into its constituent elements following the equilibrium reaction

$$(M_m{}^{y+} . A_n{}^{a-}) \rightleftharpoons mM^{y+} + nA^{a-}$$

which is interpreted by the law of mass action by the relation

$$\frac{(M^{y+})_m \times (A^{a-})_n}{(M_m{}^{y+} . A_n{}^{a-})} = k$$

The smaller the value of k, the more stable the complex: k is the instability coefficient of the complex ion; it is dependent on the pH.

A large number of metals form complex oxalates in the same way as iron: chromium, manganese, cobalt, copper platinum, iridium, titanium, vanadium, uranium, etc. Chromium for example gives the blue chromioxalate with the formula

$$K_3[Cr(C_2O_4)_3]$$

and another red compound with a slightly different constitution

$$K[Cr(C_2O_4)_2] . 2H_2O$$

In the same way as oxalic acid, the other organic acids like *tartaric acid* and *citric acid* give complex salts with these metals. A large number of these oxalic, tartaric and citric compounds, particularly the iron ones, are sensitive to light.

The most sensitive salts are the oxalates, then the tartrates. The citrates are the most stable of them.

The sensitivity appears greater if, instead of using the pure salt, a mixture of ferric chloride and an excess of the corresponding acid is used.

Under the action of light, the ferric ion of the complex group loses a valency and becomes a ferrous ion: the ferr*i*oxalates, ferr*i*tartrate and ferr*i*citrate became the ferr*o*oxalates, ferr*o*tartrates and ferr*o*citrates, which are all reducers.

It becomes evident that if these ferrous compounds are in the presence of compounds which are reducible, then they reduce the latter and show their presence. For example, *ferric ammonium tartrate* $(NH_4)_3[Fe(C_4H_4O_6)_3]$—prepared by dissolving ferric hydroxide $Fe(OH)_3$ in tartaric acid, saturating with ammonia and evaporating after filtration—is converted, in the solid state as well as in solution, into ferr*ous* ammonium tartrate which can reduce silver nitrate and Fehling's solution.

The reducing power of organic ferric and cobaltic salts has been used in practice in the following systems: iron-silver, iron-mercury, iron-platinum, iron-gold, iron-ferricyanide, cobalt-ferricyanide, which will be dealt with briefly. We would finally mention the light sensitivity of *iron carbonyl*, a compound of iron and carbon monoxide which provides images which can be toned.

APPLICATIONS OF ORGANIC COMPLEX SALTS

392. Iron-organic system

This system is used in the *ferrogallate process.*

A ferric salt, exposed to light under a negative, gives a positive image of the corresponding ferrous salt. This image is rendered visible by treatment with gallic acid which combines with the ferrous salt to give a black compound similar to iron ink.

Ferrogallate paper is preferably prepared with the following mixture:

Ferric sulphate	3 g
Water	40 cc
Tartaric acid	5 g
Water	40 cc
Gum arabic	6 g
Water	80 cc
Ferric chloride	7·5 cc

The sensitized paper is dried and must be kept away from moisture otherwise it deteriorates very rapidly.

After exposure, the image is developed in

Gallic acid 0·2%	100 cc
Oxalic acid 0·1%	5 cc

Rinse, fix in 2% hypo and wash.

Kögel(8) disclosed a paper sensitizing formula using ferric salts in the presence of *α-naphthoquinone sulphonic acid* and a mordant. The ferrous salt formed in the photochemical reduction forms a coloured compound with the naphthoquinone.

Gay used a mixture of ferric salt and *starch* paste and developed the image in *potassium iodide.*

393. Iron-silver system (sepia paper).

A paper sensitized with a solution of ferrioxalate, tartrate or citrate containing *silver nitrate*, and exposed to light, gives an image by reduction of the silver salt, in the presence of moisture, by the process already described. The excess ferric complex is removed by washing.

The following two formulas can be used on gelatin(9) or gum coated paper:

Ferric ammonium citrate—green(10)	80 g	200 g
Silver nitrate	12 g	66 g
Citric acid	15 g	66 g
Water	1000 cc	1000 cc

The silver nitrate is dissolved separately in part of the water.

The image is developed in water, washed, fixed in 2% hypo and again washed. It can be toned.

Ferric oxalate with silver nitrate in the presence of mercury salt catalysts has also been used.(11)

The ferric salt used alone gives a latent image which can be developed in ammoniacal silver nitrate, then fixed.

The old '*iron paper*' was made by sensitizing paper with a mixture such as:

Water	100 cc.
Ferric nitrate	5 g
Silver nitrate	5 g
Tartaric acid	25 g

394. Iron-mercury system

The reducible substance in this case is a mercurous salt, preferably the oxalate. The paper is sensitized, for example, with a solution of ferric oxalate and mercurous oxalate in the presence of gum arabic. In this case, after a long exposure to light (15–60 mins) insoluble ferrous oxalate is formed which can only react in a 5% potassium oxalate solution in which it is soluble (formation of ferro-oxalate). It is therefore better to use simple ferric ferrioxalate and then develop in water.

The deep brown image, washed with oxalic acid, then with water, can be fixed in 10% ammonium chloride which converts the residual mercurous oxalate to mercurous chloride.

395. Iron-platinum system (Platinum process)

The principle of this once widely used system, which has the advantage of giving permanent prints of a good black colour, is similar to the preceding ones:

(*a*) an organic ferric salt (the oxalate) is reduced by exposure to light to the ferrous salt.

(*b*) the ferrous salt formed in turn reduces potassium chloroplatinite $K_2[PtCl_4]$ or $Pt\,Cl_2 . 2KCl$, which gives metallic platinum by the reaction:

$$\underset{\text{Ferrous oxalate}}{6FeC_2O_4} + \underset{\text{Platinous chloride}}{3Pt\,Cl_2} = \underset{\text{Platinum}}{3Pt} + \underset{\text{Ferric chloride}}{2FeCl_3} + \underset{\text{Ferric oxalate}}{2Fe_2(C_2O_4)_3}$$

The chloroplatinite is used, as platinous chloride is insoluble.

A mixture of chloroplatinite and ferric oxalate, coated on paper and exposed to light, gives a grey-violet image which must be developed as the ferrous oxalate produced is insoluble and cannot reduce the chloroplatinite. To dissolve the ferrous oxalate it must be converted to a ferro-oxalate by bathing the exposed paper in a solution of neutral potassium oxalate. By replacing the ferric oxalate in the sensitizing solution with an alkali ferri-oxalate, the reducing ferro-oxalate is obtained directly and only water treatment is necessary. The solutions must be slightly acid (by adding an organic acid) to prevent the formation of basic iron salts which would make the paper yellow.

The sensitizing mixture must contain substantially equal quantities of chloroplatinite and ferric oxalate.

Operating procedure

Gelatin coated paper is sensitized with the solution

Potassium chloroplatinite 10%	250 cc
Ferric oxalate 30%	100 cc
Potassium chlorate saturated soln.	100 cc
Oxalic acid 10%	10 cc

For less contrasty images omit the chlorate and increase the ferric solution.

Printing is continued until a light brown image, full of detail is obtained. It is then developed in:

20° C	Water	1000 cc
	Neutral potassium oxalate	350 g
	Tartaric acid	100 g

This solution is suitable for sepia images. For black tones replace it with

Potassium oxalate	70 g
Oxalic acid	3 g
Disodium phosphate	10 g
Water	1000 cc

Wash, fix in 1–2% hydrochloric acid, again wash and dry.

For *sepia tones* replace part of the platinum with *iridium* and size the paper with arrowroot.

The platinum process is not used due to the high price of this metal. In addition, the sensitized paper does not keep well, the reduction of the ferric salt to the ferrous taking place in the dark with the least trace of moisture.

396. Iron-gold system

Results similar to those of the platinum process are obtained by replacing the chloroplatinite by sodium chloroaurate (double chloride of sodium and gold) $Na\,[AuCl_4]\,.\,2H_2O$. This is reduced to metallic gold by the photolytic ferrous salt. The images are always warm toned.

Printing takes much longer than for the platinum process. Tranchant formula for brown-black tones:

Water	80 cc
Sodium chloroaurate	10 g
Water	50 g
Ferric oxalate	50 g
Water	50 cc
Potassium chlorate	50 g
Tartaric acid	50 g

Red-violet to red-brown tones are obtained by adding 10–40 cc of a saturated solution of stannous chloride $SnCl_2$.

The image which appears by printing is developed in a bath of potassium oxalate and fixed in hydrochloric acid. If stannous chloride has been used, it is necessary to wash again and fix a second time in 5% acetic acid.

397. Iron-ferricyanide systems

Ferrous and ferric salts, treated respectively with an alkali cyanide give precipitates of ferrous and ferric cyanides $Fe(CN)_2$ and $Fe(CN)_3$ which redissolve in excess cyanide to give two complexes—the ferrocyanide and ferricyanide, such as $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, and in which the bivalent and trivalent iron exists in the complex ions $[Fe(CN)_6]^{----}$ and $[Fe(CN)_6]^{---}$.

The change from one to the other of these complexes is easy to bring about as we have already explained: the resulting valency of the complex ion is equal to that of the negative radical $(CN)_6$ less the valency of the metal ion, which in this case is 2 for ferrous iron and 3 for ferric iron. This makes the ferr*o*cyanide ion corresponding to ferrous iron, tetravalent; whilst the ferr*i*cyanide ion corresponding to ferric iron is trivalent. When the iron ion Fe^{++} of the ferr*o* complex changes to valency 3 by losing an electron to form Fe^{+++} the ferro ion is converted to the trivalent ferr*i* ion

$$\underset{\text{Ferrocyanide ion}}{[Fe^{++}(CN)_6{}^{6-}]^{----}} - \underset{\text{electron}}{e} = \underset{\text{Ferricyanide ion}}{[Fe^{+++}(CN)_6{}^{6-}]^{---}}$$

Conversely, if the ferric ion of the ferr*i*cyanide receives an electron, it passes to the ferrous state which brings about the change of the ferri ion to ferrocyanide.

The ferr*o*cyanide ion is a *reducer* and in this capacity becomes *oxidized* to ferricyanide. The ferr*i*cyanide ion on the other hand is an oxidizing agent which during oxidation becomes reduced to the ferro state. We know in fact, that a *reducer* is a compound capable of giving electrons easily whilst an *oxidizing* agent is a compound with an affinity for electrons in the same way that a dehydrating agent is one with an affinity for water.

The ferro and ferricyanide ions give salts, the ferrocyanides and the ferricyanides. The alkali salts are soluble; the others generally insoluble, coloured, and decomposed by alkalis. Ferrous salts form a bluish-white precipitate with the ferrocyanides, which is ferrous ferrocyanide; ferric salts give an intense blue precipitate of ferric ferrocyanide, or *Prussian blue*

$$\underset{\substack{\text{Ferric}\\\text{chloride}}}{4FeCl_3} + \underset{\substack{\text{Potassium}\\\text{ferrocyanide}}}{3K_4[Fe(CN)_6]} = \underset{\substack{\text{Ferric}\\\text{ferrocyanide}}}{Fe_4[Fe(CN)_6]_3} + \underset{\substack{\text{Potassium}\\\text{chloride}}}{12\ KCl}$$

Potassium ferricyanide does not precipitate pure ferric salts. With ferrous salts it gives an insoluble blue ferrous ferricyanide (Turnbull's blue).

At one time potassium ferrocyanide was prepared by heating nitrogenous organic compounds with potassium carbonate and iron residues, but it is now prepared from the by-products of coal-gas. Ferricyanide is obtained from the ferrocyanide by electrolytic or chlorine oxidation.

Potassium ferr*o*cyanide occurs as yellow crystals, containing $3H_2O$, which are very soluble in water. The ferr*i*cyanide crystallizes in red prisms which are very soluble in water. Its solutions are unstable to light.

398. Ferroprussiate paper

A *ferric salt*, exposed to light, is reduced to a *ferrous salt*. The negative ferrous image treated with a potassium ferr*i*cyanide solution is coloured blue due to the formation of a precipitate of ferrous ferricyanide (Turnbull's blue). If, on the contrary it is treated with a solution of potassium ferr*o*cyanide, the unchanged ferric salt reacts to form a blue precipitate of ferric ferrocyanide (Prussian blue) whilst the ferrous image produces a bluish-white precipitate which is superimposed on the other and reduces the positive image (*cyanotype* paper).

If a mixture of a ferric salt and potassium ferricyanide were exposed to light to give a negative blue image of ferr*ous* ferr*i*cyanide directly, it would be too unstable and would react spontaneously. The ferric salt must be stabilized by incorporating it as an *organic complex*: ferric ammonium or potassium citrate or oxalate. In fact, the sensitizing mixture is made up of a ferric organic complex and potassium ferricyanide which is coated on paper.

The ferrioxalate for example, is reduced by light to the ferrooxalate, losing a molecule of oxalic acid which is decomposed to CO_2.

$$\underset{\text{Ferrioxalate ion}}{[\mathrm{Fe(COO\,.\,COO)_3}]^{---}} + e^- \rightarrow \underset{\text{Ferrooxalate ion}}{[\mathrm{Fe(COO\,.\,COO)_2}]^{--}} + 2\mathrm{CO_2}$$

But the ferrooxalate is a reducer: it can locally convert the ferr*i*cyanide to ferr*o*cyanide and precipitate with the latter as ferric ferr*o*cyanide (Prussian blue). This is not all: *potassium ferricyanide is itself light sensitive.* Exposed to light it is reduced to ferrocyanide which reacts with ferric salts to form ferric ferrocyanide.

The photosensitivity of the ferrioxalates is related to their photoconductivity. Suzuki has worked on this.(11b)

The importance of the stability of the ferrous complex is in each case made evident by the fact that the ferrotartrate produced by photochemical decomposition of ferric potassium tartrate does not, contrary to published information, give a blue precipitate, but simply a soluble violet complex. This is because the ferrotartrate is much more stable than the ferrooxalate or the ferrocitrate.

399. Sensitizing formulas

Paper sensitized with ferric potassium oxalate is faster than the ferricitrate paper but it does not keep as long. In each case gelatin sized paper must be completely free from reducing substances which would quickly fog the sensitive layer. It must be thoroughly dried at a temperature below 55°C and keeps for 3 months.

Ferric potassium oxalate formulas(12)

Author's formula

pH − 1	A	Ferric potassium oxalate 12%	240 cc
		Oxalic acid 20%	50 cc
		Ammonium tartrate 35%	30 cc
	B	Potassium ferricyanide 10%	70 cc

Tomoda's formula (12b)

Water	80–260 cc
Ferric ammonium oxalate	12 g
Oxalic acid	0·5 g
Neutral potassium oxalate	0·75 g
Ammonium dichromate	0·2 g
Dextrin	0·75 g
Potassium ferricyanide	2 g

Ferric ammonium citrate formulas:

pH < 2·3	Ferric ammonium citrate (green) 25%	100 cc
	Potassium ferricyanide 12%	100 cc
pH > 2·3	Ferric ammonium citrate (Brown) 20%	100 cc
	Potassium ferricyanide 16%	100 cc
	Ammonia	1–4 cc

The addition of small quantities of dichromate increases the contrast. Triethanolamine (1 cc) increases the sensitivity and reduces the contrast.

Prints are fixed merely by washing which dissolves the excess sensitizer. The final wash is acidified slightly with hydrochloric acid, to prevent decomposition of the ferroprussiate into iron oxide.

Modification of ferroprussiate colours. The material is first treated in weak alkali such as 1% sodium carbonate, which decomposes the ferric ferrocyanide to ferric hydroxide and soluble alkali ferrocyanide: the blue colour is destroyed leaving only a faint pink image.

The decolorized paper is washed and treated in a solution of tanin(13) which reacts with the iron hydrooxide to give a highly coloured image, similar to ordinary ink. The colour of the image depends on the variety of tanin:

with *gallic acid*, or gall-nut tanin, the image is black.

with *oak* tanin the image is violet.

with *catechu* tanin the image is brown. A little boric acid is added to this bath.

400. Other photosensitive systems

Systems similar to the iron-ferricyanide ones can be obtained, on one hand by replacing the potassium ferricyanide by *potassium cobalticyanide* $K_3[Co(CN)_6]$, and on the other, by replacing the ferri-organic complex by an analogous cobalt or copper compound: thus one can use *cobaltic ammonium oxalate* $(NH_3)_3 . [Co(C_2O_4)_3]$ obtained by electrolytic oxidation of cobaltic oxalate in ammonia, or *cupric ammonium (or potassium) citrate.* Photochemically produced cobalt ferrocyanide, and complexes of Cr and Mn have been used in ceramics to obtain glazed colours.

Manganic salts like the ferric, cobaltic and cupric ones are reduced by light to the lower valency manganous ones. Most of the inorganic manganic salts are unstable, and it is therefore better to use the organic salts: oxalate, tartrate, citrate, lactate, etc. They are obtained by treating potassium permanganate with an excess of organic acid. *Manganic tartrate*, coated on gelatinated paper, becomes discoloured by light, giving a positive image which can oxidize o-toluidine hydrochloride: the image becomes blue-green.

401. Photoceramics

It is possible to impregnate porous pottery with a light sensitive mixture. After exposure under a negative, it is sufficient to wash and fire. The compound which forms the image is destroyed by the heat but leaves in its place a metallic oxide. It is then glazed.

The ferroprussiate solution can be used, but the iron oxide produced is soluble in porcelain glazing compounds. Jorgensen(13b) recommends the following formula:

Potassium cobalticyanide	3 g
Hot water	8 cc
Glycerin	1 g

after cooling to below 40°C add:

Ammonium colbaltioxalate	6 g
Ferric citrate	0·5 g
Citric acid	0·3 g

Use immediately.

Using cobalt, chromium and manganese, multicolour effects can be obtained.

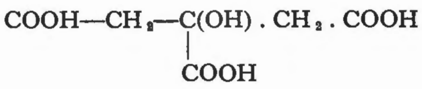
402. Preparation of ferric oxalates and citrates

1. *Ferric oxalate* $Fe_2(C_2O_4)_3$. Ferric hydroxide, precipitated from a solution of the chloride or sulphate with ammonia, is washed and then dissolved in a hot solution of oxalic acid (the hydroxide being in excess). The solution of ferric oxalate is filtered and concentrated by evaporation to a syrupy liquid which precipitates oily droplets on the addition of alcohol. Solid ferric oxalate is obtained as brown granules. Its solutions must be kept in the dark.

2. *Ferric potassium oxalate* $K_3[Fe(C_2O_4)_3]$. A mixture of concentrated solutions of ferric chloride and neutral potassium oxalate, when slowly cooled, deposits green crystals of ferric potassium oxalate which can be washed and recrystallized. It is also obtained by mixing ferric and potassium oxalates.

3. *Normal ferric citrate.* This compound does not seem to exist.(14)

4. *Ferric ammonium citrates.* Citric acid,



$$\mathrm{COOH{-}CH_2{-}\underset{\displaystyle COOH}{\underset{|}{C}}(OH)\,.\,CH_2\,.\,COOH}$$

treated with ferric hydrate forms a complex cation:

$$[Fe_3(C_6H_5O_7)_2(OH)_2(H_2O)_2]^+$$

which can give salts like the chloroplatinate or the citrate. The latter is obtained in the presence of excess acid and crystallizes with $18H_2O$.

$$[Fe_3(C_6H_5O_7)_2(OH)_2(H_2O)_2]_3\ C_6H_5O_7\ .\ 18H_2O$$

To prepare it, freshly precipitated ferric hydroxide is dissolved in 3N citric acid at 50°C, then evaporated at this temperature until a surface skin forms. The citrate is precipitated with 95% alcohol, dried at 50°C and redissolved in water and crystallized at a moderate temperature. Red-brown scales are obtained.

5. Ammonia converts this complex citrate to *brown ferric ammonium citrate* which is believed to be the citrate of the complex ion:

$$[Fe(C_6H_4\ .\ FeO\ .\ O_7)_2(NH_4)_2(H_2O)_2]^+$$

A solution of the complex ferric citrate is mixed with a slight excess of ammonia and concentrated on the water bath below 50°C, when it deposits a brown ferric ammonium citrate with $15H_2O$. This compound is heated for an hour at 90–100°C to give another brown citrate containing $6H_2O$ as deep red scales. By further prolonged heating the remaining $6H_2O$ are removed. The complex ion begins to decompose at 120°C.

The brown ferric citrates appear to form colloidal solutions in water, which do not exist until the pH is 2·3.

Commercially, the brown ferric citrate is prepared by treating 41 parts of ferric hydroxide (containing 11% Fe_2O_3) with 10 parts of citric acid and 6 parts of ammonia (20% NH_3).

6. *Green iron citrates.* The addition of citric acid or an alkali citrate to brown ferric citrates converts them to green ferric citrates, such as *green ferric ammonium citrate* from which the brown salt can be obtained again by treating with ammonia.

The green salts come from *ferricitric acid* with the formula $H_3[Fe_2(C_6H_5O_7)_3$ which is prepared by dissolving ferric hydroxide in cold citric acid and evaporating at a low temperature until yellow-brown scales are obtained. By replacing the 3H of the acid with ammonia or potash in the appropriate quantities the green ferric ammonium (or potassium) citrates are obtained. The same result is obtained by mixing the theoretical quantities of citric acid, ferric hydroxide and ammonia or potash. The solution is then concentrated on the water-bath at a low temperature until the deliquescent green scales are produced. A mixture of ferric chloride and alkali citrate deposits the same compound after evaporation. The green citrates always have an acid reaction.

Commercially this material is prepared from 25 parts of ferric hydroxide (11% Fe_2O_3), 10 parts of citric acid and 5 parts of ammonia (20% NH_3).

The green citrate contains 14–15% Fe whilst the brown citrate contains 21·7–22·4%.

SPECIAL TECHNIQUES

403. Sensitive layers adsorbed on glass

Grebenesikow has shown that water attacks glass to form superficially a very thin film of colloidal silica having a very high absorptive power. Burmistrow (*Phot. Jour.*, April 1936) made use of this property to prepare glass plates with a sensitized surface, without using organic colloids. The photosensitive compound can be silver nitrate, silver nitrate precipitated with an already adsorbed halide, or colloidal silver chlorinated with $CuCl_2$ after adsorption.

Physical development in a solution of silver nitrate and hydroquinone is used.

1% ferric chloride attacks the glass to produce a silica layer ten times as thick as that from pure water. However, the thickness varies with the glass and the action is increased by heating.

A glass plate can be suitably sensitized by successive treatments in nitric acid, tincture of iodine and dilute ammonia followed by bathing in 10% silver nitrate, washing and drying. It gives an image with 30 minutes exposure at 3 feet from a 15A arc, then 15 minutes physical development before fixing in 25% hypo.

The layer thickness varies from 5 to 20 mμ. Resolving power —2·5 x that of a Lippmann emulsion separating two lines 0·25 μ apart.

Application—graticule preparation. The surface must be protected with a varnish or well hardened by heating to 350°C and polishing.

It should be added that the success of the method given above is very critical: the image is often too weak or too fragile. Leiztner reports having had only failures,(15) but Loening and Farnell,(15b) obtained satisfactory results with precipitated silica.

404. Sensitized anodized aluminium

Aluminium, covered with a thin superficial layer of alumina by electrolytic oxidation (anodizing), can hold in its pores without a protective colloid, various photosensitive mixtures: precipitated silver salts, soluble silver and iron salts, ferricyanide etc., which have already been dealt with earlier.(16)

The alumina layer, exposed under a negative, or by optical projection can then be developed and fixed without difficulty depending on the nature of the sensitizer used. The resulting image, silver or otherwise, is stable and resistant to shock.

The images can be coloured by dyeing the oxide layer using the usual resist methods.

Sheet or foil aluminium without an oxide layer can be coated with a ferric sensitizer in a resin(17) dissolved in an organic solvent and printed.

For anodizing, Kirilov and Kheinman(18) used the following technique: aluminium sheets containing at least 99·4% Al are polished, and degreased in a hydrocarbon containing alcohol, then in a solution containing disodium orthophosphate 46 g, caustic soda 8 g and soldium silicate 28 g per litre for 2–3 minutes at 50°–60°C. They are then oxidized by electrolysis in 10% sulphuric acid at 30°C. The aluminium plates form the anode (+) whilst the cathode (−) is lead. Current density 1·5 A/dm^2. The voltage (6–18 V) is adjusted so that the alumina layer formed is suitable after 30–40 minutes. If the acid concentration is increased or the temperature is raised, the oxide is attacked and the layer is thinner. A greater dilution makes the oxide brittle and porous. The thickness increases noticeably with the duration of electrolysis; if, for example, it is 15 μ after 45 minutes it will be 25 μ at 60 minutes.

The aluminium can also be oxidized in oxalic or chromic acid. In the latter case, the solution generally contains 50–100 g per litre chromic acid, 0·1 g sodium chloride and 0·4 g sulphuric acid. Voltage 10–40 V, temperature 30–40°C, current density 0·15–0·6 A/dm^2 (at 40 V), time about 30 minutes At higher temperatures the oxide film becomes powdery.

Sensitizing. The oxidized aluminium plate is sensitized by immersing alternately in solutions of 10% potassium bromide, then silver nitrate. Kirilov and Kheinman did this 39 times before filling up 1/3 of the volume of the alumina pores. Fog due to spontaneously formed silver specks is overcome by treating for 5 minutes in a solution containing 50 g of ferricyanide and 50 g potassium bromide per litre. After washing, drying and exposing for 1–2 seconds at 20 cm from a 500 W lamp, development is carried out in a solution containing 5 g amidol, 25 g anhydrous sulphite, 1–10 g of potassium bromide and 4 g 40% lactic acid (anti-oxidant). The image is yellow-brown—or sometimes black. Owing to the low contrast, intensification is necessary.

Diazo sensitization can be used but reproducible results are difficult to obtain.

Sensitization in the oxide pores requires care. Furthermore it gives plates which do not keep well and are slow.

Pure aluminium plates, suitably oxidized can have a mirror surface. They can then receive a layer of *photographic emulsion*—chloride or bromide. These plates, when treated like photographic papers give beautiful images on a metallic base which look like Daguerrotypes. Another available type has a white under-layer for the production of dials or industrial plates.

An unhardened emulsion freshly coated on anodized aluminium, then developed in a tanning developer can be used for photomechanical work to repel greasy inks after hot water development. Printing must be prolonged to expose the gelatin in contact with the metal.

Another technique used by the writer is to coat the sensitizing emulsion on dyed anodized aluminium (black, blue or other colour). After development, the image, is attacked by a hydrogen peroxide bath (see para 596) which leaves a cavity where the silver was. The washed print is then immersed for a few seconds in a bleaching solution—hypochlorite for example—which destroys the dye staining the base wherever there is a cavity, in proportion to the thickness of the residual gelatin.

Among the dyes which can dye anodized aluminium are: nigrosine (J and JB), Niagara direct blue, Pontamine fast turquoise blue 8 GL, naphthol green B, naphthalene green V, quinoline yellow, polar yellow, azorubine, neolan red, etc. Dyeing time 30–60 minutes in a 1–5 g per litre solution containing 1 cc acetic acid, and at a temperature of 80–92°C. Finishing in a mordant of 5 g per litre nickel acetate at 95°C is often carried out for 15 minutes. Immersion in boiling water for 30 minutes improves the fastness of the dye.

405. Photographic tracing on sheet metal

Tracings on sheet metal for fabrication or for the preparation of templets are frequently made photographically (by contact or projection), after sensitization of the previously varnished sheet. The sensitive layer can be either an emulsion applied with a spray-gun or an emulsion already coated on a temporary paper support and transferred to the sheet.

(*a*) *Coating method.* The washed and dried metal is coated with a resin layer rich in plasticizer, then two other layers with decreasing plasticizer content but containing a white pigment. The photographic emulsion, in small pieces kept at 7°C (45°F) or in powder (which is dissolved in water), is heated to 37°C (99°F) and sprayed with compressed air. After drying at 35°C (95°F), the sensitized sheets are exposed under negatives and developed in large tanks.

(*b*) *Transfer process.* The metal surface is first covered with two layers of white varnish. The varnish is dried and made tacky by swelling, then the paper carrying the emulsion is applied with a roller or with an automatic machine. The support is stripped off dry and the image is printed onto the transferred emulsion and then developed in an M.Q. developer.

The transfer paper can be prepared by coating a layer of beeswax (dissolved in trichlorethylene) on the base, then an emulsion and finally a nitrocullulose layer containing a rubber ester (as an adhesive layer). High contrast process emulsions are used (B.P. 559,843).

(*c*) *Copying.* The original drawing must be dimensionally stable. It can be drawn in reverse on plate glass or vinyl sheet covered with a white opaque varnish. To avoid drawing in reverse, it can be reflex printed from an original, the right way round on a sheet of white aluminium. The copy is made on plate glass for large sizes or on gummed paper.

It is possible to make the copy with a phosphorescent layer which is excited by X-rays before being placed in contact with the drawing and the sensitive material. The degreased aluminium plate is coated successively with a clear lacquer, a black lacquer, then a phosphorescent paint on which the drawing is made after matting with special glasspaper. Excitation is by X-rays from a 200-kV 20 mA source for two minutes. The phosphorescent image is then placed in contact with the sensitized surface for 3 minutes, or reflex printed.

406. Reversal transfer

Reversal transfer is a process in which silver bromide *diffuses* from a photographic layer into another gelatin layer containing *development centres* of colloidal silver, in the presence of a *solvent.* If the solvent contains a developing agent a new image is formed at the same time in the transfer layer by physical development brought about by the development centres.(18b)

The emulsion layer and the transfer layer can be superimposed on the same base or can be on two separate sheets. In the former case (Gevaert Diaversal), the base is first coated with a layer of hardened gelatin containing a suspension of colloidal silver, then a coating of fast unhardened emulsion. After exposure and negative development, the paper, still containing the developer, is immersed without agitation in a solvent bath. The residual silver bromide is dissolved and diffuses into the lower layer, where it is reduced imagewise. The upper emulsion layer is then removed in hot water. A brownish image remains. Resolving power, 10 lines per mm. (A. Rott's process, F.P. 873,507 and Add. cert. 53,404, 53,502, 53,513, 53,515.)

Agfa Copyrapid paper is the result of E. Weyde's work carried out at the same time as Rott's, and consists of a system using two separate papers, one negative carrying a silver bromide emulsion, and the other a positive paper carrying a gelatin layer containing development centres.

As the negative is exposed via the base for reflex copying, the emulsion must be very contrasty, with a very short toe to the characteristic curve. Orthochromatic chloride reflex papers are very suitable for reversal transfer although they contain more silver halide than necessary. The Copyrapid negative emulsion is very thin (which makes it cheaper).

The paper is exposed in a reflex printer emulsion towards the document. It is then placed face to face with the positive paper and inserted into a developing machine. This consists, in principle, of two rollers which press the moistened sheets together. Development is complete in a few seconds with a concentrated caustic soda developer containing a solvent for silver halides. When transfer is complete, it is only necessary to part the papers if only limited keeping is necessary. Otherwise, it is better to wash before drying. The image is yellow-brown on a white ground when washed, or yellow when not washed.

The development centres of the positive transfer paper are generally of colloidal silver, silver sulphide, gold, etc. A faint image can be obtained merely by using fixed out, washed and dried photographic paper.

407. Polaroid-Land process

This process for obtaining a negative and a positive simultaneously is used mainly in the U.S.A. to obtain a 'picture in a minute'. It is controversial whether Rott or the Agfa laboratories have priority over Land for the image transfer idea. Whatever it is, the Land process deserves mention because of the orginality with which it is applied, and the quality of the results. This is the principle:

A paper support, which is the final positive, is unrolled in the camera and brought into contact by two rollers with the exposed negative material. A viscous developer contained in a pod attached to the paper is spread between the two materials when the pod is burst passing through the rollers. The resulting sandwich pack is withdrawn from the camera through a slit fitted with a knife. The two supports must each be opaque. One minute after being brought into contact the positive is complete.

The viscous developer contains hydroquinone, caustic soda, sodium sulphate and hypo, or a developer such as benzylsulphonylhydrazine (Woodward); its viscosity is increased with a soluble cellulose compound. Development is very rapid, and at the same time the undeveloped silver bromide is dissolved by the hypo to diffuse into the positive layer where it is reduced to form a brown or black positive image.

For the process to be possible, development must be more rapid than the formation of the transferable complex. Furthermore, it is essential that the complex is only reduced in contact with the positive material. The positive negative ratio depends on the ratio of the rates of complex formation and development. The yield is at an optimum when the two are in equilibrium.

Furthermore for the precipitation of the silver from the argentothiosulphate to take place before the solution is saturated with silver, metallic, or preferably sulphide or selenide ions must be present, producing development centres of silver sulphide or selenide. The concentration of these ions must not exceed 10^{-10} or the positive will have low density and contrast, and will not be black. The difficulty is overcome by dispersing a slightly soluble sulphide on the surface of the positive material.

The positive image can be stabilized with a viscous solution containing acetic acid and a zinc salt: colourless sulphide ions are formed (F.P. 1,105,617). An antioxidant, such as ascorbic acid+ethyl tartrate is added to the stabilizer.

Obtaining several prints. A print uses only 14% of the silver present in the layer. If the negative, put in contact with a second positive, is developed again, there is no image. But A. J. Sievers noted that when the solvent (hypo) is reduced to an optimum value, three more copies can be obtained. Theoretically, the maximum number is seven.(18c)

408. Xerography

Xerography is the local destruction by light of an *electrostatic charge* on a metal plate coated with a semiconductor. The image is made visible with a powder which is then transferred to paper by electrostatic discharge.

Selenyi disclosed in 1935(19) the principle of this method, and the idea was taken up again by Carlson in 1938. The process acquired by the Haloid Company was perfected by Schaffert and Oughton at the Battelle Memorial Institute.(20)

One starts with an aluminium sheet covered with *selenium* whose dark resistance is $10^{15}\ \Omega$ cm and $10^{10}\ \Omega$ cm in the light. The selenium is deposited by vacuum sublimation. Theoretically it can be replaced by sulphur or anthracene. The plate is charged (or sensitized) by passing, 1 cm from its surface, a stretched metal wire at an E.M.F. of 4000 to 7000 V. The semi-conductor is charged by the Couronne effect, the metal being earthed. The electrostatic charge acquired in this way is unchanged for seven hours and then starts to discharge slowly in the dark.

By exposing to light behind a photographic lens, the *selenium becomes conductive* where it has been exposed. It locally conducts its superficial charge to the metal support. The discharge continues slowly after exposure but the image contrast is not appreciably reduced. The visible radiation can be replaced by X-rays. In this case the exposure is 1–7 times shorter than with a fine-grain X-ray film without a screen. Resolving power in visible radiations: 10 lines/mm.

Development. The surface of the plate is covered with a *resinous powder* (diam. 0·1–20 μ) containing *crystalline grains* about 300 μ diameter. These grains can be of tartaric acid or ammonium chloride, if the plate is positively charged. The resin is negatively charged by friction. (The resin powder, however, can be charged by direct electrical means, giving better half tones.)

Thus the negatively charged resinous powder is attracted to the positively charged image and makes it visible. The exposed plate is placed at the bottom of a dish containing the powder mixture, and is moved about until a satisfactory contrast is obtained.

Metcalfe(20b) develops with a liquid (petrol, turpentine, carbon tetrachloride) containing a dispersed pigment. Time: 1 to 10 seconds.

Transfer. This only consists in applying to the image a negatively charged sheet of paper and pressing the combination between two metal plates and heating to melt the resin and attach it to its new support.

The selenium-covered plate can be used again after wiping the surface with powdered sodium chloride.

In this way a photographic print can be obtained two minutes after exposure.

Reversal. When a pigment is blown between the exposed plate and a parallel electrode charged to 300 V, a reversed image is obtained. (Rayford: *Phot. Engng.*, 1955, 173–182.)

408b. Electrofax. This process, similar to Xerography, was worked out by Young and Greig of the R.C.A. Corp.(20c) A layer of zinc oxide ZnO (0·25–0·35 μ diam), dispersed in a resin, is coated on baryta paper. The sheet is negatively charged with a high tension charge. When exposed to light, ZnO becomes a conductor; the charges are dissipated in the exposed areas. To develop the image, a positively charged pigment is used, which adheres to the non-exposed regions. Then the resin is softened by heat, making the pigment stick. Minimum voltage between the exposed and unexposed areas: 150 V. In practice, the sensitized sheet is charged to 300–600 V, by passing it under a wire at 3–7 kV, the sheet being placed on a metal plate connected to the earth. Efficient λ: 320 to 420 mμ. Zinc oxide can be rendered colour-sensitive with a dye such as rose Bengal, eosin, fluorescein, acridine orange, methylene blue. Sensitivity is influenced by moisture; however, it is sufficient to make photographic enlargements.

408c. Berchtold process. Whilst, in Xerography and Electrofax, the residual charge of a photoconductor is used, here this is the photoconductor which emits a current under the action of light.(20d) A selenium or thallium sulphide photoelectric layer, covered by a transparent electrode, is coated on a special plate having unidirectional conductivity exclusively perpendicular to the plane of the plate. This is obtained by sawing a block of parallel varnished metal wires, cemented together. Under the plate, is placed a sheet of paper sensitive to electric current, such as diazo paper, the pH of which can vary by electrolysis (or a system reacting to redox phenomena). The back of the paper must lay on a counter-electrode made of graphite containing rubber. Twenty-two volts are applied to the entire block, during exposure which must be intermittent. Time: 60 secs. with 600 lux.

408d. Thermofax (Minnesota Mnfg. Co.). A translucent sheet of paper is covered with a substance which blackens when heated, then with a white pigment, the layers containing a spirit-soluble resin. Under the action of intense infra-red rays, the sensitive layer darkens locally (blue-black image on yellow background). Application: document reproduction.

409. Ferrography

Ferrography is the *magnetic recording* of an image on tape, after analyzing with a cathode *iconoscope* of the type used in television cameras, then copying on a *cylindrical steel sleeve*. A *magnetic powder* is sprayed onto the cylinder and adheres in proportion to the intensity of the field and makes the image visible; the image can then be transferred onto paper as in xerography. A print is thus obtained with a 48 lines per cm pattern in about a minute. For further details, see the works of Atkinson and Ellis.(21)

The transcription can also be made direct from the iconoscope to the steel cylinder or from the magnetic tape onto a machine for printing a half-tone image point by point.

410. Photosensitive glass

Glass capable of producing an image by exposure to light was perfected by the Corning Glass Works following the work of Dalton, Stookey and Armistead. Dalton(22) was the first to notice that copper ruby glasses are more quickly coloured when exposed to U.V. radiation before firing. He then disclosed that an image could be formed of metallic particles after exposure and firing.

The photosensitive glasses must contain a photosensitive metal such as silver, gold, copper or cerium. After 10 minutes exposure to an arc lamp, the glass is heated to 650°C to obtain an image through the glass. A glass studied before 1943(23) had the composition: SiO_2 – 100; Na_2CO_3 – 37; Al_2O_3 – 3·3; $BaCO_3$ – 15; $NaNO_3$ – 6; cryolite – 10; CeO_2 – 0·05; Au – 0·014; and gave a blue to red image depending on the exposure time, before firing for 30 minutes at 550°C, depending on whether the coagulation is superficial or deep in the glass. A point source favours the production of a deep image.(24)

The region of spectral sensitivity is between 300 and 370 mμ for copper or silver glasses.(25) It is below 254 mμ for gold glasses, but the addition of cerium raises the limit to 350 mμ.

The glasses must be free from lead, but more than 5% of an alkali oxide is necessary. Borates and phosphates give spontaneous colouring on firing. Baryta is beneficial to gold sensitizing. Traces of tin and bismuth increase sensitivity but reduce contrast. Cerium compounds act by absorbing the active radiations.

Latent image: this is formed by the electrons given out by the photosensitive ions which are kept in an active metastable state by the traps made by the faults in the glass lattice, or by the metallic ions. During firing, the metallic ions acquire electrons to become atoms, which aggregate to produce metallic particles. A brief heating destroys the latent image by thermal agitation.

Opal glasses. The metallic silver particles produced by exposure to light can bring about, during firing, the crystallization of non-metallic particles which finally give a milky image on a clear ground. Some opalized glasses are more quickly attacked by hydrofluoric acid than the untreated glass.

Transparent glasses. Transparent glasses with a coloured image can be of two types: gold glasses giving blue, purple or ruby images and gold+palladium for sepia images, used mainly in stained glass.

Transferring a silver image to glass. Stookey(26) disclosed a process for transferring a photographic image onto glass in which the procedure is as follows: the silver image in gelatin is applied to the glass surface and covered with a special paste of ferric sulphate (25%) and yellow ochre (75%) in a liquid binder (oil or water). Drying is followed by baking at 450°C for 30 minutes. A latent silver image is then formed on the glass surface. To make it visible, the glass must be heated in a reducing atmosphere (mixture of hydrogen and nitrogen) for an hour between 450 and 500°C, which transforms the silver ions to metal. The ferric sulphate oxidizes the silver whilst the ochre prevents the deformation of the image during the decomposition of the gelatin.

1. Goetz A. and Inn E. C. Y. made a photosensitive system [silver oxide adsorbed onto zinc oxide or titanium oxide] dispersed in a concentration of 20 mg per sq. ft. Black to yellowish images are produced depending on the state of subdivision. (*Rev. Mod. Physics.*, 1948, 131–142.)
2. Namias: *Bull. Soc. Fr. Phot.*, 1895, 117. The photosensitivity of the mercury salts was studied by Bergmann in 1779.

2b. Van der Meulen and Countryman studied a similar preparation of mercurous oxalate dispersed in gelatin and developed by heating to 120°C, after exposure. Fierce heating produces an explosion of the mercurous oxalate. Maximum sensitivity between 230 and 320 mμ. (*Phot. Eng.*, 1953, 104–112.)

3. Mercury oxalate can also be converted to an *amino complex* and introduced into the gelatin. It is sensitized by metals like silver, gold, thallium, etc. and by eosin. Images by development or by printing out can be obtained in this way. I.G.F.: G.P. 470,611 and 619.
4. F.P. 728,099.
5. Reissaus: G.P. 540,888. Weyl and Cramer: *J.O.S.A.*, 1949, 889.
6. F.P. 730,043, 730,876.

6b. Arens and Eggert: *Sci. Ind. Phot.*, **2,** 381. Eggert J.: *Bristol Phot. Conf.*, 1950, 94–98. Eggert J.: *Sci. Ind. Phot.*, 1953, 377–385. Berchtold J. and Eggert J.: *Naturwiss.*, 1953, 55. Berchtold J.: Thesis No. 2376, *Phot. Inst. ETH*, Zurich, 60 pages.

7. Except when it is extremely pure and dry.
8. F.P. 665,491 (1928).
9. F.P. 874,014 (1942).
10. For the preparation of organic ferric salts, see para. 402.
11. G.P. 261,342 (1910), 366,068 (1922).

11b. Suzuki S.: *R.P.S. Phot. Conf.*, London 1953.

12. For the preparation of organic ferric salts, see para. 402.

12b. Tomoda Y.: *Jl. Soc. Phot. Japan*, May 1951, 161.

13. The tanins are glucosides, combinations of glucose and gallic acid derivatives.

13b. Jorgensen C. V.: *Kem. Maanedsblad*, 1939, 201; *Nordiske Kemikermode*, 1939, 254.
14. Belloni: *Gaz. Chim. Ital.*, **50,** II, 190 and 210.
15. *Phot. Engng.*, 1950, 7–15.
15b. *Phot. Jl.*, 1952, 187–194.
16. Mason R. B.: U.S.P. 2,115,342 (1932).
17. Philips: F.P. 864,723.
18. *Zh. Prikl. Khimii*, 1951, 4019–4025.
18b. Stevens and Norrish: (*Sci. et Ind. Phot.*, **9(2),** 334) had noted, in 1938, that the images of an emulsion layer can diffuse in a gelatin layer, in close contact. Frln. E. Weyde made the same observation with a baryta coated paper.
18c. Sievers A. J.: *Phot. Sci. and Techn.*, May 1955, 75.
19. Selenyi P.: *Zeitz. Techn. Phys.*, 1935, 607.
20. Schaffert R. M. and Oughton C. D.: *J.O.S.A.*, 1948, 991–998. McMaster R. C.: *Non Destr. Testing*, 1951, 8–25.
20b. Metcalfe K. A.: *Jl. Sci. Instrum.*, 1955, 74.
20c. Young C. J. and Greig H. G.: *R.C.A. Review*, 1954, 469–484.
20d. Berchtold J.: *Sci. et Ind. Phot.*, 1955, 465–471.
21. Atkinson R. B. and Ellis S. G.: *Jl. Frank. Inst.*, 1951, 373–381.
22. U.S.P. 2,326,012 and 2,422,472.
23. B.P. 597,089 (1943).
24. Stookey S. D.: *P.S.A. Jl.*, 1948, 399.
25. Stookey S. D.: *Ind. and Eng. Chem.*, 1949, 856–861.
26. Stookey S. D.: *Ind. and Eng. Chem.*, 1954, 174–176.

Chapter XXV

PHOTOGRAPHIC BASE MATERIALS

PHOTOGRAPHIC PAPER

411. Constitution of cellulose

Cellulose is the essential constituent of all vegetable material. It is found in many varieties, and in various degrees of purity. It is almost pure in *cotton*, and in wood is mixed with lignine, proteins, resins, waxes and inorganic matter.

In practice cellulose is divided into three types, designated by α, β and γ:

α-cellulose: insoluble in 18% soda, constitutes 98·5–99% of cotton.

β-cellulose: soluble in 18% soda, but is reprecipitated by adding acid.

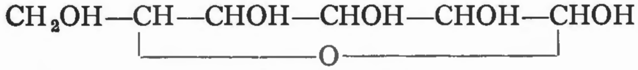
γ-cellulose: soluble in 18% soda and is not reprecipitated on acidifying.

The β and γ varieties are termed *hemicelluloses*. Photographic paper should contain less than 4% of them.

Cellulose is a derivative of *glucose*, a pentahydroxyaldehyde, in the form of its anhydride

$$\mathrm{CH_2OH—CHOH—CHOH—CHOH—CHOH—CHO}$$

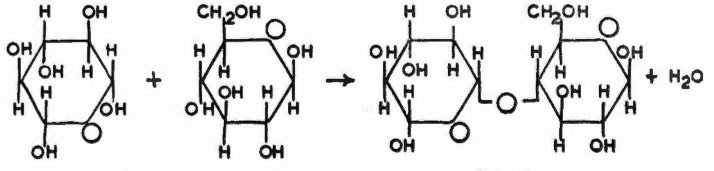
Glucose



$$\mathrm{CH_2OH—\underbrace{CH—CHOH—CHOH—CHOH—CHOH}_{O}}$$

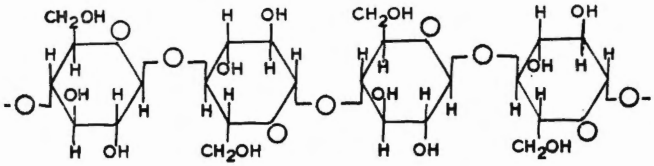
Glucosic anhydride

Glucosic anhydride, or α-glucopyranone is represented schematically by a hexagon, one of whose peaks is occupied by an oxygen atom. Two or more molecules of α-glucopyranone unite in a chain via the oxygen to give a *cellobiose*, a *cellotriose*, *cellotetrose*, *cellohexose*, etc.



α-glucopyranone Cellobiose

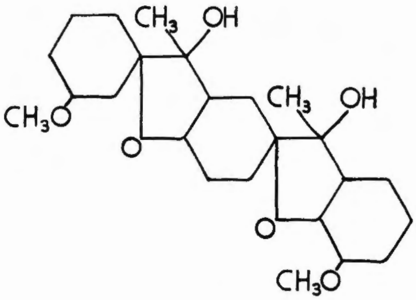
Cellulose is a very long chain of glucopyranic nuclei, on the cellobiose model, the number of these nuclei being 100 to 200.



Cellulose

The X-ray diffraction spectra show that cellulose is in the crystalline state, the simple crystals, or crystallites, having dimensions and shapes which vary with the nature of the fibre. Furthermore, the chains which make up the crystallites are themselves made up of groups of smaller chains, each containing four glucosic nuclei.

Lignine, which impregnates the cellulose in wood appears to be a polymer of benzofurfurane, formed from a ketol by migration of an H and cyclization with loss of water. *Pectin* is formed by the union of many substances: pentoses, hexoses, galaturonic acid, acetic acid, methanol.



Lignine

Cellulose is hydrolyzed by acids into simpler degradation products, the final product being glucose. Controlled hydrolysis produces intermediate products. With sulphuric acid and acetic anhydride the principal product is octaacetylcellobiose.

When cellulose is pure, as in cotton, its treatment is simple but when it is associated with lignine in wood, it is necessary to solubilize the latter. Use is made of the relative inertness of cellulose to *sodium bisulphite* and *chlorine*: the *lignine* combines with the bisulphite giving soluble sulphonates. With chlorine, chloroderivatives are formed which can be solubilized with soda. The soda also dissolves resins, waxes, fats and proteins.

412. Paper

Paper is made up of a tangle of cellulose fibres. Many starting materials are normally used in its manufacture: rags and textile clippings, wood, straw, esparto, cane, etc.

For photographic use, however, paper must have certain properties which can only be achieved by judicious choice of materials, and manufacturing processes. The water, which is used in very great amounts (1000–2000 litres per kilo of rags, and 200–450 litres per kilo of of bisulphite paste) must be very pure and non radioactive.

For photographic paper, the principal sources of cellulose are a mixture of *rag pulp* or *cotton* with *bisulphite wood pulp*.

Rag pulp. The rags should be *cotton* or *linen* exclusively, but sometimes hemp is included. Cotton has fibres which stretch relatively little in water, and whose chemical resistance is relatively high. Linen, with its tangled fibres, ensures great mechanical stability.

The sorted and cleaned rags are washed with an alkali: caustic soda or a mixture of chalk and sodium carbonate. They are bleached with chlorine whose excess is neutralized with an antichlor such as sodium sulphite.

The carefully washed fibres are then separated and chopped in a Dutch beating trough equipped with a drum of blades (Fig. 51).

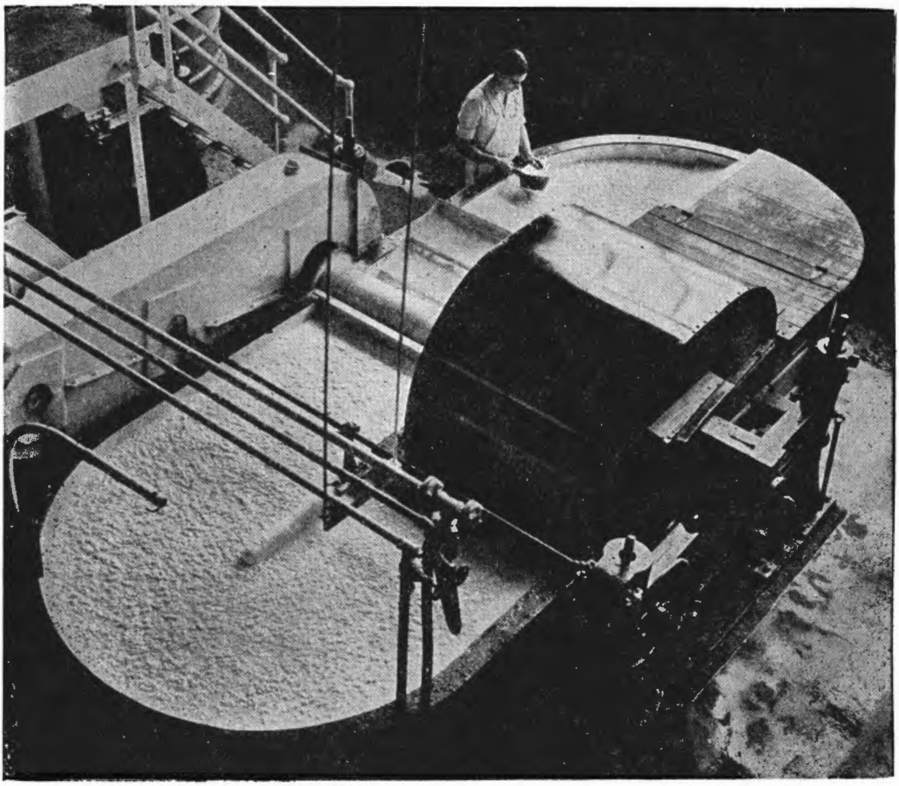


FIG. 51. Treating the paper pulp. *Photo: Eastman-Kodak, Rochester, U.S.A.*

Bisulphite pulp. This is usually obtained from fir and spruce. It must be stirred hot, and under pressure, with calcium bisulphite in the presence of excess sulphur dioxide. The bark is then removed and the wood reduced to chips and treated in large washing vats lined with acid-resistant bricks. The sulphonated lignine dissolves. At the same time, aldehyde groups are produced from the side chains. To prevent their liberation with darkening of the mass by polymerization the bisulphite must be maintained in excess.(1)

The wood is then washed and bleached with chlorine or hypochlorite (hot in the second case). Brick-lined concrete beaters in which the pulp is circulated around baffles are used. The process is completed with thorough washing, after an alkali bath if chlorine has been used.

The pulp if incompletely cooked, then processed, gives waterproof papers.

The yield is 45% of the weight of the dry wood whilst rag pulp gives 70–90%.

Other methods. The *soda process* is applicable to all woods, but it is more expensive than the bisulphite process as 20–30% of reagent is required. Papers obtained from birch, aspen and chestnut are slightly absorbent. They must be bleached.

Straw, rye, esparto and bamboo treated with soda, or chlorine and soda alternatively give fibres with interesting properties: those from straw are waterproof, translucent and stiff, from esparto they are bulky and absorbent, whilst bamboo produces tough porous papers.

The treatment of papers with soda obtained from *sodium sulphate* and lime produces sodium sulphide which is ruinous for photographic papers. Furthermore, the bleaching of these high-coloured pulps, called 'kraft', reduces their principal qualities, namely great strength and flexibility.

Finally we would note that half the world's paper consumption, particularly newsprints, is obtained by mechanical breaking down of wood.

413. Sizing

To make the paper resistant, binders and fillers must be added to the cellulose pulp.

The binder is made up of several of the following materials: gelatin, casein, colophony, melamine, starch.

Colophony, which is the commonest binder is generally accompanied by aluminium sulphate which lowers the pH to 4·5. The source of the colophony can influence its photographic behaviour. Red or brown stains must not be produced when the paper is treated with diazonium compounds after several hours. To make the resin inert it should be treated with nitrous acid or a nitrate.

To produce very resistant papers it is advisable to size with 3% *melamine*(1b) even together with colophony and aluminium sulphate. Paraformaldehyde is added to the melamine, which is first dissolved in water containing hydrochloric acid, and ripened for 24–48 hours. It is incompatible with casein.

A method of analyzing the sizing substances has been perfected by Sève.(2) Extracts are made with boiling acidified alcohol (colophony), acidified water (gelatin), ammoniacal water (casein) and boiling acetic acid (melamine).

Filler. This is generally kaolin.

Dyes. These beling to the *indanthrene* group: indanthrene (or solanthrene) blue and brilliant pink or sirius pink K.L., to tint whites; and indanthrene orange or Hansa yellow G.I. for cream and ivory.

Testing the absence of iron and copper. The paper pulp, added to potassium ferrocyanide must not give bluish or reddish stains. Iron content: less than 0·1 mg per kilo.

414. Baryta coating

The paper, and the emulsion which later covers it, are separated by a layer of gelatin containing a suspension of *barium sulphate* ($BaSO_4$) in extremely fine particles (0·5–1 μ). The barium sulphate increases the reflecting power of the paper, and gives it a perfectly white surface covering all the faults. The baryta solution is often tinted.

The barium sulphate is obtained by precipitating barium chloride with sodium sulphate at 55°C. The dilution of the reagents, the temperature and the agitation determine the fineness of the precipitate, and hence the degree of mattness of the paper. Precipitation in the presence of glycerin gives a very fine precipitate. This becomes more difficult to wash as the particles decrease in size. The water content is reduced to 30–50%.

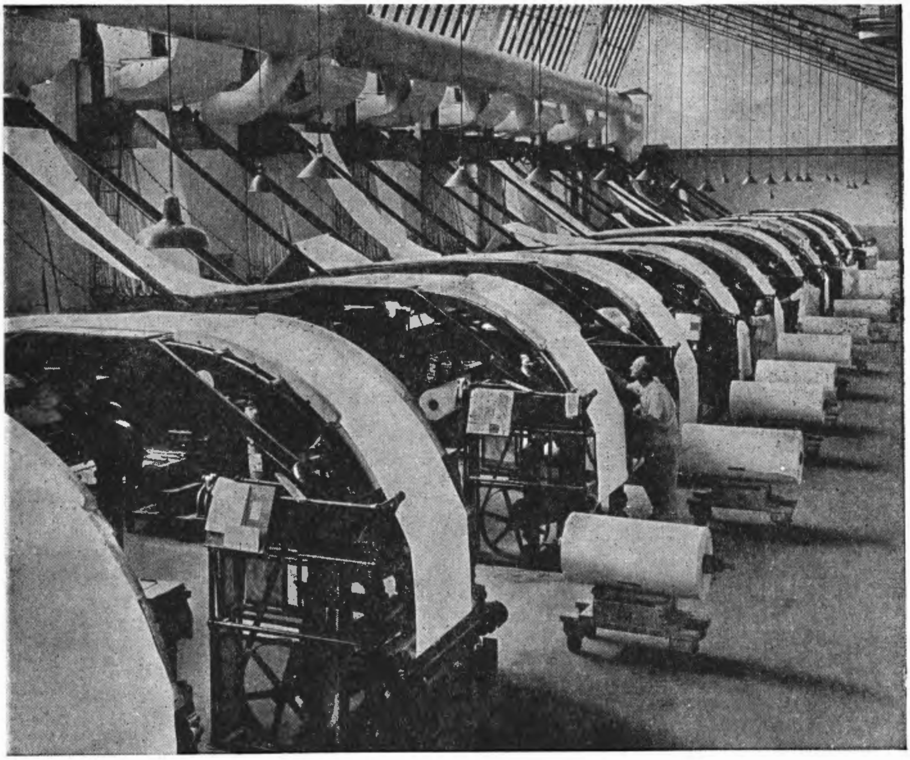


FIG. 52. Reeling up the Baryta coated paper. *Photo: Eastman-Kodak, Rochester, U.S.A.*

Baryta coating is carried out by applying the mixture with brushes, which spread it over the paper which goes past them around a large drum. The wet paper is led into a tunnel where it is arranged in long festoons which move slowly. Linear speed: 90 to 150 feet per minute.

The paper is dried with a current of warm filtered air during its passage through the tunnel, (which can accommodate 3000–6000 feet) and after rehumidifying to 18°C is reeled up (Fig. 52).

The operation can be repeated several times depending on the gloss required.

Baryta formulas	Trumm		Agfa	Schoeller
	Gloss	Matt		
Baryta paste (water %)	120 kg 50%	50 kg 50%	180 kg 30%	100 kg 44%
Baryta powder	—	5 kg	—	—
Water	20 l	25 l	30 l	70 l
Glycerin	0·6 l	0·3 l	6 l	1·25 l
Water	30 l	15 l	75 l	?
Gelatin	4·5 kg	1·5 kg	18 kg	5 kg
Water	1 l	1 l	170 l	—
Chrome alum 10%	1·5 l	1 l	6 l	1·5 l
Formalin 30%	—	—	100 cc	+
Milk	2·5 l	—	4 l	—
Alcohol	2 l	2 l	—	—
Citric acid 10%	1 l	0·2 l	—	—
Dye solution 5%	0·1 l	0·15 l	+	+
Saponin 5%	+	+	+	+

Coarse-grain baryta is suitable for matt surfaces. Note that the percentage in the paste indicates water and not barium sulphate. The milk is an anti-frothing agent; it must be boiled. Citric acid is only used when the pH must be reduced.

The purity of the water must be carefully controlled. If necessary, it must be filtered over active carbon, then distilled. The gelatin must be photographically inert. Its selection is important.

Method of preparation. The white baryta paste is mixed in a Werner mill with the water, glycerin and dye for 20 minutes at 30 r.p.m. The gelatin solution (filtered through cloth at a pressure of 1 kg) is then added, and mixing is continued for 15 minutes more. The mud is filtered through stainless steel gauze using a brush, then the remaining solutions are added.

Number of baryta layers. Matt surfaces 1, half matt 2, glossy 3 or 4. Weight of $BaSO_4$ per m^2 per layer : 10–11 g.

Calendering. The coated paper is treated at 80°C in a 5- or 7-roller calender at a pressure of 3 tons (Fig. 53). Glossy surfaces three times, semi-matt twice and matt surfaces, once or not at all. Wait one month, to let the baryta layer harden, before coating the emulsion. (Fig. 54).

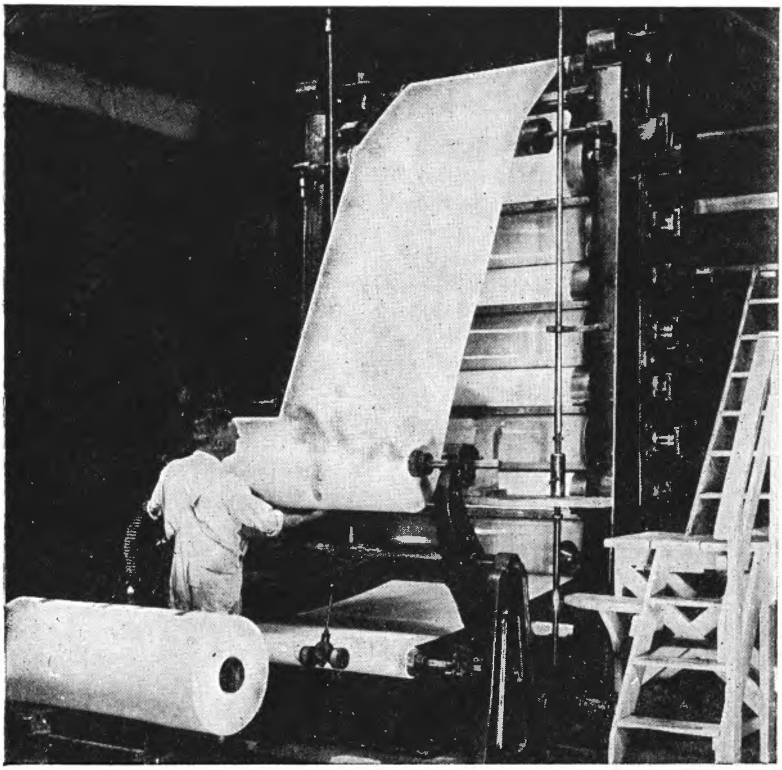


FIG. 53. Calendering the photographic paper.

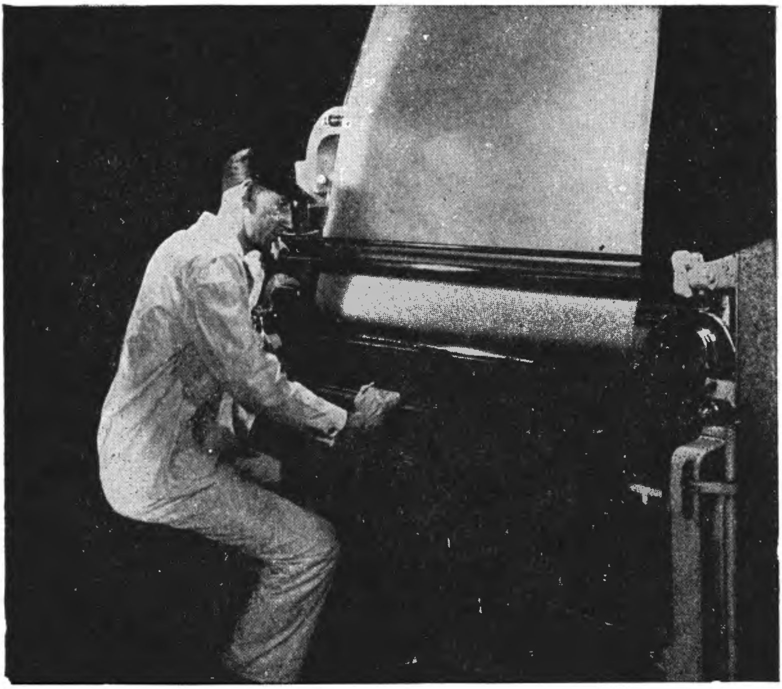


FIG. 54. Coating the emulsion.

Photos: Eastman-Kodak, Rochester, U.S.A.

415. Waterproof paper

Waterproof paper is used for continuous printing of aerial photographs, reversal identity photographs and the production of transparent photographic scales.

Cellulose, vinyl or acrylic lacquer can be used, if surface application with a solvent is used. It is, however, possible to make the paper waterproof by incorporating the compound in the pulp: melamine, vinyl acetate emulsion, vinyl copolymer, or preferably vinyl chloride emulsion plasticized with butadiene nitrile (Geon or Breon). These emulsions can also be applied superficially. Some of them need curing at 120°C to fuse the resin particles; others are film-forming when cold.

In all cases the lacquered paper must be coated with a *substratum*, otherwise the emulsion would not adhere. This substratum can be a resin emulsion mixed with gelatin. For example, for an acrylic lacquer, an acrylic emulsion with gelatin and chrome alum can be used.(3) If necessary, several subbing layers can be used with increasing proportions of gelatin.

The paper can even be waterproofed by exposure to vapour of tetra ethyl or methyl silicate, followed by water treatment.(4) This fixes silicon atoms on the lateral chains.

Transparent waterproof photographic paper. Both sides of a long-fibre paper (90 gm/m^2) are coated with a nitrocellulose lacquer such as: Nitrocellulose 20, ethanol 15, butanol 10, acetone 20, ethyl acetate 27, tricresyl phosphate 4 and castor oil 4. Amount—100 g per m^2. The emulsion surface is subbed with: gelatin 2, water 2, acetic acid 10, methanol 76, amyl alcohol 10. Anti-halo: 5% gelatin coloured with acid fuchsine (60 cc/m^2).(5)

416. Tests on papers

All papers, baryta coated or otherwise, which are to be used for photographic purposes must be subjected to many control tests—chemical, mechanical, optical and photographic.

Ash content (fillers)
Weight of size
Weight of baryta
Humidity
Degree of water absorption on wetting
Presence of iron, copper, etc.
Presence of oxidizing or reducing agents
pH
Grease and other spots
Occluded air content
Dust (organic, mineral and metallic)
Moulds
Sticking marks in rolls
Weight per sq. metre
Density
Thickness
Microscopic examination of cross-section
Length and orientation of fibres
Homogeneity (holes)
Resistance to breaking, wet and dry
Stretching with wetting (two directions)
Resistance to tearing, wet and dry
Resistance to wear (rubbing).
Crumpling
Pliability
Bursting
Swelling in water
Shrinkage on slow drying (two directions) and rapid drying (two directions)
Flatness after drying (deformation)
Resistance to photographic baths and flatness
Formation of blisters
Uniformity of baryta coating (brushing streaks)
Colour and whiteness (colorimetric measurement)(6)
Gloss and grain (in all directions)

Tests with photographic emulsion-check:

Absence of white spots with centres (desensitizing dust).
Absence of black dots with craters (dye which is a red light sensitizer).
Variations in speed and contrast compared with a standard paper.
Fog, after 30 days at 40°C in dry oven, compared with standard paper.

Weight of paper. Ordinary photographic paper is supplied in two thicknesses: *Paper* (properly named) 135–150 g/m^2 and *card*, 230–250 g/m^2.

Document papers are generally 80 g but they can be lighter or heavier.

CELLULOSE ESTER FILMS

417. Cellulose esters

Cellulose, which, as we have seen, is an oxidation polymer of glucosic anhydride, contains three hydroxyl groups per unit in its molecule: two OH are directly attached to the pyranic nucleus and a third via a $—CH_2—$. These three OH groups therefore have not the same activity. The action of acids esterifies the alcohol groups to give, according to conditions, cellulose mono-, di-, and tri- esters, whose chemical properties differ. Frequently, it is simpler to obtain the tri-ester first and then hydrolyze back.

Cellulose combines with most known acids, giving a very large number of possible esters. The most interesting, as a photographic base is the triacetate, which has replaced the dangerous nitrate.

The structure of cellulose derivatives is studied with X-rays, and ultra-violet and infra-red radiation. In this way the hydroxyl, aldehyde, ketone and acid groups which may be present can be identified and enumerated.(7) The X-ray diffraction spectra show the degree of crystallinity. If the ester has been prepared in a homogeneous medium (in a solvent) it no longer has the fibrous structure of cellulose. On the contrary, when a non-solvent diluent is used, the resulting product retains the structure of the original material, which imparts beneficial mechanical properties. The size of a main link is 10·3 Å, but the distance between two parallel chains depends on the number of attached groups. In the presence of a solvent, the ester first dissolves these—it is said to gelatinize—which brings about the separation of the chains following the attachment of a solvent molecule on an acyl group (by a hexose group). The parallel chains then become mobile relative to each other; they can then disperse if excess solvent is added.

418. Cellulose acetates

Cellulose which is completely esterified with acetic acid is the *triacetate* which contains 62·5% of acid combined in the form $CH_3 . CO . O . R$. Ordinary non-inflammable base is intermediate between diacetate and triacetate, and is obtained by partial hydrolysis of triacetate. Triacetate is superior to it in mechanical strength, and it alone is used for professional positive ciné film. When correctly prepared, it is less deformed by processing than diacetate or nitrate.

Distinguishing. Acetate safety base can be distinguished from nitrate base by its ultra-violet fluorescence. Another method is to place a piece of film in trichlorethylene. The heavier nitrate (D 1·52) sinks whilst the lighter acetate (D 1·25) floats.

There are three main methods of preparing the cellulose acetates:

(*a*) Acetylation in homogeneous medium by acetic anhydride in acetic acid, in the presence of a catalyst such as sulphuric acid. Pre-treatment is necessary to swell the fibres (acetic acid + sulphuric acid).

(*b*) Acetylation in suspension in a diluent (heterogeneous medium), in the presence of a catalyst—sulphuric acid or zinc chloride. Pre-treatment is also necessary.

(*c*) Acetylation with acetyl chloride in pyridine, or, preferably, dioxane.(8)

Acetylation in suspension, in which the cellulose fibrous structure is retained, is preferable for film base.

Separation of the acetates. An acetone solution of cellulose acetate will throw down the most acetylated fractions when water is added; when ethylene chloride or dichloroethane is added, the less acetylated portions come out.(8b)

Physical properties. The density of the cellulose acetates increases with the degree of acetylation from 1·2 to 1·35. Refractive index, 1·5. Resistance to heat 175–200°C. Decomposes at 250°C. It does not continue to burn.

The acetates will disperse in certain saline solutions such as zinc chloride and calcium bromide or thiocyanate.

The addition of 10–30% alcohol to solvents increases the solution rate. The number of possible solvents decreases as the acetyl content increases.

Acetic acid content	Acetone	Ethyl acetate	Methylene chloride +20% alcohol
51%	soluble	sl. soluble	soluble
54%	soluble	mod. soluble	soluble
56%	soluble	soluble	soluble
58%	soluble	soluble	soluble
59%	sl. soluble	sl. soluble	soluble
62·5%	insoluble	insoluble	soluble

Methyl formate and concentrated acetic acid dissolve all the acetates from 50 to 62·5%.

Viscosity. The viscosity of cellulose acetate solutions depends on the molecular weight, the degree of esterification, the solvent and the moisture content. This reduces the viscosity.

419. Preparation of cellulose acetate in homogeneous medium

Pre-treatment. The cellulose is treated in the following bath:

Acetic acid	4 kg
Sulphuric acid	0·020 kg
Cotton	1 kg

for half an hour between 30 and 40°C. It is left for another hour between 25 and 30°C, drained, washed and dried.

Acetylation. The hydrocellulose is acetylated at 40°C in:

Acetic acid	80 parts
Acetic anhydride	100 parts
Zinc chloride	20 parts

or at 70°C in:

Acetic anhydride	500 parts
Sulphuric acid S.G. 1·82	25 parts

which can be used for 125 parts of hydrocellulose. An acetate with 60% acetyl content is obtained.

In all cases the anhydride must be kept in excess. The reaction is carried out slowly, with cooling to avoid any rise in temperature. The operation is complete when all the cellulose is dissolved. It must then be stopped so that the product is not gellified.

Hydrolysis. Five to 10% of water is added to the drained triacetate to decompose the anhydride. Precipitation of the acetate is avoided by adding this water as dilute acetic acid. The mass is left for 12 hours.

The hydrolysis proper is carried out with more or less dilute sulphuric acid —70% for example, at a constant temperature, generally above the ambient. The more dilute the acid, the less hydrolysis: the degree of hydrolysis can therefore be regulated at will. With concentrated acid, de-esterification cannot be continued below 30% acetyl. With more dilute acid acting for a longer time it can be carried down to 20%; the product then becomes water-soluble, and is precipitated by alcohol or acetone. At 13% acetyl, the product decomposes and regenerates insoluble cellulose.

The hydrolyzed acetate is precipitated with water. The viscosity of the mass is first reduced by adding dilute acetic acid, followed by a large volume of water. The acetate precipitates. It is washed with water to recover the acid, and sometimes it is treated with alcohol. The acetate, washed as pulp, is dried.

420. Preparation of cellulose acetate in suspension (heterogeneous medium)

Pre-treatment. The cellulose, dried to 3–6% moisture, is introduced into the stainless-steel pre-treatment vessel. Thirty-five parts acetic acid to 100 parts of cellulose is added, and the mass is stirred for one or two hours.

The swelling of the cellulose can be accelerated by adding some sulphuric or phosphoric acid. The acetic acid is then partly displaced with carbon tetrachloride (Eastman-Kodak).

Acetylation. This is catalyzed by sulphuric acid. The chloride has the disadvantage of gelling the resulting ester.

The cellulose, in a second vessel (of bronze—95% Cu and 5% Sn) is mixed with 300 parts of acetic anhydride, 400 parts of methylene chloride and 1 part of 98% acid to 100 parts cellulose. The reagent mixture is added in fractions. For a cellulose containing 3% water these will be:

Acetic anhydride	1/2	1/4	1/4	of the total
CH_2Cl_2	2/3	1/6	1/6	
Sulphuric acid	1/4	1/4	1/2	

Each addition is made after the temperature has dropped; a water jacket may be used to assist this. A reflux condenser returns the methylene chloride. After 4–6 hours all fibres have disappeared, indicating the end of the process. The temperature is kept at 45°C until the required viscosity is obtained.[(8c)]

The diluent could theoretically be benzene, toluene, xylene, trichlorethylene, carbon tetrachloride, pyridine, etc.

Triacetate. The triacetate thus obtained must be washed and dried. To avoid hydrolysis, the sulphuric groups present must be displaced by acetyl groups. Sindl used ethyl acetate for this as it does not dissolve triacetate.[(8d)]

Fifty-eight to *59% acetate.* The triacetate is partially hydrolyzed. Eighty to 100 parts of water mixed with 65 parts of sulphuric acid is added to the mass. The temperature is raised to 55–60°C. When the acetyl content has dropped to 59%, the acetate is pumped from the hydrolysis vessel and is neutralized with sodium acetate. The operation takes 6 hours at 53–58°C. To obtain an acetyl content of 58% the product must dissolve completely in a mixture of equal weights of methylene chloride and acetone. To achieve this the hydrolysis is continued for a further 20 minutes. For 56% acetate, the testing solvent is 9 parts of acetone and one part of ethanol.

When hydrolysis is judged to be complete, the temperature is raised to 80°C for a short time to remove the methylene chloride. The acetate is then precipitated. If a low viscosity is required, water is added, with stirring. For photographic acetate, 600–700 parts of 6% acetic acid is added, stirring only for the first minute. After precipitation, stirring is continued for a further 10 minutes.

The precipitate is broken up and the suspension is drained on a moving perforated band for 1 hour. The acetate is carried to a mixer where it is ground with 10% of its weight of 30–35% acetic acid. The new suspension is pumped onto a second perforated band where it is drained and washed with eleven successive jets of acetic acid of decreasing concentration, and finally with a jet of water. Each wash water is used in the previous treatment.

The resulting mass is centrifuged, which still leaves 150% of water. It is dried at 60–70°C and at 10–20 mm pressure until its moisture content is 0·5–3%. Drying time: 6 hours.

Construction materials: acetylation and precipitation—bronze. Other stages, stainless steel, except the blower, piping and drier, which are aluminium.

421. Cellulose raw material

The starting materials for the manufacture of cellulose esters are *cotton linters* and *wood pulp*.

Cotton linters is the short down on the cotton seed left after the main stripping. Manufacturing scraps are added to it. The fibres are first beaten to remove the husk and earth, and are then degreased with trichlorethylene. They are then purified by cooking for several hours in autoclaves containing 3% sodium carbonate, which removes the waxes and pectic materials (the same result can be obtained with 3% caustic at normal pressure). The mass is then successively washed, bleached, acidified, re-washed, dried and carded. Nor more than 0·3% ash and 0·2% fats must remain in the linters, which must contain 98·5% α-cellulose and have a moisture content of 1%.

Wood pulp. Wood pulp obtained from fir or beech by the bisulphite or the alkali process must be as pure as possible. It is quite difficult to reach 96% α-cellulose. The pulp generally contains $\leqslant 1\%$ ash, $\leqslant 0{\cdot}5\%$ waxes and fats, $\leqslant 2\%$ pentosanes. Pulp sheets 1–2 mm thick must be shredded before esterification.

Purification of cellulose is absolutely essential for the preparation of cellulose nitrate. Crude cellulose containing lignine, fats and waxes can ignite spontaneously when nitrated.

422. Cellulose acetopropionate and acetobutyrate

Propionic $CH_3—CH_2—CO.OH$, butyric $CH_3—CH_2—CH_2—CO.OH$ and isobutyric $(CH_3)_2:CH—CO.OH$ acids esterify cellulose to form plastic materials similar to the acetates. The general method of preparation is to react a mixture of the corresponding acids and anhydrides on hydrocellulose in the presence of a catalyst. Another standard method uses the acid chloride in the presence of the corresponding magnesium salt: mix, for example, 162 parts of regenerated cellulose with 198 parts of magnesium butyrate, dry, and add 213 parts of butyryl chloride and 25 parts of butyric anhydride. The mass thickens rapidly and the temperature rises. It is diluted with nitrobenzene, then poured into water, which precipitates the cellulose butyrate. For various other methods, see (9).

The *acetobutyrates* and to a less extent, the *acetopropionates* are preferred to these simple esters, as they give films which are very resistant to deformation by heat and moisture.(9b) They are prepared as follows:

Action of propionic or butyric anhydride on partially hydrolyzed cellulose acetate.

Action of a mixture of propionic or butyric acid and anhydride on cellulose previously heated for 4 hours at 45°C in acetic acid.(10)

Action of a mixture of acetic and propionic (or butyric) anhydrides on pretreated cellulose. The reaction can be catalyzed with monochloracetic acid and magnesium perchlorate.

Action of propionic or butyric acid on partially hydrolyzed cellulose acetate in the presence of monochloracetic anhydride.

Action of propionyl or butyryl chloride on partially hydrolyzed cellulose acetate in pyridine.

Action of propionyl or butyryl chloride and acetic anhydride on cellulose in the presence of a tertiary organic base.

Action of a mixture of acetyl chloride, acetic anhydride and magnesium propionate or butyrate on regenerated cellulose.

See also the following patents[(11)] and a study of the preparation and properties of the acetobutyrate by Sato, Lodai, and Kodama.[(12)]

Finally, here is the method used in Germany for the preparation of *cellulose acetobutyrate*.

The cellulose is pre-treated with acetic acid as above. Esterification is carried out in the mixture:

Acetic anhydride	50 parts
Acetobutyric anhydride	300 parts
Methylene chloride	350 parts
Sulphuric acid 98%	1 part

Esterification time: 7–10 hours. Temperature the same as for acetylation. The final product contains 16–18% butyric acid and 43–44% acetic acid.

Acetic acid, dehydrated at a high temperature and low pressure in the presence of triphenyl phosphate gives a product CH_2CO called ketene, which with butyric acid gives an acetobutyric anhydride $C_3H_7 . CO—O—CO . CH_3$.

The acetobutyrates and acetopropionates are soluble in acetone, ethyl acetate, butyl acetate, ethyl lactate, methyl glycol acetate, diacetone, alcohol, dioxane, methylene chloride, propylene chloride + 10% alcohol, etc.

423. Other cellulose organic esters

Cellulose esters other than the acetate, acetopropionate and acetobutyrate are not used for the manufacture of films. Some of them, however, have been tried for the formation of auxiliary layers:

Cellulose formate, less stable than the acetate.

The esters of fatty acids such as *cellulose palmitate*, obtained by the action of the corresponding acid chlorides.

Cellulose phthalate. Phthalic anhydride combines with cellulose in the presence of pyridine to give a triphthalate whose sodium salts are soluble.

The *cellulose ethers* result from the union of alkyl radicals to the cellulose nucleus *via* an oxygen atom, following the scheme Cellulose—O—R. The radical is generally methyl, ethyl, or benzyl. They are prepared by reacting the alkyl sulphate or iodide on alkali cellulose, hot, and in the presence of excess caustic soda.

The most important ethers are *methyl cellulose*, *ethyl cellulose* and *benzyl cellulose*. Methyl cellulose with 13–18% $—OCH_3$ is soluble in cold water.

Carboxymethyl cellulose, or sodium cellulose glycollate, Cellulose—O—$—CH_2—CO . ONa$, is produced by the action of monochloracetic acid on alkali cellulose. It is water soluble, giving very viscous solutions, and is used as a thickener.

Alkali cellulose is obtained by heating cellulose with 35% caustic soda. The drained mass is dissolved in water from which it is precipitated with sulphuric or acetic acid after filtration. The hydrocellulose is redissolved in soda lye: 8% NaOH and 8% cellulose (see para. 433: *Cellophane*).

424. Cellulose nitrate

Cellulose nitrate is little used today except for roll- and sheet-film base, and even in this role it has been largely replaced by acetate. Cellulose nitrate film has excellent mechanical properties and its price is much lower than acetate, qualities which have justified its choice despite its inflammability.

Cellulose, treated with fuming nitric acid in the presence of sulphuric acid, is converted to the nitrate, but the nitrogen content varies with the operating conditions. In general it increases with the acid concentration.

Its solubility depends on the degree of nitration:

Nitrogen content	Alcohol +ether	Acetone	Ethyl acetate	Amyl acetate
9·5%	ins.	mod. sol.	mod. sol.	mod. sol.
10·5%	sl. sol.	sol.	sol.	sol.
11·5%	sol.	sol.	sol.	sol.
12·5%	mod. sol.	sol.	sol.	sol.
12·9%	gelat.	sol.	sol.	sol.
13·5%	ins.	sol.	sol.	sol.

Complete nitration corresponds to 14·14% nitrogen. This requires nitric acid whose concentration is greater than 85%. For the usual lower degrees, Lunge and Bebie give the following nitration mixtures:

Nitrogen content	Nitric acid	Sulphuric acid	Water
9·31	39·78	36·72	23·50
9·76	40·30	37·20	22·50
10·93	41·31	38·43	20·26
11·59	42·15	38·95	18·90
12·05	42·73	39·45	17·82
12·31	43·25	40·14	16·61
12·58	43·85	40·66	15·49
12·76	44·45	41·03	14·52
13·21	46·01	42·61	11·38
13·65	49·07	45·31	5·62

The *viscosity* of cellulose nitrate solutions depends not on the degree of nitration, but on the *nitration temperature*. The viscosity falls as this temperature rises. It also depends of course on the *solvent*. The *alcohol-ether ratio* is a characteristic for a certain nitrocellulose to obtain the minimum viscosity. More alcohol can be added as the nitrogen content falls. The moisture content must be borne in mind as it affects the viscosity of solutions.

The cellulose nitrates in current use contain 11–12·5% nitrogen (optimum 11·5–12%). Their viscosities vary from 0·5 to 200 seconds (ball method). The low viscosity grades give thick even films most readily, whilst the viscous varieties give stronger films.

Manufacture. Cellulose nitrate is made from wood pulp, or preferably, cotton linters, purified by methods already given. This purification with hot alkali is essential, or the mass may ignite when nitrated due to the formation of unstable nitroderivatives.

Nitration can be performed with the usual nitro sulphuric mixtures given above, or by a variation such as the following (which gives a product very soluble in alcohol-ether): nitric acid 23·7% sulphuric acid 61·71%, water 14·6%. Nitrating time: 30 minutes maximum. Twenty-eight kg of acids are required to give 1 kg nitrate.

It is, however, better to nitrate in the presence of nitrogen peroxide N_2O_4 (B. Pt. 21·6°C) which retains the fibrous structure of the cellulose. To avoid degrading the cellulose, the peroxide is dissolved in the nitric acid. The nitrogen content depends on the percentage of peroxide: with 30%, a content of 13·7% N is obtained. A nitro-sulphuric mixture containing the peroxide can also be used, for example, nitric acid 22, sulphuric acid 57, nitrogen peroxide 2, water 19. Nitrating time: 45 minutes at 30°C.

Cellulose nitrates with a high nitrogen content are also prepared with acetonitric and phosphonitric acid mixtures.

The nitration acid mixtures must always be cooled before use. The nitro cotton is then drained (but not completely) and *washed* for several days in a large amount of water. To *stabilize* it, it is boiled in 0·5% sulphuric or hydrochloric acid for two days. After washing and pulping, it must be *bleached* in 1% hypochlorite or chlorine water, neutralized with bisulphite, again thoroughly washed, and then drained. To *dehydrate* the mass, it is squeezed in a press. By *imbibing* 95% *alcohol*, and again pressing, the water is removed; this can be repeated. Cellulose nitrate must *not* be dried.

Together with *camphor*, it gives celluloid.

425. Plasticizers

A plasticizer is a substance which can soften a polymer by jellifying it. It is located between the side members of the molecular chains (and particularly the ester groups) which enables the chains to shift by sliding over each other.

Plasticizers are generally high boiling solvents (low vapour pressure). They must be resistant to heat and light, be colourless, insoluble and not hydrolyzable.

By combining a solvent, having *keto* and *ester* groups, with a *heavy nucleus* it is possible to obtain these qualities. Thus with *phthalic acid* $C_6H_4(CO.OH)_2$ and fatty alcohols, phthalic esters are obtained which are excellent plasticizers:

Ethyl phthalate	$C_6H_4(CO.OC_2H_5)_2$
Butyl phthalate	$C_6H_4(CO.OC_4H_9)_2$
Isoamyl phthalate	$C_6H_4(CO.OC_5H_{11})_2$
Octyl phthalate	$C_6H_4(CO.OC_8H_{17})_2$

Ethyl phthlate, which boils at 298·5°C can advantageously be replaced by the less volatile higher homologues. The amount added to cellulose acetate should not exceed 10%.

Another group of placitizers in current use are the *phosphates*: triphenyl phosphate $(C_6H_5)_3PO_4$ (M.Pt. 48·8°C) and m-tricresylphosphate $(C_6H_4CH_3)_3PO_4$ (B.Pt. 420°C). Up to 25% can be used in an acetate. The jellifying properties of tricresylphosphate are attributed to the flexible pyramid shape of its molecule.

Among the other plasticizers the most interesting are:

Tartrates – butyl (B.Pt. 300°C) and especially *amyl* (B.Pt. 400°C). Miscible in all proportions with cellulose esters.

Glycerin esters: triacetin (or glycerin triacetate) and the tripropionate and tributyrate. They have the disadvantage that they hydrolyze. More stable products are obtained by combining diacetin with phthalic acid, or glycerin with abietic acid derivatives. The tribenzoate is also a good plasticizer (M.Pt. 71°C).

Sulphamides, such as monoethyl-p-toluene sulphamide $CH_3 . C_6H_4 . SO_2 . NH . C_2H_5$ or Elastol (M.Pt. 63°C). They have been criticized for producing brittle films.

The esters of fatty acids are not volatile, but the length of their chains reduces their jellifying power. They can only be used as additives. Butyl oleate (B.Pt. 357–370°C) with benzyl alcohol, butyl stearate (M.Pt. 18–20°C) mixed with phthalates or tartrates, amyl borate, etc.

Cellulose acetopropionates and acetobutyrates are placticized like the acetates. The following have also been recommended, however: octyl phthalate, tributyl phosphate, cyclohexyl adipate, p-toluene sulphamide, camphor, tetrahydrofurfuryl furoate, glycol furoate,(14) furfuryloxyacetic esters,(15) alkyl acetamides,(16) glycol dilactates,(17) glycolic esters of 3 : 4 : 5-trimethylbenzoic acid,(18) the ester-amides(19) and triethanolamine esters.(20)

Plasticizers for cellulose nitrate. The best and most common plasticizer for cellulose nitrate is *camphor*.(21) Good results are also obtained with *butyl phthalate* (up to 50%), ethylene glycol phthalate (cellosolve phthalate) (B.Pt. 345°C), butylene glycol phthalate (B.Pt. 370°C), ethylacetanilide $C_6H_5 . N(C_2H_5) CO . CH_3$, a camphor substitute called Mannol (M.Pt. 54°C, B.Pt. 258°C), hydroxynaphthalide-2 : 3 (Mittel P.H.), symmetrical diethyldiphenylurea $(C_6H_5)(C_2H_5)N—CO—N(C_6H_5)(C_2H_5)$, (Mollit I) (M.Pt. 72°C, B.Pt. 325°C).

The action of many plasticizers on various cellulose esters has been studied in detail by many writers, to whom reference should be made.(22)

426. Dopes for film casting

The dopes for film making are prepared by dissolving the *cellulose ester* and the *plasticizer* in a *volatile solvent* which preferably contains a heavier solvent to avoid reticulation during drying.

Cellulose triacetate—58% and over. Eighty-five parts of acetate are plasticized, for example, with 15 parts of a mixture of triphenyl phosphate and diethyl phthalate, in a solvent made up of methylene chloride 85, chloroform 10, amyl alcohol 5, or a mixture of methylene chloride and butanol or ethanol, or methylene chloride, acetone and methanol. A suitable mixture contains: methylene chloride 90, methanol 3, n-butanol 7.(22b)

A non-solvent (e.g. amyl alcohol) produces a gel which improves the initial rigidity.

Acetate—56% and less. The solvent is generally acetone; anhydrous ethanol and toluene can be added, for example: acetone 85, alcohol 10 and toluene 5. Plasticizers: triphenyl phosphate and ethyl (or other) phthalate. Seventy-seven parts of solvent to 20 of acetate and 3 of plasticizer are required.

A formula attributed to Schleussner contains acetate 25, acetone 100, triphenyl phosphate 3, tricresyl phosphate 0·1, phthalic ester 0·2, p-toluene sulphamide 2.

The volatile solvent can be partly or completely replaced by methyl or ethyl formate or acetate. Unlike the nitrate, cellulose acetate is insoluble in amyl acetate.

Cellulose acetobutyrate. In acetone solution. The same plasticizers as acetate, or those already given.

Cellulose nitrate. The solvent is *acetone* or anhydrous *methanol.* Example: cellulose nitrate 18, camphor 4, butyl phthalate 0·5, acetone 77·5.

Another formula includes: cellulose nitrate 25, camphor 3·8, tricresyl phosphate 0·05, phthalic ester 0·1, butanol 2·5, ethanol 13·5.

Amyl or butyl acetate can be added to the solvent. It is also well known that cellulose nitrate forms a dope with an *alcohol-ether* mixture.

The dopes are prepared in mixers, filtered by pumping through cotton, and degassed by standing. Slight heating speeds up the ascent of the bubbles.(22c) It is then led to the reservoirs of the coating machines.

427. Solvents

As stated above, the main solvent for 58% triacetate is methylene chloride CH_2Cl_2. It is a very volatile non-inflammable liquid, but it is toxic. Its use necessitates well-sealed machinery and good ventilation. Compared with ether and acetone, the evaporation times are: ether 1, methylene chloride 1·8, acetone 2·1.

Boiling points of cellulose ester solvents (A = acetate, N = nitrate, E = ethyl cellulose, B = benzyl cellulose).(23)

	°C
Methyl formate (A, N)	32
Ether (N + alcohol)	34–35
Methylene chloride (A + alcohol)	40–42
Ethyl formate	54
Acetone (A, N) (acetobutyrate)	55–56
Methyl acetate (A, N) (E with solvents)	56–62
Chloroform (A)	61
Methanol (N, E)	64–65
Ethyl acetate (N) (A + alcohol) (acetobutyrate)	74–77
Ethanol (E) (B + benzene)	78
Methyl ethyl ketone (A, N)	79
Isopropanol	82
Isopropyl acetate (N)	84–93
n-propyl acetate (N)	97–101
n-propanol	96–98
Dioxane (A) (N + alcohol) (acetobutyrate)	101
Isobutanol	104–107
Toluene (E)	109–110
Trichloroethane (A)	110–115
Epichlorhydrin (A)	117
n-butanol	114–118
Isobutyl acetate (N)	116
Acetic acid (A, N)	118
Glycol diethyl ether (N)	121
Ethyl butyrate (N)	122
Amyl formate (N)	123
n-butyl acetate (N, E)	121–127
Mesityl oxide (A, N)	129
Methyl cellosolve (ethylene glycol monomethyl ether) (A, N)	115–130
Isoamyl alcohol (E)	132
Cellosolve (ethylene glycol monoethyl ether) (N)	126–138
Isoamyl acetate (N) (E + alcohol)	138
Methyl cellosolve acetate (A, N)	138–145
n-propyl ketone (butyrone)(A, N)	144
Cellosolve acetate (N)	149–160
Cyclohexanone (A, N)	150–165

	°C
Diacetone alcohol (A, N)	150–165
Cyclohexanol (B)	155–170
Ethyl lactate (A, N)	155–163
Furfurol (A, N)	160–165
Methylcyclohexanone (A, N)	165–171
Isoamyl butyrate (N)	179
Cyclohexyl acetate (A, N)	170–180
Furfuryl alcohol (N)	177
Tetrahydrofurfuryl alcohol (N)	177
Ethylene glycol diacetate (A, N)	186–190
Butyl lactate (N) (acetate diluent)	170–195
Ethylene glycol monoacetate (A, N)	178–195
Ethyl acetylglycolate (A, N)	181–195
Carbitol (diethylene glycol monoethyl ether) (N)	180–200
Benzyl alcohol (A, N, E)	204–208
Ethyl benzoate (A, N)	212–215
Diethylene glycol (N)	244
Diacetin and triacetin (A)	258–259
Butyl tartrate (A, N)	298
Butyl tartrate (A, N)	325
Amyl tartrate (A, N)	400

It should be remembered that the use of solvents requires *stringent precautions* against their *toxicity* and *inflammability*. In general, solvents should be regarded as dangerous, for either long or short periods. The chlorinated compounds are the most toxic, together with the benzene hydrocarbons, methanol, the formates, dioxane and mesityl oxide.

The *inflammability* is determined by the flash point. The solvents having a boiling point below 115°C can form *explosive mixtures* at room temperature. The chlorinated compounds are practically non-inflammable, but at high temperatures the poisonous phosgene can be produced.

The highly inflammable liquids can be ignited by static discharge, produced for example, by the friction of the product in a casting tube. For this reason all vessels must be earthed.

Measurement of the viscosity of dopes. The viscosity of dopes is generally measured by the time taken for a steel ball to fall between two marks in a vertical glass tube. The viscosity in poises is given by the equation

$$v = K(D - d)t$$

where D is the density of the ball (7·65 for steel), d is the density of the viscous liquid, t the falling time in seconds and K the constant of the instrument. Glycerin can be used as the standard liquid.

The dimensions of the apparatus are:

	Tube diam.	Distance	Tube length	Distance to upper mark	Ball diam.
U.S.A.	1 in. (25·4 mm)	10 in. (254 mm)	14 in. (355·6mm)	2 in. (50·8 mm)	5/16 in. (7·93 mm)
Brit. Eng. St. Ass.	32 mm	150 mm	260 mm	55 mm	$\frac{1}{8}$ in. (3·16 mm) $\frac{1}{16}$ in. (1·58 mm)

The viscosity can also be measured by the other methods given in para. 358.

428. Film-base casting

Film base is prepared by spreading the dope on a polished moving metal surface. The metal surface can be either a drum or an endless belt. The dope is poured through a hopper of variable height in a layer of constant thickness, which on steady drying gives a thin transparent film.

Drums with a diameter of 12 to 20 feet (Fig. 55) revolve continuously at about two revolutions per hour, giving an output of about 90 feet of film, 4 to 5 feet wide. Smaller 6-foot drums are also used for casting triacetate from methylene chloride. The drum surface is silvered, and perfectly polished. The film is removed from the heated drum before it is completely dry, by a system of other rollers which completes the removal of solvent.

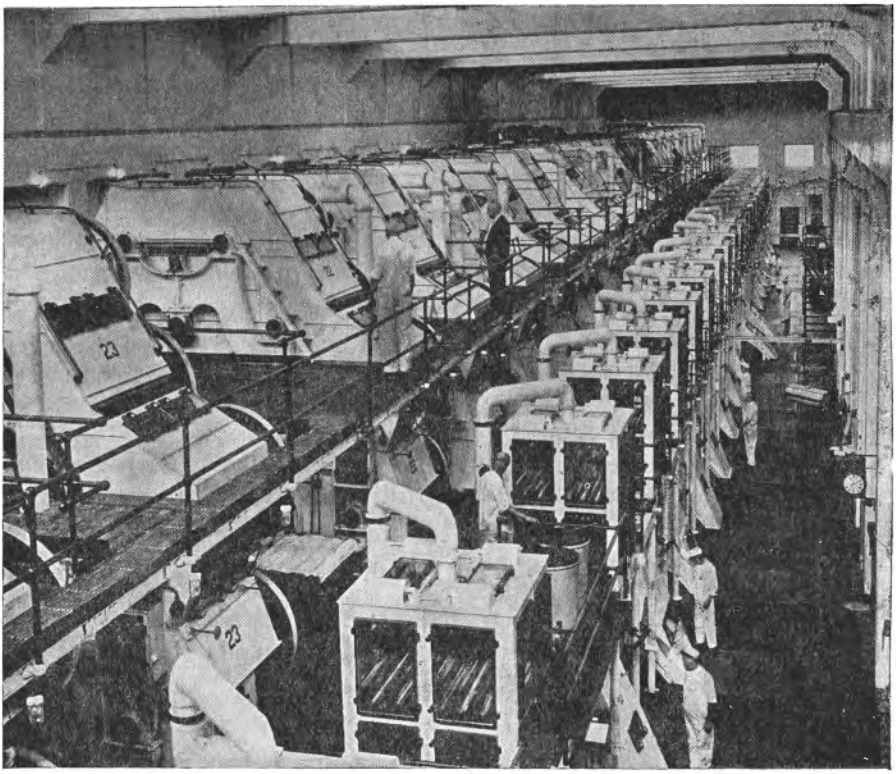


FIG. 55. Manufacture of film base by casting on to metal drums.
(Photograph: Eastman-Kodak, Rochester, U.S.A.)

Casting is a very critical operation which requires precise control of the operating conditions. The viscosity of the dope must be kept constant, the drying temperature and speed of rotation, uniform, and the air must be thoroughly filtered. If the solvent is removed too rapidly, a surface skin may form, which reticulates. The presence of water can result in the film blooming. The rate of evaporation of each solvent depends on its vapour pressure and the working temperature.

Endless band machines are used more in Europe. They consist of a nickel or copper band supported by two drums. These bands are about 4 ft. 9 in. wide and 75–100 feet long. The dope is generally spread over about 48 in. and trimmed to 42 in. Speed: 150–300 feet per hour. The electrolytic copper bands are 0·03 inches thick and are silver soldered, smoothed and undergo many tests. Nickel bands 0·02 inches thick are to be preferred. The machine carrying the band must permit its thermal expansion. The surface of the bands must be repolished every two or three years owing to pitting by corrosion.

Copper belts have a layer of gelatin applied to them for acetate casting or hydrolyzed cellulose acetate for nitrate. Nickel ones are not protected. The drying tunnel is at 40°C and the first drum at 35°C. The film is dried completely at 60–70°C after removal from the band. It can be subbed whilst it still contains 5–8% of solvent. The drying rate depends more on the temperature of the air than on its velocity. When highly inflammable solvents are used, it is advisable to reduce the oxygen content of the air to below 8% by introducing nitrogen into the drying air.

In all cases, the solvent vapour content must be lower than that corresponding to the lower explosive limit or higher than that corresponding to the higher explosive limit. A mixture of inflammable gas with air will not burn if it is too poor or too rich.

The solvent is recovered either by absorption with active carbon, or by condensation (cooling to below 10°C). It is then purified. Active carbon is regenerated with live steam.

Static electricity is eliminated either with electrical apparatus using the corona effect (Chapman, Skimex, Calorit, Corona, Simco, etc.) or by α-ray bombardment using polonium (United States Radium Corp.). The half life of this metal is 136 days.

Setting method. A cellulose ester, dissolved only in an active solvent above a certain temperature will set when it is cooled. It can then be stripped and dried on both sides. For example, cellulose acetate, triphenyl phosphate, propylene chloride and isopropyl alcohol; the solution is coated at 60°C and cooled to 10°C. The set film still containing 20% solvent is separated and dried.(24)

Coagulation method. The dope is coagulated in a hot damp atmosphere.

Sizes of film base. Width 41–54 inches. Thickness: roll-film ·003 in., ciné film ·005 in., sheet film ·008 in.

429. Deformation of films

Cellulose esters absorb 2–3% of water.

They expand, then contract on drying with unequal *shrinkage* in the two *perpendicular* directions. Drying stresses, by orienting the linear molecules, shrink the film in this direction by releasing the mechanical tension.

Hysteresis phenomena affect re-wetting. Furthermore, the emulsion swells eight times more than the base. The size variations by wetting are reversible. Those due to loss of solvents and release of mechanical stresses are not.

The shrinkage of a film must not exceed 1% after 10 days at 40°C, 50–55% R.H. This shrinkage is increasing by *ageing*, but it may be irregular, depending on variations of temperature and humidity. It should be less than 0·3%.

The new *triacetate* films only shrink 0·15% in length and 0·2% in width after two years at 25°C and 50% R.H. For photogrammetry, however, *acetobutyrate* films are preferred as their shrinkage is only 0·04%. Shrinkage on keeping for one year is 0·01%. The difference between the length and width shrinkage is less than 0·01%. Swelling is $7{\cdot}10^{-5}$ per degree Centigrade and $8{\cdot}10^{-5}$ per hygrometric degree.

The longitudinal and lateral shrinkage by *processing* and the expansion on *moistening* and *heating* of several commercial films was measured by Fordyce, Calhoun and Moyer.(24c)

	Per cent shrinkage after processing		Per cent expansion for an increase of			
			10% RH		5·5°C	
	long.	lat.	long.	lat.	long.	lat.
Negative (B. and W, and colour)	0·06	0·07	0·07	0·08	0·03	0·035
Positive (B and W, and sound)	0·05	0·05	0·05	0·06	0·03	0·035
Eastman colour prints	0·07	0·08	0·06	0·07	0·03	0·035
Kodachrome 16 mm (acetopropionate)	0·09	0·10	0·08	0·10	0·035	0·04

For printing on continuous printers, the pitch of the perforations must be +0·5%, −0·2% of that of the positive raw stock.

All films are *distorted by being wound* on spools. The difference in these deformations in the two directions is, after four months:

0·01% emulsion in.

0·05% emulsion out.

Drying with alcohol increases shrinkage. It is least with isopropyl alcohol, but age shrinkage increases.

Mechanical tests on films. The mechanical tests show the following properties.

Breaking strength per mm² (about 12 kg).

Stretch to breaking (45%).

Number of folds (80 for nitrate).

The figures are relative to nitrate which has the best mechanical strength. The resistance of triacetate approaches nitrate, but diacetate can only be folded forty times at the most.

To these main tests, others for hardness, elasticity, perforation, tearing from a started cut, resistance of perforations, and the effect of high and very low temperatures can be added. Note the softening and decomposition temperatures (80°C and 130°C for nitrate).

The best-known apparatus for determining these physical characteristics is made by Louis Schopper (Leipzig).

Degradation by light. Ultra-violet radiation depolymerizes cellulose, cellulose nitrate, cellulose acetate, and other esters like acetobutyrate with discolouring and reduction of mechanical strength. The chains are ruptured with a reduction in molecular weight. Depolymerization is accelerated by oxygen.

430. Burning and decomposition of films

The cellulose esters are not perfectly stable systems. For many reasons they are subject to changes. Also the storage of films, particularly developed ones, necessitates certain precautions.

Of all the esters the *nitrate* is the least stable. The ease with which it is decomposed and ignited is well known. It readily gives off nitrous fumes which attack the gelatin in the presence of moisture. A freshly made nitrate film will not decompose after 20 days in an oven at 80°C,(25) but if it is old, nitrogen peroxide is evolved after 3 days. If it is *impregnated with hypo it will ignite at* 80°C *after one or two days*—a danger of incomplete washing of nitrate films.

It is usual to distinguish between the *ignition temperature* at which combustible gas is evolved, and the *temperature of spontaneous combustion.* The test can be carried out either in an oven, in a test-tube slowly heated in an oil bath, or in a current of air whose temperature is raised.(26) With the latter method, the ignition and spontaneous combustion figures following are obtained:

Celluloid, 141 and 141°C (instead of 130 and 180°C).

Cellulose acetate, 305 and 475°C.

The stability of an ester is also determined by the loss of weight after at least 48 hours in an oven at 105°C: $<10\%$ for nitrate.

Films which are to be kept for a long time must be examined periodically. An official method is to heat a 6-mm diameter sample from the leader, weighing 7 mg in a tube in an oven at 134°C.(27) The stopper of the tube is fitted with a piece of alizarin red paper. The acid vapours decolorize the paper to a height of 3 mm.

Decolorizing time	Film can be kept
10–30 mins.	6 months
30–60 mins.	1 year
>60 mins.	Repeat test after 2 years

If decoloration is very rapid, another print must be made immediately.

Nitrate films should be kept in a cooled, well-ventilated place at 2–4°C and 50% R.H., and in non-metallic containers.

Acetate films can be kept at 18°C without harm.

431. Gelatin removal

This is used for recovery of film base, and three main methods are used.

(*a*) Immersion in a solution of *caustic soda*. This method is unsuitable for hardened gelatin. It has the disadvantage of hydrolyzing the base, and with cellulose nitrate, there is the danger of spontaneous ignition of the recovered base.

(*b*) Immersion in a solution of *sodium hypochlorite*. Effective even with hardened gelatin. Stripping takes place in a few minutes.

(*c*) Treatment with a *protein attacking enzyme*. In work on the action of Rhozyme P 11, Gansel(29) found that the activity was quadrupled by raising the pH from 5 to 8, and doubled from 40 to 50°C. He also tried Serizyme and Takamine.

Denitration of films: Nitrate film scraps, dissolved and cast in sheets, are denitrated by treating for an hour in a solution of magnesium acid sulphide, in the presence of an ammonium salt. The role of the latter is to avoid precipitation of magnesia. After washing and drying sheets of regenerated cellulose, which still contains 0·5% nitrogen, are obtained.

432. Analysis of cellulose esters

The determination of the combined acid in cellulose esters is carried out either by alkaline saponification or by acid hydrolysis. The estimation can be carried out on the solid ester, but it is better if the ester is in solution.(30)

(*a*) Saponification with hot caustic, and estimation of the excess alkali with HCl (Eberstadt's method). The ester is first heated at 50–60°C for 30 minutes in 75% alcohol. It is then heated for 15 minutes with 0·5 N caustic, then, after 48 hours titrate with 0·5 N HCl. Wait several hours for the end of the reaction.(31) Values too high.

(*b*) Koevenagel and Koenig heat the ester for 90 minutes in alcohol, then agitate for 24–48 hours with cold 0·5 N NaOH. Back titrate with H_2SO_4.

(*c*) Saponify with alcoholic caustic, 24 hours, at 25–30°C. Back-titrate with an acid. This method can be used for all esters.

(*d*) Saponification of the ester dissolved in acetone (Barnett's method).

(*e*) Saponification of the ester dissolved in pyridine (Battegay and Peuche).

(*f*) Hydrolysis with 50% sulphuric acid followed by distillation of the organic acid *in vacuo*, after adding sodium phosphate (Hess), or by steam distillation (Ost and Katayama). The distillate is titrated with soda or back-titrated with H_2SO_4.

(*g*) Separation as methyl esters by treating with sodium methoxide in the presence of excess p-toluene sulphonic acid which acts as a catalyst. The volatile products are distilled into an alkali.(32)

Determination of the nitrogen content of cellulose nitrate.

If the nitrocellulose is free from plasticizer it can be decomposed with mercury in concentrated sulphuric acid. Nitric oxide is evolved and its volume is measured:

$$2HNO_3 + 3H_2SO_4 + 3Hg \rightarrow 2NO + 3HgSO_4 + 4H_2O$$

The Schultz-Teeman method uses ferrous chloride in hydrochloric acid. The reaction takes place in a flask connected to a graduated tube filled with caustic soda, which absorbs the carbon dioxide.

$$2HNO_3 + 3FeCl_3 + 3HCl \rightarrow NO + 3FeCl_3 + 2H_2O$$

Extraction and determination of plasticizers in cellulose acetate. This is done in a microsoxhlet with 0·5 g of material.(33)

433. Cellophane

Cellophane is a transparent, hygrometric and extensible material made of *regenerated cellulose*. It can be used as a temporary support for carbon images, and as a *sensitized silver salt layer* (see para. 340) and for diazo processes. Cellophane contains 15% plasticizer, mainly glycerin. Its surfaces can be coated with an impermeable layer. It is made by coagulating *viscose* with dilute sulphuric acid.

NON-CELLULOSE FILMS

434. Polyethylene terephthalate films

Polyethylene terephthalate, studied by Whinfield and Dickson in 1940, is a new plastic substance with remarkable properties. Known by the names Dacron and Mylar (Du Pont), Terylene (I.C.I.) and Tergal (France), it can give film bases which are much more resistant than cellulose bases. These new bases are specially manufactured by Du Pont under the name *Cronar*.

Polyethylene terephthalate is a high polymer with a molecular weight as high as 15,000. Its density is 1·4 and it softens between 220 and 240°C and melts at 260°C. It can be welded and is three times as reistant to heat as cellulose triacetate. Furthermore, at low temperatures it loses none of its qualities.

A polyethylene terephthalate film is *dimensionally* very stable as it contains no plasticizer. The water take-up at 25°C and 65% R.H. is 0·4%. The expansion produced by 1% R.H. is 0·001 mm per metre against 0·004 for acetate. Expansion per °C is 0·036 mm against 0·041.(33b)

The *tensile strength* is particularly high: 1,330 kg per cm^2 against 880 for triacetate. Resistance to tearing is double that of other plastics. Impact strength is 75 kg/cm^2 against 3 for acetate. Abrasion resistance: 100, polyamides 150, other films 5–25. Resistance to alternate flexing is equal to Nylon. In short, the life of the film is trebled compared with other cellulose films. Because of this exceptional resistance the thickness can be easily reduced by 25% enabling the amount on a spool to be increased.

The *resistance to light* is equal, but not better than that of other films. However, the harmful radiations are between 300 and 360 mμ and can be absorbed by a sheet of glass. Transmission limit: 315 mμ.

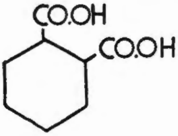
Terephthalate is not very inflammable. It burns only slowly releasing burning droplets which extinguish themselves.

Chemical properties. Terephthalate is not readily hydrolyzed, except by hot concentrated alkali. Oxidizing and reducing agents have little effect. It is not affected by acids. Organic solvents have no effect, except phenols and chlorophenols.

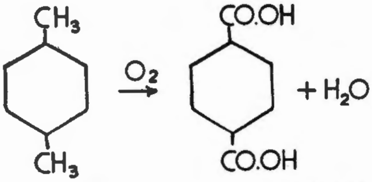
435. Constitution and manufacture of polyethylene terephthalate

Terephthalic acid is an aromatic para diacid corresponding to phthalic acid, which is the equivalent ortho acid. It is produced by aerial oxidation, in liquid medium of p-xylene, from petroleum refineries, at 130–140°C in the presence of a cobalt salt as catalyst. The accompanying o- and m-xylene and the ethylbenzene are previously removed by crystallization, distillation, then recrystallization or sulphonation.

The terephthalic acid is first esterified to *methyl terephthalate* which is purified. This is then heated with excess *ethylene glycol* in the presence of a catalyst—zinc borate or litharge (PbO).(33c) In this reaction, a mixture of

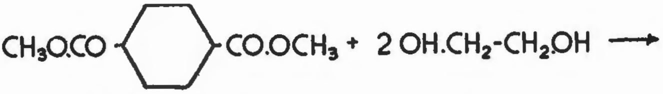


Phthalic acid

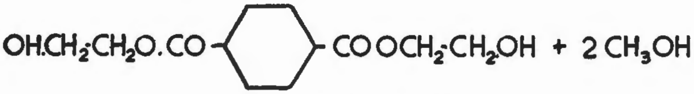


p-xylene Terephthalic acid

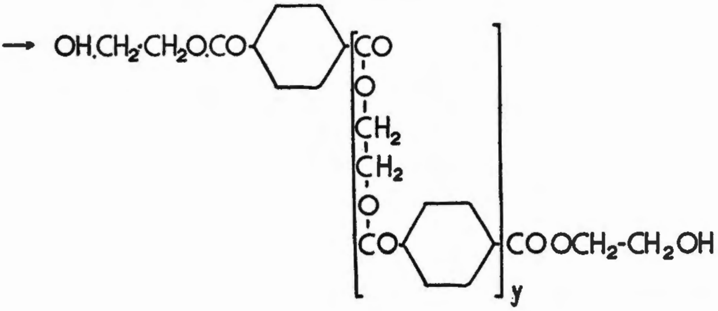
hydroxyethyl terephthalate and low molecular weight polymers is formed. The excess ethylene glycol is eliminated by vacuum distillation whilst the condensation gives long polymer chains of 40–55 units.



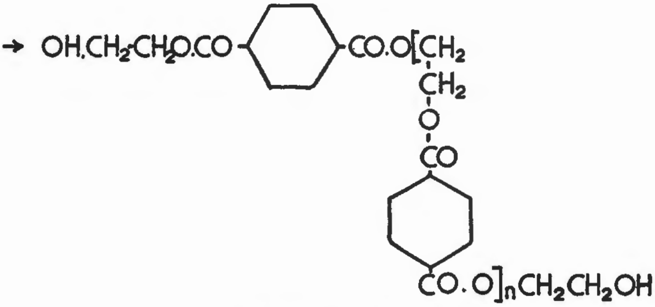
Methyl terephthalate Ethylene glycol



Hydroxyethyl terephthalate



Low polymer (y = 1–4)



High polymer (u = 40–55)

Polyethylene terephthalate

Manufacture of terephthalate film. The molten mass of plastic is coated by extrusion, without the use of solvents, onto a polished surface. If the film is stretched in two perpendicular directions its physical characteristics are modified with an increase of mechanical resistance. To retain this modified condition, it is necessary to heat the base to about its softening point resulting in a reorientation of the recrystallized macromolecules. The same treatment on a filament changes its properties from those of linen to those of silk.

The thickness of the resulting terephthalate films varies from 6 to 200 μ (·0003–·01 inches).

436. Other film bases

A large number of other plastic materials can be used to prepare film bases, or transparent or translucent sheets. These supports, however, lack mechanical resistance or elasticity, although they could be coated. The principal ones are:

Polyvinyl chloride and its co-polymers with polyvinyl acetate. The films are obtained by extrusion.

Polyvinylidene chloride or Saran.

Methyacrylate resins (Perspex) and stearyl methacrylate (Rohm and Haas).

Polystyrene in transparent plates: the films are brittle.

Polyamides: Nylon, Rilsan.

Polyurethanes: Perlon.

Rubber hydrochloride (Pliofilm).

Polyethylene (soft and translucent).

Trifluorochlorethylene (Kel-F).

Tetrafluoroethylene (Teflon).

The use of these bases involves emulsion adhesion difficulties, particularly with the fluoro derivatives.

AUXILIARY LAYERS

437. The substratum

The photographic emulsion will not adhere directly to cellulose nitrate or acetate supports.

Before coating the emulsion, the cellulose film is covered with a very thin layer of a *substratum* which facilitates the mutual adhesion of the two materials.

Subbing consists in principle of introducing a small amount of gelatin into the base surface, swollen by alcohol. Koslow and Podgorodetzki have shown that gelatin applied in aqueous solution to a nitrocellulose film previously immersed in alcohol, adheres perfectly. Adhesion can also be achieved by superficial saponification with 25% caustic soda at 50–65°C for a few seconds.

In practice gelatin is used as a weak solution in alcohol containing acetic acid and a little water. The acetic acid enables the gelatin to be dissolved in the alcohol, which is essential. The water content is also critical; if there is too much water the base does not swell, and the gelatin does not stick, but if there is not enough, the gelatin precipitates and no longer sticks.

Cellulose nitrate. A thin layer of substratum is applied from the following solution:

Gelatin	1·2 g
Acetic acid	2 g
Water	5 cc
Methanol 99·5%	92 cc

The gelatin is first dissolved in a mixture of the water and acetic acid by heating on the water-bath after soaking for several hours. The methanol is then added little by little. If the emulsion does not adhere well, reduce the water; if a white deposit is formed, increase it.

Cellulose acetate below 56%. There are several ways of subbing ordinary cellulose acetate.

(*a*) It is first coated with a thin layer of nitrate, which may contain a little acetate, followed by a substratum for nitrate as above.

(*b*) Gelatin-nitrocellulose substratum.

Gelatin	1 g
Acetic acid	2 g
Water	4 cc
Nitrocellulose	1 g
Acetone	60 cc
Methanol	32 cc

(*c*) Gelatin-chrome alum substratum⁽³⁴⁾

Gelatin	0·6 g
Chrome alum	0·06 g
Water	4 cc
Acetic acid	2 g
Ethanol	12 cc
Methanol	34 cc
Acetone	48 cc

(*d*) Add 5 cc methylene chloride to the above recipe.

(*e*) Acetic acid as a gelatin solvent has the great disadvantage that it is difficult to remove by evaporation. Any remaining after drying may change the pH of the emulsion and alter its characteristics. The same is true of *salicylic* and *phthalic* acids: being non-volatile, they diffuse into the emulsion.

Nadeau⁽³⁵⁾ solved the problem by using β-keto acids, which decompose with moderate heating into the ketone, which has no effect on the emulsion, and carbon dioxide. Thus benzoylacetic, methylacetoacetic and trimethylacetoacetic acids decompose respectively into acetophenone, methyl ethyl ketone and pinacolone:

$$\underset{\text{Benzoylacetic acid}}{C_6H_5\text{—}CO\text{—}CH_2\text{—}CO\,.\,OH} \rightarrow \underset{\text{Acetophenone}}{C_6H_5\text{—}CO\text{—}CH_3} + CO_2$$

$$\underset{\text{Methylacetoacetic acid}}{CH_3\text{—}CO\text{—}CH(CH_3)\text{—}CO\,.\,OH} \rightarrow \underset{\text{Methyl-ethyl ketone}}{CH_3\text{—}CO\text{—}C_2H_5} + CO_2$$

$$\underset{\text{Trimethylacetoacetic acid}}{(CH_3)_3 \vdots C\text{—}CO\text{—}CH_2\text{—}CO\,.\,OH} \rightarrow \underset{\text{Pinacolone}}{(CH_3)_3 \vdots C\text{—}CO\text{—}CH_3} + CO_2$$

The acetate film is subbed, for example, with the following solution:

Gelatin	1 g
Benzoylacetic acid	2 g
Water	4 g
Methanol 99·5%	28 g
Acetone	65 g

to which 0·1 g chrome alum may be added. The film is then quickly heated to 82–135°C to decompose the acid. Nadeau and Stark add chromium chloride or nitrate to the organic solutions (acetic or otherwise) to increase adhesion.(36)

Cellulose triacetate, propionate and butyrate. It is difficult to sub these esters. Several coats a few microns thick of the same ester, more and more hydrolyzed, until a normal adhesion layer is obtained can be applied. The last coat is treated with an ordinary substratum. For triacetate the gelatin can be dissolved in formic acid and chloral hydrate, and add to this solution a mixture of methylene chloride, glycol chlorhydrin and ethanol.(37)

Superficial hydrolysis of the film before subbing has also been suggested.

Vinyl chloride. Dimitriev(38) subbed Astralon film by first coating a solution of 1% perspex in dichlorethylene, then a gelatin-celluloid solution: gelatin 1·8 g, water 3·75 cc, and after dissolving acetic acid 1 cc, methanol 10 cc; add a solution of 2 g celluloid in 70 cc methanol and 70 cc acetone.

Some patents propose the use of a mixture of gelatin and polyvinyl acetate, in a layer 2·5 μ thick, then a layer of gelatin,(39) or a mixture of gelatin and incompletely esterified polyvinyl acetate.(40)

Another substratum for vinyl chloride, and for polystyrene, is to coat two layers of a methacrylate.(41)

Methacrylate (Perspex) with a low carboxyl group content has greater adhesive power when it is recovered with a methacrylate with more carboxyl groups. Fillins(42) recommends an acrylic emulsion mixed with a gelatin solution in one or more progressive layers.

Nylon: solution of gelatin in a phenol.(43) For example: gelatin, water, m-cresol and formalin in methanol.

Glass plates. The glass is washed in soda and rinsed, before subbing with an aqueous solution of gelatin and chrome alum, using a wad of cotton or flannel.

Gelatin	0·5 g
Water	100 cc
Chrome alum 10%	1 cc

Optionally 10% of 2% alcoholic thymol can be added.

Aluminium. Aluminium sheets are subbed by superficial electrolytic oxidation (para. 404) or chemical attack by an acid: phosphoric, molybdic, or fluosilicic in the presence of ammonium nitrate.(44) Similar treatment can be used for zinc.

438. Halation

Halation is light-scattering produced by reflection of light rays from the rear face of the base. It only occurs beyond a certain exposure intensity: the image of the brightest parts of the subject is more or less spread, and bounded at some distance by a halo whose outer limit diffuses towards neighbouring areas.

To determine the exposure limit at which halation is produced, *Mauge's method* is used. The sensitive layer is placed behind a 12 cm wedge with a constant of 0·5 to 0·6; between the wedge and the sensitive layer is a mask with a 1 mm slit down the centre. The layer is exposed to light so that solarization is almost reached on the clear part of the wedge. The developed material shows an image of the slit which becomes wider at high exposures (irradiation); after a certain point the image is bordered by two other parallel bands due to halation, which become bigger and bigger, finally joining to produce a greatly spread patch.

With an unprotected layer, halation appears at an exposure of about eighty times the threshold. With a layer having an absorbing backing halation does not appear until exposures above 3,000 times the threshold are given.

Determination of halation with a screen. Von Kujawa, then Watter (44b) have proposed the determination of halation objectively using a uni-directional screen together with a sensitometric wedge. The characteristic curves with and without the screen are compared. If the sensitive layer shows no halation, the clear lines corresponding to the opaque parts of the screen are quite transparent. In the opposite case, halation has the effect of increasing the density obtained under the screen. It is stronger as the distance between the two characteristic curves decreases.

A wedge with a constant of 0·3, or a DIN wedge is used, half of which is covered by a 20 line per cm screen. The wedge—screen—sensitive layer pack is exposed to a point source, then, after development, the curves are drawn in the region of D = 1. For colour films, a colour densitometer is used to determine the halation for each layer. If the halation value is given by the antilog of the distance between the two curves, the Agfacolor figures are:

	Without anti-halo	With anti-halo
Yellow	34	1620
Magenta	4	331
Cyan	3·5	89

Halation is avoided by using bases having a coloured backing or intermediate layer which can be decolorized or eliminated.

439. Anti-halo layers for photographic films

Photographic films always have a backing layer of coloured gelatin. This acts not only as an anti-halo layer, but also prevents the film from curling.

The dye used in the rear gelatin layer must be readily decolorized by the developer alkali or sulphite. It is generally an acid dye.

For ortho films it is generally pink, and for pan films, blue, green or yellow-brown.

Matt backing is obtained by incorporating starch previously pasted with warm water.

Pink anti-halo. Water 1000 cc, gelatin 110 g, 10% acid fuchsine 60 cc, 5% chrome alum 18 cc, 5% saponin 4 cc, alcohol 30 cc. Coat at 36°C.

Green anti-halo. Instead of fuchsine use 100 cc of 5% *sulpho green.* After development, sulpho green leaves an insoluble greenish residue in the gelatin, which in acid solution may re-form the dye. It is therefore preferable to use other dyes including: *methyl green* (2 g per litre) whose colour is bluish, or *Helvetia* or *acid green.* For blue, *Hoechst New Blue,* and for violet, *Benzyl violet 4B.*(45)

Acid green is prepared in the following way: 1. Formation of dimethoxytriphenylmethane by dropwise addition of cold sulphuric acid to a mixture of anisole and benzaldehyde in concentrated acetic acid. 2. Oxidation to dimethoxytriphenyl-carbinol with PbO_2 in acetic acid. 3. Drying at 110°C with benzoic acid, and the action of 6-chloro-3-amino benzoic acid. The dye is extracted with water, and purified by dissolving in NaOH and precipitating with HCl.

A *yellow dye,* flavaniline S is decolorized by alkalis. It can be prepared by heating one part of acetanilide, two parts of aniline hydrochloride and two parts of zinc chloride to 230–250°C. Boil in water to separate the zinc chloride. The residue is dissolved in a dilute acid, filtered, and the dye is precipitated with sodium chloride. It is then sulphonated with fuming sulphuric acid. Flavaniline S is sulphonated α-p-aminolepidine. (Rowe Index 803).

Azamethine dyes which are decolorized by alkalis are obtained by condensing equimolecular parts of aromatic or heterocyclic aldehydes with substituted amines, then combining with organic acids containing at least one salt-forming —OH or —CO . OH group.(46)

Sheppard and Houck(47) have disclosed dyes of the murexide type of which the most common is the ammonium salt of purpuric acid. These dyes are decolorized in acid fixers with a pH of 4 by tautomeric transformation to the keto derivative which then hydrolyzes.

By condensing pyrazolones, rhodanines, oxindoles, etc. with 1 : 3-diketones in a solvent, decolorizable oxa-oxythrimethine dyes are obtained.(48)

Yellow-brown anti-halo. Permanganate is reduced by organic materials to the brown dioxide. A yellow-brown anti-halo layer which is very effective is readily obtained by adding an alkaline permanganate solution to a warm gelatin solution(48b) containing an organic reducer (glucose or tartaric acid). It is best to noodle and wash the mass, and add further gelatin before coating.

440. Anti-halo layers for cine films

Cinė films have no gelatin backing. The coloured anti-halo layer is applied as a backing varnish soluble in the developer or in a solvent which does not affect the base, or as an underlying layer.

The backing varnish is grey-violet, blue-grey or black. The interlayer can be made of brown or black silver dispersed in a colloid. It is only used for reversal films.

The backing varnish must be soluble in the developer, but not in plain water, and must be sufficiently resistant in a thin layer. It is applied from a solution in an organic solvent. A suitable varnish can be made from de-waxed or hard *shellac* in alcohol, *polyvinyl phthalate* in butyl acetate,(49) a *polyacrylic acid* or a *polystyrene-maleic* acid.(49b)

Agfa anti-halo backing varnishes which are non-decolorizable were made of gelatin in an organic solvent:

	Grey	Blue
Gelatin	660 g	660 g
Water	1·32 l	1·32 l
Phthalic anhydride (10% in methanol)	1·25 l	1·25 l
Methanol	72 l	77 l
Acetone	11 l	11 l
Baryta white	5 l	—
Lacquer black extra	80 g	9·3 g
Flavazines E+GL extra conc.	57 g	—
Rhodamine Ponceau GG extra	1·6 g	—
Aniline blue BB	—	13·4 g

The dyes are previously dissolved in alcohol.

A colorizable backing varnish is based on a co-polymer of maleic anhydride and vinyl ester (Povimal BA).

	Nitrate	Acetate
Povimal BA	487 g	609 g
Isopropyl alcohol	50 l	—
Isobutyl alcohol	50 l	25 l
Methyl phthalate	80 cc	100 cc
Ethanol	—	75 l
Acid green (para. 438)	324 g	405 g

It takes two hours for the resin to dissolve at 65°C.

Anti-halo dyes are produced by coupling a phenolic resin with a diazonium compound, the resin having in the para position to the hydroxyl a replaceable H which can couple with the azo group.(50) The same resins can be combined to give indophenol blues.(51)

Dyed base. The anti-halo backing varnish of negative and miniature ciné films is often replaced by dyeing the whole base grey, blue-grey or violet-grey.

Reversal films. The backing layer of a reversal film may be a varnish which is developer-soluble or is decolorized in the oxidizing reversal bath. When an under-layer forms the anti-halo layer the colouring matter is usually colloidal silver, thickness 2 μ.

The *brown colloidal silver* is obtained by reducing a gelatinous solution of silver nitrate with amidol then setting and washing. *Black colloidal silver* is produced by reducing silver hydroxide, formed by pouring silver nitrate into a caustic solution of dextrine, with hydroquinone. After adding gelatin, the mass is washed. It can also be prepared by developing a fogged photographic emulsion.

441. Anti-halo backing for plates

A plate-backing must be readily soluble in the developer, and must not prevent the plates from being cut. Furthermore, it must be readily applied to the plates and must not dirty the developer. These various requirements rule out gelatin, dextrine, cellulose derivatives and other colloidal substances.

Ordinary and ortho plates are backed with an alcoholic solution of *rosolic acid* (orange red). Rosolic acid is a trihydroxytriphenyl carbinol.

The addition of a green dye, very soluble in alcohol and non-crystallizing such as *naphthalene green*, to rosolic acid, enables very dark, almost black, layers to be obtained, which are suitable for panchromatic plates.

The backing is brighter and more resistant to rubbing if 0·5% ammonia is added.

442. Antistatic layers

The greatest source of chance troubles in the manufacture of photographic layers is the formation of *discharges* of static electricity.

The coated film is charged by rubbing, and is the parting of two layers or a strip on an insulating roller which produces flashes.

The polarization of a film is made up of the residual charges resulting from the influence of an electric field. This polarization can be measured on the two sides of a film independently of any temporary charge, with an electrostatic voltmeter.(51b)

The potential resulting from reeling an acetate film at a speed of 90 feet per minute under a mechanical tension of 1 kg reaches 4–5 kV. The polarization potential is below this value, but sparks are produced when the polarization charges accumulate on the successive layers of a roll of film.

The flashes are mainly produced during slitting, inspection and reeling. *Manual inspection should be avoided* as it causes a large number of these discharges.

Precautions are generally taken during the manipulation of films: *humidification of the air*, *earthing the machines*, *rubber rollers made conducting* by incorporating graphite, brushing a film with '*angel's hair*' in aluminium joined to earth. These precautions are not very effective; they are not always carried out, and furthermore, the discharged film can be immediately recharged and produce flashes in the camera or on rapid unwinding before development.

Static discharge is not produced in ionized air. Unfortunately neither the electrically produced corona effect, nor ionization by α-rays from polonium, or with a flame, can be used with films due to the danger of fog and the difficulties of the systems.

The only practical way of avoiding flashing is to use an antistatic base, that is, one which is difficult to charge.

One objectionable process is to keep moisture in the emulsion, with glycerin or a hygroscopic salt like lithium chloride. A more interesting method is the application to both sides of the film of a quaternary ammonium salt like trimethyloctadecylammonium methyl sulphate in an organic solvent,(52) or sodium ethyl phosphate dispersed in cellulose-di-n-butylamine sulphate.(52b)

Superficial hydrolysis of the base with alkali has been disclosed by Stinchfield.(53) It is preferable, however, to apply a surface *film of a different type*. For example, benzyl cellulose, ethyl cellulose or cellulose nitroacetate on nitrate, or for acetate, polymerized carboxylic acids⁽⁵⁴⁾ such as polyacrylic acids, cellulose carbamates,⁽⁵⁵⁾ abietic esters,⁽⁵⁶⁾ zein (maize casein),⁽⁵⁷⁾ etc.

Acrylic antistatic layer. This is based on a mixture of 60% polymethyl methacrylate $(CH_2 = CH—CO.OCH_3)_n$ and 40% polyacrylonitrile $(CH_2 = CH—CN)_m$, partially saponified until it has adequate solubility.⁽⁵⁸⁾ The resulting resin, called Meniviskol, is dissolved in four hours at the boil: methanol 19·3 l., water 4 l., N caustic potash in methanol 6·67 l., Meniviskol 1·33 kg. For use take 23·7 l. of this stock solution and 211 l. of methanol.

Cellulose acetomaleate antistatic layers.⁽⁵⁹⁾ The starting material is a 44–45% acetyl cellulose acetate (Serikose) prepared by hydrolysis of triacetate with sulphuric acid. To maintain a high molecular weight for the acetate, the acetylation temperature must be kept relatively low, maximum 50°C (cf. para. 420). The hydrolyzed acetate is treated for 3 hours at 100–105°C in the following mixture: maleic anhydride 23 kg, citric acid 8 kg, triacetin 10 kg, cellulose acetate 17 kg. After cooling, the product is precipitated with water, washed and dried.

One kg of this resin is dissolved in 15 l. of distilled water and 25 l. toluene below 75°C, then a further 140 l. toluene and 45 l. distilled water is added. The resin is then partially saponified by adding 2·5 l. of N/2 caustic soda. The solution is decanted after 16 hours, and filtered before being applied to the base.

443. Anti-abrasion layer

The photographic emulsion, coated on paper or film is generally re-coated with a thin layer of gelatin a few microns thick.

Films are coated, after the emulsion is applied, with:

27°C	Water	1 l
	Gelatin	30 g
	Alum, 5%	10 cc
	Saponin 5%	5 cc
	Alcohol	280 cc

444. Stripping layers

Some photographic layers are coated on temporary supports, so that they can be transferred after development, to permanent supports, for example, in photogravure.

The temporary support is generally paper, but may be acetate sheet. The paper is first coated with a layer of nitrocellulose⁽⁶⁰⁾ which is subbed. Above this, a gelatin or gum arabic adhesive layer is coated, containing a little glycerin. The permanent support consists of a relatively thick layer of nitrocellulose. This is subbed and coated with emulsion. After development the emulsion can be detached from its temporary paper support by prolonged immersion in water.

Another system is to coat the paper first with gum dammar, which is waterproof, then with emulsion, and finally with nitrocellulose (which is the final support). This nitrocellulose layer is itself coated with a thermoplastic resin,(61) vinyl acetate, for example. By hot pressure against a metal plate, the resin sticks, enabling the paper to be removed.

A temporary triacetate support, covered with 20 μ of nitrocellulose, then with the emulsion, enables dry stripping to be carried out, after surface lacquering.

445. Two-colour backing paper

The two-colour backing paper for roll-film is lacquered on the green-, red-, grey- or yellow-coloured side.

The figures and instructions are first *printed*: in a dark colour with a gum-arabic base ink containing *solanthrene blue* or *carbon black*, or in a light colour with a gum-arabic ink containing very fine *titanium white*. A kilo of ink containing 180 g of blue pigment (previously ground with a little glycerin) can print 10,000 m of 6·5 cm wide paper.

The printed face is then protected on the same machine with a *layer of lacquer*: *nitrocellulose* in acetone and butyl acetate, *zein* (maize casein) in alcohol, *polystyrene* plasticized with octyl phthalate in trichlorethylene, etc.

Lacquered backing paper must be tested for *inertness towards the emulsion* by an oven test. The printed figures must not be transferred onto the emulsion, and the increase in fog must be practically nil, compared with a similarly treated blank without the backing paper. It should be noted that excessive activity can result from poor quality *paper pulp*.

446. Film splicing

Cellulose nitrate films are readily spliced with a solution of celluloid in a mixture of acetone and amyl or butyl acetate. The emulsion must be scraped off first.

Acetate films of 56% acetyl and below need a solution of acetate in a mixture of acetone and ethyl acetate. Other solvents are methyl ethyl ketone (B.Pt. 79°C), cellosolve (B.Pt. 115–130°C) and cellosolve acetate (B.Pt. 138–145°C).

For triacetate films (*56% and over*) a mixture of methylene chloride and alcohol must be used. Add a little toluene if necessary.

Splicing acetate films without cement. Herzig(63) has described a welding process of joining end to end, without scraping or overlapping. The necessary apparatus has a nichrome band heating element of 16 W/cm. The films to be joined are pressed against the band with a pressure of 14 kg/cm^2. A mica sheet insulates them from the teflon pressure plate. It is advisable to moisten the ends of triacetate with plasticizer to compensate for evaporation.

Splicing terephthalate (*Cronar*) *films* is done with an adhesive Mylar ribbon, without scraping. The joint resists 1000 projections.(64)

447. Film cleaning

Carbon tetrachloride, which is normally used for cleaning developed films(65) can be advantageously replaced by Freon 113, which is a fluorinated hydrocarbon with the formula $C.ClF_2—C.Cl_2F$. It is volatile, non-flam and almost non-toxic. As a powerful organic grease-solvent, it can cause irritation to the hands if used without gloves.

The film can be *protected* at the same time as it is cleaned by adding 0·1% beeswax or cetyl alcohol to the solvent. A recommended mixture includes 0·03% Carnauba wax, 0·025% beeswax and 0·075% ethyl cellulose.

447b. Protective lacquers

The purpose of using protective lacquers on prints is to protect them against abrasion and chemical action.

The old recipes are all based on natural resins, which have the disadvantages of being either brittle or soft and sticky: *dammar* 10 g, benzine 50cc, carbon tetrachloride 50 cc; or *sandarac* 100 g, castor oil 1 g, alcoho to 1000 cc (with the optional addition of 50 g benzoin). For hot lacquerlng: *sandarac* 55 g, *bleached shellac* 83 g, castor oil 20 g, turpentine 10 cc, alcioho to 1000 cc. For an opalescent layer: *sandarac* 103 g, *mastic* 23 g, ether 1000 cc, benzine 25–750 cc depending on the opalescence desired (very inflammable lacquer).

For retouching: clear colophony 230 g, dammar 100 g, mastic 23 g, lavender oil 1 g, turpentine 1000–2000 cc—or sandarac 113 g, lavender oil 85 cc, alcohol 800 cc (matt the dry layer by rubbing, after powdering with pulverized colophony if desired).

The *synthetic resin* industry now offers a wide range of products from which excellent varnishes can be made: transparent phenolic resins which are alcohol soluble, *coumarone*, *glycerophthalic*, *maleic and acrylic* resins, etc. For example, *Alresate* 177 dissolved in toluene or solvent naphtha gives a tough film whose properties can be modified with a plasticizer (para. 425). The *coumarone* resins are soluble in benzene and carbon tetrachloride, sometimes in acetone; the *methacrylates* in acetone, ethyl acetate and benzene; *polystyrene* in all chlorinated solvents; *polyvinyl acetate* in alcohol, ethyl acetate and the chloro solvents; *polyvinyl acetals* in alcohol, acetone, ethyl acetate and benzene; *polyvinyl chloride* in dichlorethylene; *chlorinated rubber* in ethyl acetate, benzene and dichlorethylene; the *alkyd resins*, simple or modified, in acetone.

Resins which are too soft should be avoided as they give tacky layers: this happens with polyvinyl acetate, which is preferably replaced by a polyvinyl acetate-chloride copolymer.

The *cellulose esters* can give lacquers with interesting properties: *nitrocellulose*, *cellulose acetate and benzyl cellulose* in particular. Nitro-cellulose is compatible with copal gum (Manilla) in methanol, butanol and cellosolve; with Kauri gum in methanol, butanol and butyl acetate, with dammar and mastic in butyl acetate and solvent naphtha. It is also compatible with phenolic resins like the Albertols, some maleic resins (Synresols) and the pentaerythrole esters. The solution may contain a plasticizer (such as castor oil). Plasticized *benzyl cellulose* gives flexible glossy films; it is soluble in a mixture of 90 parts toluene and 10 alcohol.

The following formula(66) contains a vinyl copolymer. To avoid yellowing, an ultra-violet *stabilizer* has been added: 2 : 2′-dihydroxybenzophenone with triethanolamine. The plasticizer is tricresyl phosphate. In this case, nitrocellulose is included to enhance adhesion.

Cellulose nitrate ('half-second' viscosity)	1
Vinylite VYGC (40% solution in butyl acetate)	6·3
Tricresyl phosphate	2
Butyl acetate	6
Butyl alcohol	1
Ethyl acetate	1
Ethanol	1
Toluene	15
Triethanolamine	1·6
2 : 2′-dihydroxybenzophenone	0·1
Microcrystalline wax (not specified)	0·3

Vinylite VYGC is manufactured by Union Carbide and Carbon Co.

Geon (*or Breon*) *652* emulsion (Goodrich Chemical Co.), made from polyvinyl chloride and butadiene-nitrile rubber, gives transparent, glossy, supple films by simple application, but they are not sufficiently resistant to rubbing.

Fungicide for tropical countries.(67) Treat negatives for archives in 0·5–1% *zinc fluosilicate* solution for 3 minutes and dry. Zinc fluosilicate is very poisonous and contact with the skin must be avoided. Avoid direct handling of treated negatives by a very clear warning. The method is not applicable to papers because of yellowing.

448. Mountants

To stick paper to plate glass or metal plates, use the following mixture:

Gelatin	60 g
Syrup (sugar)	60 g
Glycerin	60 g
Chrome alum	1 g
Water to	1000 cc

The alum is dissolved separately in a little cold water. Amount used: 40–50 cc per sq. ft. The liquid sets after about 24 hours and cannot be remelted.

Cold soft adhesives

	A	*B*	*C*	*D*
Hercolyn (methyl dihydro abietate)(68)	42	40	40	38
Hydrogenated colophony	50	50	—	—
Rubber	—	10	—	—
Ordinary colophony	—	—	52	—
Ethyl cellulose	8	—	8	—
Dammar	—	—	—	50
Chlorinated rubber	—	—	—	12
Microcrystalline wax	10	—	—	—

The Hercolyn and hydrogenated colophony are heated to 140–160°C. The ethyl cellulose is added slowly with stirring.

Hot adhesive. An acetate film 0·06 mm thick covered with a hot adhesive substance is commercially available (Kodak).

A recommended plastic mixture includes Hercolyn 42p, Staybelit No. 10 50p, ethylcellulose 8p, and microcrystalline wax 5–20p. Staybelit is an hydrogenated colophony.(68)

448b. Stripping negatives

To transfer a film image to glass, the image is first stuck onto a subbed plate with liquid 10% gelatin containing 2% formalin under pressure. After drying for 24 hours, the backing is removed in 40% caustic soda at 50°C, or better, in sodium hypochlorite. Rinse, blot, then dissolve the base in acetone, ethyl acetate or methyl cellosolve. Rather than stick the negative directly onto the glass, the image can merely be protected by applying several layers of rubber (in benzene solution). By sticking a sheet of paper under, double transfer can be effected.

Sterry process. A negative on film or glass can be stripped in the following way: immerse the negative in potassium carbonate 40 g, 40% formalin 25 cc, glycerin 20 g, water to 1000 cc for 30 minutes. Drain and dry. Cut around the border to the base 2 mm from the edge. Immerse the negative, treated thus, in 5% hydrochloric acid, which results in the formation of bubbles of carbon dioxide. Apply under water to the image side a sheet of moistened sulphided paper. Remove the pack and squeegee out the air bubbles and gently strip off the paper at an angle, carrying with it the image layer. Transfer to a second paper immersed in a dish full of water. Remove excess liquid with a roller and strip off the first paper. The image can then be re-transferred to a glass plate coated with a warm 3% gelatin solution.

Hydrofluoric acid process (for negatives on glass). Cut all round the image and 3 mm from the edge. Place the plate on three levelling screws, and pour onto it a solution of: alcohol 25 cc, water 1 cc, glycerin 1 cc (stock solution) + 6–30 drops of hydrofluoric acid (just before use). Spread the liquid with a piece of paper. After a minute, test an edge to make sure the gelatin is free, then pass a waxed wire (stretched on a bow) between the image layer and the glass. Pour on some stock solution (without acid) and then apply a sheet of waxed paper under light pressure. Remove the paper plus image from the original glass, and transfer the image to a gelatin-coated plate. A second transfer enables the image to be reversed.

A variation is to immerse the plate for 8 hours at 12°C in a solution at pH 8 containing 1·2% acetic acid, 1·64% sodium acetate and 0·2% hydrofluoric acid.(69)

Hydrofluoric acid is dangerous to handle. It is sometimes replaced with 4% sodium fluoride mixed with half its volume of formalin. Transfer is carried out in water.

Strengthening the image layer by applying a layer of gelatin or collodion (plunged into water before drying to make it permeable) is advised.

Transfer onto talc-powdered glass enables the image layer to be detached finally.

Stripping collodion negatives. Strengthen with a layer of rubber, then collodion. Cut round 5 mm from the edge. Apply moist paper with a roller. Detach the paper+image layer, starting at an angle, and helping with the point of a knife. Transfer to another moist paper then onto gelatin or gum-coated glass.

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1b. *Melamine* is a triaminotriazine of the urea family, formed from 3 $=\mathrm{N}-\mathrm{C}(\mathrm{NH}_2)=$ groups joined in a six-membered ring. It reacts with formalin to give first a methylolamine $=\mathrm{N}-\mathrm{C}(\mathrm{NH}\,.\,\mathrm{CH}_2\mathrm{OH})=$

2. Sève R.: *Résumé Trav. Lab. Kodak*, Jan. 1955, 251; *Sci. et Ind. Phot.*, 1955, 145.

3. Kodak-Pathé: F.P. 970,208 (1950).

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5. B.I.O.S. Trip No. 2133, Report II, 29th April 1947. H.M. Stationery Office, London.

6. Knipe G. F. G. and Reid J. B.: *Proc. Roy. Soc.*, 1943, 81, described a double monochromator with cells isolating the X, Y and Z regions of the C.I.E. colorimetric system, which is intended for the control of almost white papers.

7. Rowen J. W., Hunt C. M. and Plyler E. K.: *Jl. Res. Bur. of Standards*, 1947, 133–140.

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8b. Pakshver A. B. and Kopolnikova G. P.: *Zh. Prikl. Khimii*, 1951, 1052.

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8d. F.P. 755,981 (1933), 809,867 (1935).

9. B.P. 161,564 and 167,143 (1921)—U.S.P. 1,425,580/1 (1920), F.P. 672,220 (1929) and 820,270 (1937).

9b. Kodak: F.P. 834,554 (1938); *Ind. Eng. Chem.*, 1949, 695–701.

10. Kodak: U.S.P. 2,208,569 (1937).

11. F.P. 653,742 and Add. 35,278 (1928); U.S.P. 2,097,954 (1934); 2,113,304/5 (1935). Fordyce C and coll.: *Ind. Eng. Chem.*, 1936, 1310.

12. Sato H., Godai R. and Kodama H.: *Konishiroku Rev.*, 1953, 1–32 (in Japanese).

13. U.S.P. 2,093,462.

14. U.S.P. 2,186,631/2 (1939).

15. U.S.P. 2,196,746/49/51 (1938).

16. U.S.P. 2,211,327 (1939).

17. U.S.P. 2,231,729 (1939).

18. U.S.P. 2,234,706 (1940).

19. U.S.P. 2,253,064 (1938).

20. U.S.P. 2,253,065 (1938).

21. *Camphor* is a cyclic ketone derived from borneol. Natural camphor is extracted from *laurus camphora* from Japan and China. Synthetic camphor obtained from turpentine whose hydrochloride is converted to bornyl acetate then borneol, is more frequently used. The latter is oxidized to camphor.

22. Malm C. J., Fordyce C. R. and Tanner H. A.: *Ind. Eng. Chem.*, 1940, 1052; 1942, 430. Gloor W. E. and Gilbert C. B.: *Ind. Eng. Chem.*, 1941, 597.

22b. Kodak: U.S.P. 2,336,310 (1941) and F.P. 1,078,989 (U.S. prior. 1951).

22c. Carver E. K. and Kodak: U.S.P. 2,168,972 (1937).

23. The solubilities of the acetates given here refer to compounds having an acetyl content of 56% at most. The triacetates which are more completely esterified are more difficult to dissolve.
24. Kodak-Pathé: F.P. 865,189.
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28. Filter paper impregnated with 0·1% alizarin red containing 2% ammonia, dried and heated for 10 minutes in an oven to eliminate the ammonia.
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33b. White D. R. and coll.: *J.M.S.M.P.T.E.*, 1955, 674–678.
33c. Du Pont: F.P. 1,084,387 and 1,086,433 (1955) disclose the Li, Na and Ca hydrides and the organic salts of Col, Mg and Zn.
34. A Schleussner formula uses: stock solution—gelatin 54 g, water 54 cc, acetic acid 50 g, methanol 700 cc. To sub acetate take stock solution 140 cc, methanol 240 cc, acetone 700 cc. When this formula was tried a white deposit was produced on the film.
35. U.S.P. 2,066,850.
36. B.P. 545,905.
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41. Ilford: B.P. 573,917.
42. Fillins and Kodak-Pathé: F.P. 970,208 (1951).
43. Middleton E. B., Queen D. McM. and Hall J. R. (Du Pont): U.S.P. 2,341,877 (1940), B.P. 552,085 (1941).
44. Cartwright, Haigh and Smith: B.P. 545,942 and 548,716 (1940/41).
44b. Von Kujawa: *Sci. et Ind. Phot.*, **2(2)**, 411. Watter O. (Agfa): *Bild und ton*, 1954, **7**, 326; 1955, **8**, 8; *Sci. et Ind. Phot.*, 1955, 133.
45. These dyes are not commercial ones. Their Rowe Colour Index Nos. are: *Helvetia Green* No. 660, *Hoechst New Blue* No. 708 (dimethyl-diphenyl-diaminosulphofuchsone), *Benzyl violet* 4B No. 697 (dibenzyl-diethyl-dimethyltriaminotriphenyl-carbinol disulphonate).
46. Gavaert: F.P. 894,181.
47. F.P. 827,126.
48. Gaspar B.: F.P. 854,975 (1939).
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49. F.P. 852,992.
49b. F.P. 886,651.
50. Collins R. B.: B.P. 545,529.
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54. I.G.F.: G.P. 604,456 (1932); Kodak: F.P. 1,084,777 (1954).

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65. Also isopropyl alcohol.
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67. N.*: *Bull. Trop. Kodak Labo.*, 1951, 10.
68. Hercules Powder Co. (U.S.A.).
69. Dahanayaka C.: *Nuovo Cimiento*, 1955, 1251.

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