PHOTOGRAPHIC EMULSION TECHNIQUE

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INTRODUCTION

THE pioneer days of photography were noteworthy for the fact that the sensitive material which recorded the camera image was in a state of continual evolution. The dramatic change from collodion to gelatin emulsions due to Dr. Maddox in 1871, introduced a new era in the art of photography because of the mysterious increase in speed which the use of gelatin brought about. Although so many years elapsed before the nature of the gelatin sensitization was discovered, empirical work with gelatin emulsions brought about a constantly increasing sensitiveness to light, which culminated in the early part of this century in a speed of about 400 H and D, or its equivalent of 10 Weston. Twenty years later the speed of photographic plates jumped up to half as much again, and after another twenty years modern color-sensitive emulsions with their supersensitizers made another remarkable jump to something between five and ten times the old figure.

In the meantime, the application of photography to technical, industrial and scientific problems has expanded on a truly amazing scale which needs no emphasis here. Physical chemists, physicists and mathematicians have been attracted by the fascinating nature of the phenomena associated with sensitive emulsions into a new field, with which this book attempts in some part to deal.

During an experience of more than thirty-five years in the emulsion-making field, the author has been approached on numerous occasions with requests for sources of information on photographic emulsions. In many branches of experimental work and scientific research, it is felt that it would be of un-

doubted benefit and convenience if serviceable emulsions could be made on a laboratory scale, and suitably coated. As time proceeds, many newcomers enter the field of commercial production of one kind or another, and in the following pages the problems of the investigator and the manufacturer are fully discussed. The investigator is obliged to buy in the open market the available material which happens to possess characteristics nearest to his requirements. The factory laboratory, on the other hand, makes a considered choice of materials and checks up on that choice with manufacturing scale tests. Apart from actual manufacture, the making of emulsions provides a scope for experiment pregnant with possibilities. Some knowledge of emulsion chemistry is of the greatest value in the general study of photographic processes.

In the pioneer days, photographers had to make their own emulsions, and it was by the combined efforts of a small coterie of experimenters at the end of last century that the modern " dry plate " came into being. Some of these men were pure amateurs, others were practical chemists and men of scientific training. Out of this little band of experimenters came the founders of most of the original commercial emulsion-coating factories. The inevitable then happened. The businesses came into competition with one another, and further advances gradually became guarded as trade secrets. There came a spectacular lull in the hitherto prolific literature, and the textbooks of Dr. J. M. Eder and Sir William (then Captain) W. de Wivesleigh Abney were the chief fodder on which the would-be experimenter had to feed.

The interest in emulsion chemistry was renewed in 1920 and onwards. The classic work of The Svedberg and other distinguished physicists introduced new methods of attack on the morphology of the silver halide grain. A little later, at a Paris Meeting of the International Congress of Photography, Dr. S. E.

Sheppard announced his discovery of the effect of the presence in gelatin of allyl isothiocyanate — the secret of speed had been revealed. But the millennium had not arrived, for speed could not be increased *ad libitum* by just increasing the proportion of sensitizer used in the preparation of the emulsion.

The sensitiveness to light of the emulsion depends to quite an important extent on the particular gelatin used, and its inherent " impurities." But it is also dependent on the method of precipitation of the silver halides, on the method and degree of ripening, and on the digestion which the emulsion receives after the by-products and excess solvents of silver bromide have been removed by *washing*. Modern technique, however, makes it possible to control within fairly definite limits the character of an emulsion, so that by predetermined conditions the manufacturer can produce a plate or film having a long scale of gradation for the pictorial photographer, a process film suitable for line work, an emulsion specially responsive to X-rays, a soft-working bromide paper for enlargements, or a contrasty chloride paper for the photo-finisher. Add to this the power which Vogel's discovery of color-sensitizing gave to the industry, and we find a further field for experiment of vast potentialities, which has helped of course in large measure to provide the various solutions to the problem of natural-color photography, and to improve the graphic arts.

While the amateur emulsion-maker cannot compete with the manufacturer of sensitive materials, the latter cannot be expected to interrupt works routine by supplying small coatings of experimental emulsions made to some specification outside his own range of products. This book is thus intended not only to be a guide to practical emulsion making, but as a textbook for technical students, industrial chemists and photographers generally, who are anxious for their own reasons to prepare emulsions of various types and speed. With careful work, ex-

cellent results of repeatable quality can be made on a small laboratory scale, and the apparatus involved need be neither elaborate nor costly.

The great majority of formulas given in the following pages have been quoted from published communications, but it has been the special aim of the author to set out the fundamental lines upon which such formulas are based, so that the emulsion-maker can construct his own for any desired purpose. New needs for special characteristics crop up with great frequency, and there is definite scope for the manufacturer of sensitized products who is able and willing to meet these new demands, which may not necessarily run into immense production figures.

The manufacturer is helped today very largely by modern air-conditioning equipment, improved means for temperature control, excellent emulsion-making plant and coating machinery, and above all by the splendid researches in emulsion chemistry which have been carried out in recent years. With the further help of modern sensitometric work, special packing materials, checking by trained technicians, and above all the ever-growing intelligence of the photographer himself, the sensitive materials industry has reached a high state of efficiency, and its products have assumed the character of precision instruments.

Grateful acknowledgments are given to the Research Laboratories of Eastman Kodak Company, and Kodak, Ltd., for photographs kindly supplied; also to Messrs. T. H. Dixon and Co., Ltd., and Messrs. W. Watson and Sons, Ltd., for illustrations of plant and apparatus; to Burt H. Carroll and Donald Hubbard, whose research papers have been frequently quoted; and to Mr. Charles A. Silver for his assistance with the proofreading.

Chapter I

NATURE OF PHOTOGRAPHIC EMULSIONS

Introductory — Light-sensitive Silver Compounds — The Nature of an Emulsion — The Function of Ammonia — Sensitizing Properties of Gelatin — Ostwald Ripening — The Crystal Structure of Silver Bromide — Iodide in Emulsions — Grain Size and Emulsion Characteristics — The Effect of Light on Silver Bromide

THE image formed by the lens of a camera is recorded on a light-responsive surface which in present-day photography takes the form of sensitive silver salts in a film of gelatin. No visible action takes place in this film during a normal exposure. But it is capable of providing ultimately a visible and permanent image, obtained in practice by developing the invisible or *latent* image formed by the action of the light-rays in exposure. Daguerre showed that by exposing in the camera a plate made of polished silver treated with iodine vapor, an invisible latent image was formed which could be rendered visible by development with mercury vapor. The mercury deposits itself on the parts of the surface exposed to light, but does not adhere to the unexposed parts. The first reference to photographic sensitometry was probably made by Arago in his statement that " to the portions which represent the halftones the mercury affixes itself in greater or less quantity proportional to the action of the light upon these parts."

The thin film of silver iodide formed by the action of iodine vapor on silver, according to the equation

$$Ag + I = AgI,$$
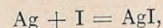
was in no sense an *emulsion*, but merely a stain similar to the discoloration of a brightly polished silver article exposed to the sulphurous atmosphere of a city. The approach was nev-

ertheless being made towards the emulsion, but it was years later when Nièpce de St. Victor coated glass plates with a mixture of albumen and starch in which were suspended the sensitive salts. Three years later came the wet-collodion process. In this, a solution of guncotton dissolved in ether and alcohol and containing soluble bromide and iodide was poured over a glass plate and sensitized by flowing a solution of silver nitrate over the set, but still damp, collodion film. The plate was exposed immediately in the camera, so that the soluble excess salts should not crystallize out.

In an effort to cut out the sensitizing process (still largely used today), the first actual emulsion was produced. This was a suspension of silver bromide or iodide in collodion, made by Bolton and Sayce. Then came the use of gelatin by Dr. Maddox, and today we find that the great bulk of sensitive photographic materials consist of gelatin " emulsions," or suspensions of silver salts in a solution of the protective colloid *gelatin,* applied to glass, celluloid or cellulose acetate film, paper, and more recently to thin aluminium alloy sheets.

It will thus be gathered that a modern photographic emulsion consists of a suspension of silver halides in gelatin, which is applied to a suitable support. It should be noted that emulsions have been made by Staud and Connelly by disp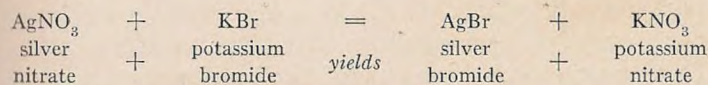ersing the silver halide in a mixture of gelatin and a water-soluble cellulose ester such as cellulose acetate or lactate,[1] while Sheppard and Houck have used the potassium salt of cellulose acetate diphthalate.[2] Agar-agar has been employed with little success. In spite of wide research, no compound or substance has yet been discovered which is anything like as sensitive to light as bromide of silver, yet extreme sensitiveness can be obtained only when it is subjected to the influence of gelatin, and if chemical fog is to be avoided on development, a small proportion of the iodide of silver must accompany the bromide.

The salts are formed by double decomposition, as for example:

$$AgNO_3 + KBr \xrightarrow{yields} AgBr + KNO_3$$

silver nitrate + potassium bromide yields silver bromide + potassium nitrate

While from the chemical equivalents it would seem that 170 parts by weight of silver nitrate would react with 119 parts of potassium bromide, it is necessary in practice to have present an excess of soluble bromide, for reasons which will be discussed later. If an excess of silver *nitrate* were present, then the emulsion would print out on sufficient exposure to daylight, giving a visible image of metallic silver; for this purpose, however, the chloride of silver in combination with an organic silver salt is commonly used. Silver chloride without excess of silver nitrate gives, on the other hand, a comparatively insensitive emulsion of the type used in making chloride or " gaslight " papers and slow transparency plates, which yield on alkaline development black and white images having great contrast and brilliance.

Thus the three halides, silver bromide, chloride, and iodide, suspended in gelatin or other suitable colloid medium, provide us with the light-sensitive emulsions of which this book will largely treat. Trivelli and Sheppard [3] describe a series of mercuric iodide emulsions, their sensitiveness and density-giving power being " much inferior to silver bromide." For printing processes on paper, certain salts of iron, copper, thallium, etc., can be used, as also can certain diazo compounds. The outstanding feature of a silver bromide emulsion containing iodide, however, is the fact that by the use of ammonia and the application of heat under controlled conditions, a remarkably extensive range of speed, density-giving power, gradation, and contrast can be obtained, which is repeatable with considerable exactness.

Reduced to its simplest form, the making of a sensitive emul-

sion has a good deal of resemblance to cooking. Solutions of the reacting salts are weighed out and mixed, one of them containing a little gelatin which acts as a protective colloid and as a means of preventing sedimentation of the halide precipitate. Any amateur cook knows the difficulty of making a good mayonnaise or hollandaise sauce. Some of the tricks of the emulsion-maker are comparable to those of the adept culinary artist, and the sensitometric characteristics of the finished emulsion largely depend on the exact method of mixing and cooking. The mixed emulsion is kept warm for a certain time, during which it is said to " ripen," more gelatin is then dissolved in it, and it is cooled until gelled.

Reference to the equation of the chemical reaction given above will show that soluble nitrate (KNO_3 in this case) is formed along with the silver bromide. Any such nitrates would crystallize out on drying, if allowed to remain in the emulsion when coated on glass or film base, and such by-products must be removed. To effect this, the emulsion is broken up in the jelly stage into small pieces, known as shreds, worms, or noodles, and these are suspended in water until the soluble by-products, together with any excess of ammonia and bromide used in the making, are washed out by diffusion. The washed gel is then dissolved by heat, fresh gelatin is usually added, and the emulsion is again cooked, this time at a higher temperature which is more or less critical, as is also the precise time of the cooking, digestion, or " finishing."

It is the variations in the proportions of ingredients, the exact method of precipitation, the time allowed for ripening, the time of cooking after washing and the temperature employed, and the character of the gelatin, which influence the final characteristics and give us the immense range of modern emulsions. These vary from the very slow silver chloride paper emulsions used for handling in Mazda light, to the exceedingly fast films

that record images in the millionth part of a second. A rough idea of the relative sensitiveness of various types of emulsions is given by Clerc [4] as follows —

Ultra-rapid negative emulsions	75,000 to	100,000 *
Positive emulsions, black tones	1,000 to	3,000
Gelatino-bromide papers, warm tones	300 to	1,000
Gelatino-chlorobromide papers	100 to	200
Transparency plates	1 to	25
Gelatino-chloride papers	1 to	5

Silver bromide emulsions made with gelatin are very much higher in sensitiveness than those made with collodion. The digestion of the silver bromide grains or crystals with the gelatin is obviously the prime cause of this difference. Clerc tells us [5] that, following from an observation by R. F. Punnett in 1924, S. E. Sheppard found that the differences in sensitive properties are due to the presence in gelatin in varying proportions (from 1 in 200,000 to 1 in 1,000,000) of *sensitizers,* among them being thiosinamin (allyl thiourea), and mustard oil (allyl isothiocyanate). The presence of these sensitizers, occurring naturally in gelatins, and in quantities varying with different makes or different batches of any one brand of gelatin, explains the great variation in quality of any given emulsion made to one formula with different samples of gelatin — a behavior which greatly perplexed the early emulsion makers and for a long time made impossible any assurance of uniformity in their products. Experiments made with gelatins rendered chemically inert, to which have been added known sensitizers, such as allyl thiocarbamide, sodium thiosulphate, etc., have given results qualitatively very similar to those made with untreated " active " gelatin, though the characteristics of active gelatin can not be explained by allyl thiocarbamide alone.[6] A great deal of research has been conducted in recent years on the chemistry

* This figure must be increased today as the result of recent advances.

of these sensitizers, and any real advance on present speeds will be due to new discoveries in this field rather than to modifications in ripening, digestion, etc. Elaborate efforts have been made, also, to produce some standard type of gelatin, with little success. As gelatin is an amphoteric colloid, capable of combining with either anions or cations depending on the hydrogen ion concentration of the solvent medium, a good deal of work has been done, by Sheppard and others, with emulsions made with iso-electric gelatin, the pH of which is 4.7. The treatment to which gelatins are subjected by certain manufacturers is kept secret, but as a general practice the choice of a batch from a number of samples by actual experiment is the accepted guide of its suitability for a particular purpose.

As an example of the versatile nature of emulsion grain sensitizing, the suggestion may be quoted of a mononuclear or polynuclear heterocyclic compound containing a hydrogen atom linked to nitrogen but replaceable by silver. The pyrimidenes, pyrazols, and purpurines are quoted as examples.

The great majority of speedy emulsions are made with ammonia, which assists in the ripening or crystal growth of the precipitated grains of silver halide and their subsequent sensitivity. In another type of emulsion, however, the suspension in gelatin is "boiled," which means actually that it is heated at a temperature somewhere between 160° F. (70° C.) and a few degrees below boiling point. Such an emulsion is an interesting one to consider at this point, because the absence of ammonia enables us to watch the process with less chemical complications. Trivelli and Smith [7] outline such a formula. Two solutions are prepared as follows:

Potassium bromide ...... 165 g   Silver nitrate .... 200 g
Potassium iodide .... 5 g   Water .... 2000 cc
Gelatin .... 65 g   Temperature, 72° C.
Water .... 1700 cc
      Temperature, 70° C.

In a series of mixings, the silver nitrate solution was added by pouring it through different sized nozzles into the salts solution, the times of precipitation varying from 31 seconds to 85 minutes, 10 seconds. The emulsion was ripened for twenty minutes at 70° C., then cooled quickly to 45° C., when 250 grams of gelatin previously washed in water was added and the whole stirred for twenty minutes at 45° C. After standing overnight in a cold storage room, it was washed and remelted to 42° C. and made up to a weight of 6.3 kilograms by the addition of 100 grams of fresh gelatin soaked in the requisite amount of water. The final pH was 6.54.

The relation between the time of precipitation and the average grain size is interesting, and is shown in the table below:

Emulsion number	Time of precipitation Min. Sec.		No. of grains $\times 10^{-9}$ per cm^3	Total surface of grains in cm^2 per cubic centimeter
8	0	31	6.85	3053
9	4	22	2.09	1957
10	10	12	0.63	1026
11	19	30	0.28	756
12	42	40	0.17	564
13	54	15	0.09	663
14	85	10	0.04	320

Figure 1 shows the relation between grain size and time taken for precipitation, reproduced from the paper quoted. It was found by Southworth [8] that there is a quantitative relation between the H and D speed (p. 208) and γ (maximum contrast on complete development), and this was found by Trivelli and Smith to hold good for a number of emulsion series with different times of development.

Let us now examine the making of the emulsion after the initial precipitation of the silver bromide, usually termed the emulsification. As already stated, a great proportion of speedy
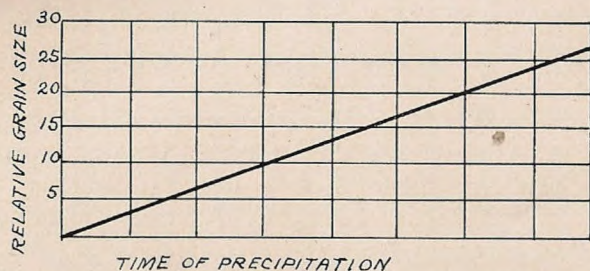
FIG. 1

emulsions are made with ammonia. In many cases the whole of the silver nitrate in the formula is treated with sufficient concentrated ammonia to redissolve the precipitate of silver hydroxide first formed. The temperature of mixing is then usually much lower. The AgBr precipitate formed in emulsification appears as minute shapeless grains under the microscope, but as ripening proceeds they grow in size and a definite crystalline shape is recognized. The crystals continue to increase in size, as time proceeds, owing to the presence of the silver bromide solvents — ammonia and the excess of soluble halide.

Silver bromide, according to von Weimarn's theory, would give a precipitate on mixing the reacting substances, the " grain size " of which would be controlled by the concentration of the reactants. The fact that the precipitation takes place in the presence of a colloid, however, must be taken into consideration, in addition to the excess of AgBr solvents. To obtain uniformity of grain, the emulsion is stirred during precipitation, this tending to reduce the size of the crystals. In some cases of ripening, the crystals are allowed to grow without agitation, especially in those cases where a mixed selection of grain sizes is needed to give photographic latitude, or a long scale of gradation.
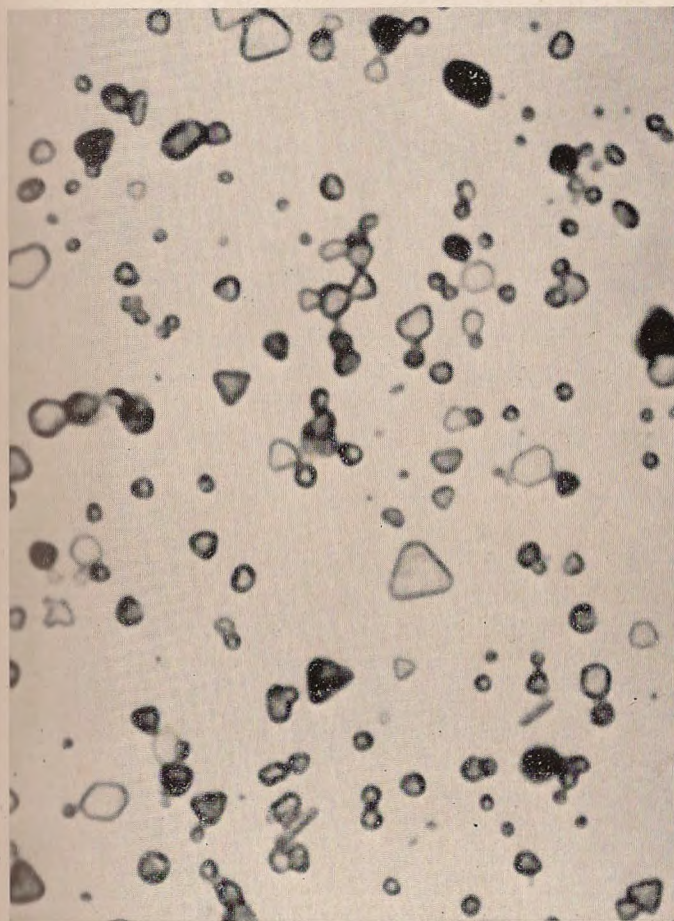
FIG. 2.   GRAINS OF A COMMERCIAL PHOTOGRAPHIC EMULSION X 5,000

In the early stages after emulsification the system tends to reduce its surface energy through any colloidal silver bromide becoming transformed into crystalling AgBr. By the so-called Ostwald ripening, the larger crystals grow at the expense of the smaller ones, and the longer the ripening proceeds, the bigger do the crystals or grains become. A certain amount of aggregation eventually takes place, unless stirring is given. A drop of emulsion can be taken on a glass rod, smeared over a clean glass slide, and thinned out with a few drops of hot water. The slide is then sharply shaken free of excess fluid, leaving only a single layer of grains adhering to the surface. The specimen, as soon as dry, can be examined with a twelfth-inch oil-immersion objective, using the concave mirror and small condenser aperture. It will usually be observed that a wide variety of grain sizes is present, appearing as hexagonal plates, triangles, needles and unresolvable particles (see Figs. 2 and 3). All of these are actually octahedra. Dr. Sheppard states that in 122 different emulsions examined at a magnification of 2,500 diameters, only octahedra could be positively identified. The equilateral hexagons which so soon become familiar to anyone examining emulsion grains with the microscope are plates developed in two directions, while needles appear which are developed principally in one direction — all, however, octahedra.

If a few drops of the ripening emulsion be smeared over a strip of glass and looked at by transmitted Mazda light, the color after emulsification will be orange. As ripening proceeds, this turns to yellow, then greenish-blue and then to blue, at which stage the maximum useful ripening will usually have been reached. If ripening be allowed to proceed further, the transmitted light may appear bluish-violet or gray; at this stage the emulsion will have overgone the mark and will probably show fog on development without having gained any advantage in speed. This method of watching the progress of ripening

FIG. 3.   GRAINS OF A PURE BROMIDE PHOTOGRAPHIC EMULSION X 5,000

was much favored by the old school of emulsion chemists, a trained eye being able to detect with considerable accuracy when the optimum stage had been reached. As the time can vary from twenty minutes or so to three or four hours with an unfortunate change in gelatins, it is a useful check in the factory when new batches come into use, even though they may have been passed as O.K. in the laboratory.

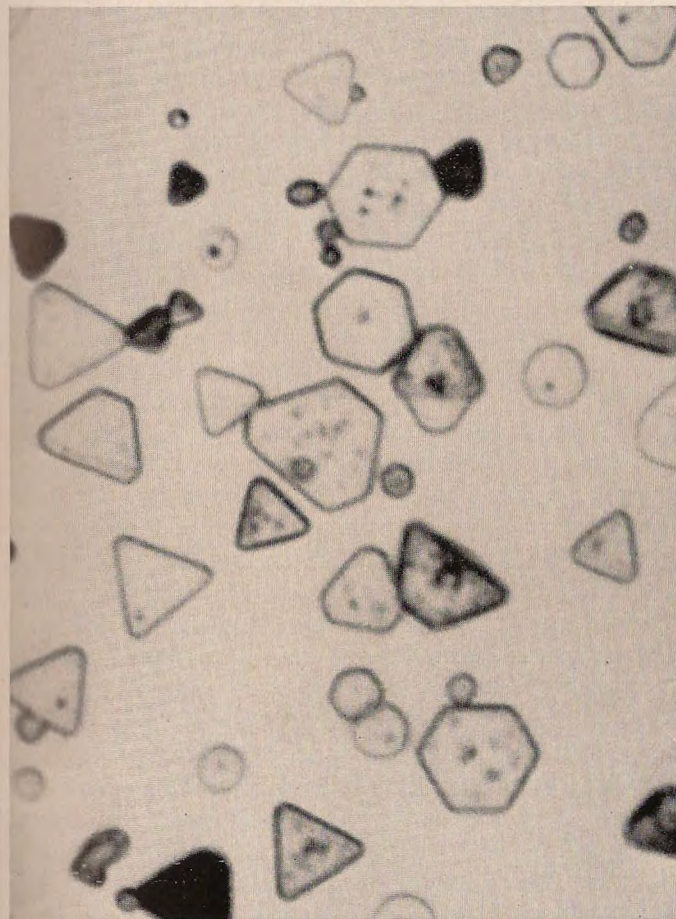So far we have said little about the iodide in an emulsion. Reference to any formula for a fast emulsion will reveal that a small amount of silver iodide is used. Whether this is formed at the time of emulsification or at a later stage, the iodide appears to take a definite part in the molecular structure of the bromide. Iodine has a greater chemical affinity than bromine for silver, and at whatever stage it is introduced, it will replace it. The term iodo-bromide is frequently used. X-ray crystal measurements of the lattice spacings indicate a complete homogeneity throughout the crystal, but the presence of the iodide ions changes the spacing, making the distance between them larger than in the pure state. This would indicate, according to Friedman,[9] that a crystal which contains iodide as well as bromide ions exists in a strained condition, the degree of strain being dependent on the concentration of the iodide ions within the crystal. To a slight extent this corresponds to the sensitivity of the resultant grain, for it has been determined that the maximum sensitivity is attained when the concentration of the iodide is approximately four mol per cent of the total halide content. Beyond this concentration the sensitivity falls off again.

The range of diameters of the crystals tells a good deal about the character of the emulsion that is to be. A wide range indicates good gradation and latitude, while if the crystals are all of similar size, a high gamma with early reversal and lack of latitude ordinarily results, except in cases of very slow emul-

sions which have had special treatment. While the grain growth in ripening is almost invariably accompanied by an increase in speed of the finished emulsion, the final sensitivity is determined more by the conditions under which emulsification took place than by the ripening itself, provided always that the final cooking or finishing is carried to completion. The early literature on emulsion making was concerned chiefly with the endeavor to get all the speed before washing. It is now an open secret, since the paper of Carroll and Hubbard was published in the *Bureau of Standards Journal of Research* in 1931, that a great deal of the final sensitivity is obtained in commercial practice by the cooking given to the *washed* emulsion. Trivelli and Smith disclose this fact still further in Communication No. 704 from the Eastman Kodak Laboratories.

The nature of the gelatin undoubtedly plays a very important part, as well as do the concentration of the reacting solutions and the method of pouring and stirring. As an example of the extraordinary effectiveness of emulsifying conditions, one may take a formula, built on lines originally published by J. M. Eder, where the silver nitrate is merely wet with water, redissolved with ammonia, and in this very concentrated condition is literally " flopped " wholesale on to the salts solution in the jar. This, of course, gives an instantaneous precipitation, the grains being of a very uniform size. No ripening time whatever is allowed, the bulk gelatin being added immediately and the emulsion set in ice water as soon as it is dissolved. Such an emulsion yields a film of very high gamma but of poor latitude, specially suited to copying black and white work. It will thus be gathered that the emulsion chemist must find out for any emulsion formula the optimum time of ripening and the necessary physical conditions to obtain the results he wants, as also the exact method of emulsification, in addition to selecting the most suitable brands of gelatin.

Let us assume now that an emulsion has been ripened and that sufficient extra gelatin has been added to give it the necessary viscosity for coating — say a total of eight or nine per cent of the volume. This viscosity is of course arranged to suit the type of plate, film or paper, and the particular coating machine and climatic conditions. The soluble by-products together with any excess of ammonia and the excess alkali halides, are next removed by washing. While this is ordinarily done in the manner described in detail in Chapter III, other methods have been suggested, such as pouring the emulsion in a fine stream into a large bulk of alcohol, thereby coagulating or precipitating the gelatino-bromide, the water with its soluble salts being taken up by the spirit. Many variations of the spirit washing method were described in the early literature, especially in the *British Journal of Photography*, towards the end of the last century.

The washed emulsion, then, is a dispersion of silver halide grains in more or less pure gelatin. The gelatin nevertheless contains sufficient sensitizers — or they have been already adsorbed to the silver bromide crystals — to insure that when the emulsion is remelted and heated the maximum sensitivity is obtained. That some sensitization has been effected within the grain in the case of mixed-grained emulsions has been shown by the fact that while after exposure the smaller grains can be rendered undevelopable (the latent image destroyed) by treatment with chromic acid, some of the larger grains still remain developable. The final cooking, when the speed of the washed emulsion can be increased many hundreds or even thousands of times in the course of thirty minutes or so, is known as digestion or finishing, and is fully dealt with in Chapter IV.

Owing to the lack of emulsion-making literature, particular interest attaches to the paper by Trivelli and Smith [10] in which are described experiments to determine the influence of grain

size on the final digestion. These experiments indicated two things; (*a*) the H and D speed of the smaller-grain emulsions increased to a greater extent than that of the large-grain emulsions; (*b*) the gamma of the smaller-grain emulsions increased less than that of the larger-grain emulsions. As an example of (*a*), the figures below are quoted from the paper of these authors:

Average grain size in μ^2	0.16	0.54	2.93
Time of finishing at 60° C. in minutes	*Increase in speed*		
10	3.4	3.8	0.8
20	4.6	5.0	0.9
30	5.2	4.4	0.9
40	5.9	4.7	1.0

Average grain size in μ^2	0.16	0.54	2.93
Time of finishing at 60° C. in minutes	*Increase in gamma*		
10	1.4	1.6	2.5
20	1.5	1.7	2.9
30	1.5	1.9	3.2
40	1.5	1.9	3.2

Admitting that grain size need not be the deciding factor in the speed of an emulsion, it has been established that within experimental limits there is a direct proportionality between the average grain size and the H and D speed in certain emulsion series. On the other hand, as the gamma of very fine-grained emulsions does not increase as much on final digestion as it does in the case of coarser-grained ones, it is usual practice to secure the high contrast (where desired) of a slow fine-grained emulsion in the mixing and ripening rather than to trust to the digestion after washing. Speed being due largely to the sen-

sitizing of the silver halide by the gelatin, it is obviously more difficult for the gelatin to function in the case of *fine* grains, which have a very large surface as compared to the coarse grains. As an example in the increase in surface area of a grain with decrease in diameter, the illustration may be given of a cube of 1 cm side, which has a free surface of 6 sq. cm. If divided up into a corresponding number of small cubes each of 0.01 thousandth of a millimeter side, the free surface of the 6 sq. cm would be expanded to an aggregate of 60,000,000 sq. cm.

Reference may be made here to the effect of very small quantities of sodium sulphite in emulsions. If this substance be introduced in quantity sufficient to reduce a few tenths of one per cent of the silver bromide present, and the emulsion be then digested, it can act as a powerful sensitizer, approaching in large measure the effect of the natural sensitizers in gelatin. As stated by Carroll and Hubbard,[11] the sensitivity nuclei formed are of metallic silver, in amounts similar to that of the silver sulphide nuclei of normal emulsions. The rate of change of sensitivity increases with increasing alkalinity, and decreases with increasing bromide-ion concentration. The rate of after-ripening with sulphite is less affected by hydrogen ion concentration than the corresponding process in active gelatin. The authors state that while many of their emulsions sensitized with sulphite were of " commercial quality," none were equal to the best obtainable by standard methods from the same type formulas.

After the emulsion has been coated on its support, a certain amount of after-ripening or ageing can go on, especially if the ripening after emulsification has not been carried to, or near to, an optimum point, or if the finishing was not carried to finality. This gradual rise in speed or gamma in a coated plate on keeping is not to be confounded with the after-ripening

which Carroll and Hubbard define as " the increase in sensitivity of photographic emulsions after washing," which we have seen depends on the effect of heat treatment upon the initially ripened grains.

The ageing of plates and films may be regarded as a continuation of digestion in the dry state and at storage temperature, but for our purpose it should be regarded more as deterioration. A coated product, after keeping for a short time to get into complete equilibrium and for the hardening agent to complete its work, should maintain the state in which it is put out for two to three years, and much longer in the case of slow materials. On the other hand, there may be a tendency in the case of films for the gradual lowering of pH, due to acid liberation, when speed will be lost. This is a matter to which due attention must be paid in commercial film manufacture. As an instance of the excellent keeping of glass plates, the case may be quoted of star drift measurements at Oxford Observatory, England, where special rapid plates were exposed in an astronomical camera on a group of stars, and without development were stored for fourteen years, and then given a second exposure at the completion of the orbit. The displacement between the two images, one having been latent for fourteen years before development, was the measure of the drift.

When light is absorbed by a grain of silver iodo-bromide, the silver halide molecule becomes dissociated, and atomic silver and free halogen are formed, the halogen being absorbed by the acceptors in the surrounding gelatin. The new system can be described as a crystal of silver iodo-bromide upon which atomic silver is adsorbed. Such a system is easily reduced to metallic silver by the action of the developer, as originally established by Carey Lea. That the reduction starts from the sensitive nuclei was shown in 1922 by the brilliant photomicrographic researches of The Svedberg.

The metallic silver grains formed from the exposed silver halide by reduction during development have been regarded as tiny coke-like masses, which link up to form aggregates or larger " grains," but it has been shown by recent work with the electron microscope that the grain formation is actually ribbon-like in character. Photomicrographic work done in the ordinary way up to magnifications of × 2000 and upwards (diam-
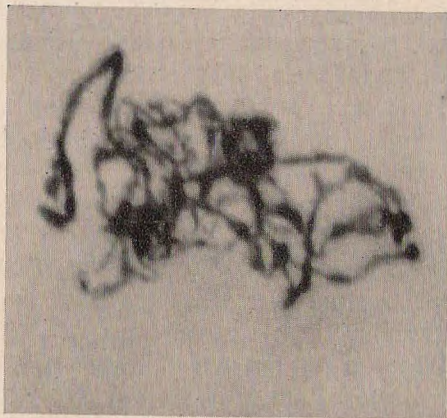

FIG. 4

eters) has never revealed, nor indicated, such a formation. But with the immensely greater magnification of × 50,000, possible with the electron microscope, definite results have been secured which may necessitate reconsideration of some of our present ideas. The image grain has now been shown (Fig. 4) to consist of a ribbon of silver crumpled up like a string, which would appear to occupy a part only of the total area of what we have regarded as the *grain* and to possess light transmitting properties rather than being completely opaque. It is more than likely that subsequent studies along these lines will show the structure to vary as regards its nonopacity with different condi-

tions of emulsification, and thereby be responsible to some extent for characteristic variations.

It is beyond the scope of this book to deal with the subject of the latent image and the theory of development, but it should be emphasized that one reason why sensitive silver emulsions have made modern photography possible and of such immense value to scientific research, is that over a long range of light intensities, depending on the individual emulsion, equal increases in exposure result in equal increases in opacity of the developed image, or equal increments of " developability."

Equal effective exposures produce equal densities under controlled development (Bunsen and Roscoe reciprocity law), except for a correction indicated by Schwarzschild which makes it necessary to substitute for the exposure $I \times T$ (intensity multiplied by time) $I \times T^p$, p being the Schwarzschild factor. An example is given by Strong,[12] showing to what extent the Bunsen and Roscoe law fails in the case of motion picture positive film. For a range of illumination intensities from 1 to 33,000, p varies from 0.68 to 1.00, the maximum intensity being 131 lumens per square meter and the exposure time varying between 18.2 hours and 2.5×10^{-4} second.

The covering power and maximum density of an emulsion depend to some extent upon the size of the reduced silver grains, their aggregation, and their number per unit area, the ratio of gelatin to silver having some effect where density measurements are made by specular light. Clerc states[13] that an optical density of 1 (transmission ten per cent) on a photographic negative, corresponds to a mass of silver of about ten milligrams per square decimeter, a mass which is variable with the grain size, conditions of development, and the wavelength of the radiations used. Trivelli and Smith showed[14] that the decrease in gamma of an emulsion is proportional to the square root of the total number of grains. They state that this de-

crease is considerably greater than the changes observed in the *resolving power* by diluting the emulsion. For recording purposes, a good black which will give sufficient differentiation in printing or on projection must be combined with high resolution, and the latter must therefore depend largely on suitable emulsion characteristics rather than on thin coating. In fine-grain emulsions, however, Trivelli and Smith find that the resolving power increases exponentially as the grain size is diminished arithmetically.

Much of the foregoing has applied to " rapid " emulsions of silver iodo-bromide having H and D speeds ranging from 25 to 2000 or more. In materials for printing, lantern-slide emulsions, and copying, speed is of little consequence. Where extrafine grain, high resolution and negligible fog are the chief desiderata, physical treatment rather than chemical is involved, and in chapters dealing with such emulsions it will be seen that the general technique of making is considerably modified.

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CHAPTER II
MATERIALS FOR EMULSION MAKING

Gelatin — Chemicals and Their Choice — Analyses and Tests — Storage — Methods of Handling Bulk Materials

GELATIN is the material which presents the most problems to the emulsion chemist. Its physical and chemical properties can be tested in the laboratory, but the physical characteristics are apt to change according to the treatment it undergoes, and the chemical properties from an emulsion-making standpoint depend to an important extent on certain constituents present only in extremely minute quantities. Bogue states [1] that the gelatin solution used in an emulsion must be so made that the dried film will have just the right porosity to electrolytes, for in all stages of development where chemicals are used it is necessary that they penetrate and impregnate the gelatin layer with considerable ease, but no trace of the precipitated silver must be permitted to escape. Gelatin acts both as a protective colloid and a vehicle for the silver haloids, and it is in fact quite astonishing what a mass of silver haloid can be suspended in a very weak solution of gelatin with comparatively slight sedimentation.

The best gelatin for emulsion-making purposes is probably that extracted from calves' hides, but other hides and other parts of the animal are used, and bones also. Hides having a high fat content are not suitable for emulsion gelatin, according to Huzii,[2] as it causes spots on the plates. If the temperature in extracting the gelatin is too high, the product will have high light sensitivity and fog-giving properties; increase in the number of extractions has similar effects.

The preparation of the gelatin involves a number of operations. The raw materials are steeped in lime water, after having been thoroughly washed free of dirt and blood. The liming process dissolves out the albuminous and mucinous constituents, and, as it is a process of alkaline hydrolysis, caustic alkali is sometimes employed. The alkali is later neutralized and a process of digestion or boiling given, followed by concentration of the liquor, bleaching, washing, etc. The final jelly is cut into sheets and dried on strings or wire nets, and here a certain amount of bacterial contamination can be contracted. Leaf gelatin is sold in the form of thin sheets, of which in the photographic quality 100 to 110 go to the pound. It may be cut into thicker sheets which are ground to powder when dry, or turned into flakes which are sometimes sold as such. The ground gelatin when sieved gives a powder of about 50 per inch mesh. Such powder is liable to contain traces of iron. Photographic gelatin, which may be looked upon as glutin and a mixture of glutin and chondromucoid, is the purest form made, being superior in quality to culinary gelatin.

A good gelatin should give a clear and nearly neutral solution. The moisture content should not be more than twenty per cent and lower in the case of " soft " gelatins. There are roughly three classes of photographic gelatins, hard, medium and soft, which can be differentiated by their setting and melting points and the quantity of water they will absorb. The ash content of a good gelatin should not exceed two per cent. Bases and heavy metals should not be present in more than traces; these may be sodium, calcium, zinc, iron, copper, arsenic, nickel. Phosphates, sulphates, sulphites, chlorides, borates and sulphur dioxide may also be present.

It is interesting to note that as early as 1847 Nièpce employed gelatin as a vehicle for coating silver iodide on glass, though this was soon dropped owing to the effect of the acid

nature of the silver bath. Eight years previously, Mungo Ponton had rendered paper sensitive to light with potassium dichromate, and later Becquerel showed this sensitivity to be due to the *size* in the paper. It was Dr. R. L. Maddox who, in 1871, first employed gelatin as a vehicle for silver bromide and so prepared the first emulsion. Its use gave an entirely new measure of speed, but it at the same time introduced a great many perplexing phenomena, some of which are still not fully understood.

Dr. S. E. Sheppard quotes in his monograph on the theory of photography, " Gelatin," a statement by V. B. Storr [3] in the *Second Annual Report of the Society of Chemical Industry* on the progress of applied chemistry, as follows: " The physical properties are a very insufficient guide to the suitability of gelatin for making photographic emulsions. There are certain chemical differences between different types of gelatin and even between different batches of the same type which are more effective in determining speed, freedom from fog, and such qualities. . . . It is very possible, if not probable, that they (chemical differences) are due to the presence or absence of very small quantities of specific substances rather than to variations in the proportions of the main constituents of the gelatin."

This statement tells a good deal of the story of gelatin, and every emulsion chemist will add to it that the only satisfactory way of testing a new sample is to make with it a semi-works-size lot of the particular emulsion for which it is to be used. It is a common occurrence, for example, for a sample which has been turned down by one maker to be accepted as excellent by another. Where results are to be repeated over long periods, or where works-batches of emulsion are being made, it is sound practice to use a blend of two or three different lots or even makes, taking care that only one of these is allowed to run out at one time, so that when a new batch of gelatin is worked in,

only a proportion of the total amount used for each making is changed.

The chemical test of most importance in selecting gelatin is for silver reduction. A one or two per cent solution of the sample is made up with distilled water, and to a measured volume is added an equal volume of ten per cent silver nitrate solution, to which has been added just sufficient concentrated ammonia to redissolve the precipitate of silver hydroxide first formed. The mixture is well stirred and is then left in the dark for a fixed time, along with a similar control test of a gelatin of known good quality. Any darkening or formation of a precipitate will give a good indication of the quality of the sample. A good gelatin will contain a relatively small proportion of non-glues. According to Stelling,[4] the non-glue extracted from gelatin by alcoholic precipitation of the glue is 3.39 per cent, 5.73 per cent from hide glues, and 10 to 16 per cent from bone glues. Arsenic has some effect on speed and fog production, and has been found to occur in eight out of twelve samples,[5] in the proportion of 0.0005 to 0.003 per cent. Copper, zinc, tin and lead may be found by the usual methods. The most important impurities are probably the sulphur compounds dealt with elsewhere. The presence of sulphur dioxide is undesirable, especially if the sample is to be used for highly color-sensitive emulsions or for the making of light filters. Where leaf gelatin is to be used for the latter purpose, it can be washed in several changes of water before use, the leaves being kept well separated, when soluble impurities will be removed.

Viscosity can be measured in a number of ways. A one per cent solution may be tested with an Engler or Ostwald viscosimeter, at a temperature of 120° F. Running the solution through a water-jacketed pipette and comparing the time taken with that of plain water is another and cruder test, but one which will give useful practical information. Thermal hys-

teresis or hydrolysis may upset physical tests, for it must be remembered that previous treatment such as heating up rapidly and cooling, gelling and remelting and so on, may alter the behavior of a gelatin solution. The viscosity of most gelatins can be very largely controlled in an emulsion by modification of the concentration, by the addition of alcohol or acetone, or by the addition of chrome alum, formalin or sodium sulphate.
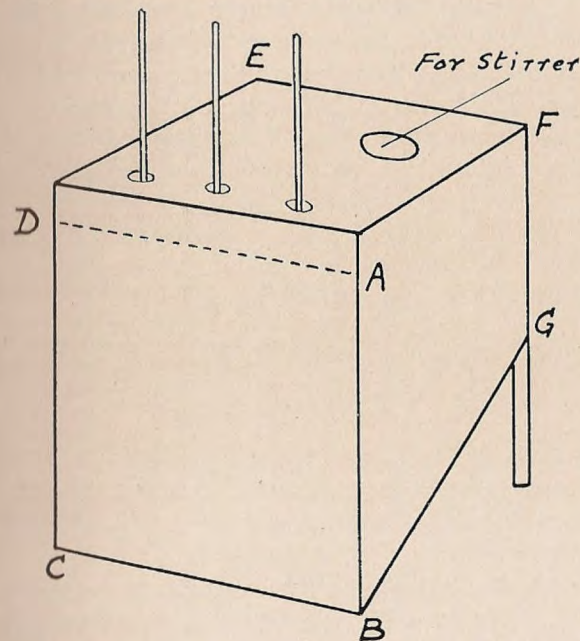

FIG. 5

The melting and setting points of a sample are of some importance. Emulsion gelatins should have a melting point somewhere between 70° and 78° F. (22° and 25° C.) and a setting point of 79° to 86° F. (26° to 30° C.). R. Child Bayley's

method of estimating melting point was to cast small discs of gelatin upon a flat metal surface, which is afterwards placed in a *vertical* position and heated. At the temperature of the melting point, the discs begin to slide downwards. The apparatus takes the form shown in Fig. 5. This is a copper tank having a plain front say twelve by eighteen inches in size, with a smaller back about nine by twelve inches, the depth *AF* being about ten inches. The bottom is inclined as shown in the diagram, so that when heat is applied to *BG* none gets to the testing surface *ABCD*. Two or three thermometers are fitted in corks placed in the top *ADEF*, the tank being filled with water and gradually warmed with an alcohol lamp or Bunsen burner after the discs have been cast. The discs can be made by pour-
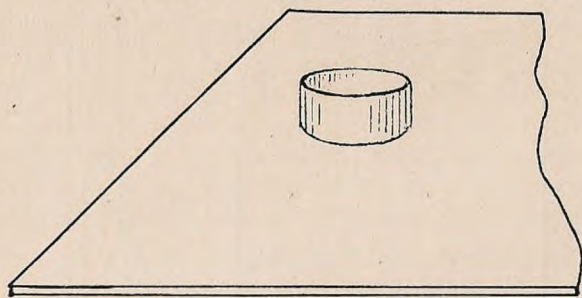

FIG. 6

ing the gelatin solution into a paper cylinder or mold set up on the surface *ABCD*, which is placed first in the horizontal position (see Fig. 6). Tests should be made with solutions of some uniform strength. E. J. Wall recommends ten per cent. The gelatin solution may be introduced into the molds with a pipette, each one being cast of the same height, about one-half inch. The tank should then be left in the cold for eight hours until the gel is thoroughly set and in equilibrium. The tank is

then set in the upright position, the paper cylinders cut round with a sharp penknife and removed, and the tank filled with water. A small motor stirrer is advisable to keep the whole front surface uniformly heated. As soon as the melting point has been reached, the little discs will begin to slide down the face of the tank, and the average temperature of all of them will give the melting point desired.

Another method, used a good deal by the author, is to introduce the gelatin solution into four little glass tubes one and one-quarter or one and one-half inches long, and about three-sixteenths-inch bore. These are set and kept cold, at about 45° F. for four hours, and are then tied around the bulb of an accurately graduated thermometer. The bulb and tubes are then suspended in a beaker of thin petroleum oil of about 0.90 specific gravity, the beaker standing in an outer water bath. A small mechanical stirrer keeps the oil in motion. The water jacket is heated, and as the oil approaches the melting point of the gelatin, the gelatin slips out of the glass tubes and drops to the bottom of the beaker. An average reading of the four tubes will then give a fairly reliable figure for the melting point.

The setting point, which is on the average eight to ten degrees Fahrenheit higher than the melting point, can be ascertained in various ways. Sheppard [6] describes one method which is stated to give results of the accuracy commonly required in emulsion making, which is as follows: Equal amounts of the solutions to be tested are placed in similar test tubes of one-inch diameter. These are then cooled in ice water and are examined at definite intervals, until the approach of solidification is indicated by the fact that the solution is hardly disturbed when the tube is tilted. When this stage is reached, the tubes are inverted at frequent short intervals. When the meniscus of the inverted sample no longer sags, a thermometer is thrust into the jelly

and the stationary temperature is taken as the setting point. The rate of setting is, of course, of considerable importance when emulsions are to be coated on any kind of machine in the factory. Generally speaking, it may be said that the rate of setting is reasonably gauged by the viscosity, or the jelly strength.[7] While the rate of setting and the setting point can be controlled to a large extent by additions of hardeners (alum, formalin, etc.) or alternatively by softeners (glycerin, etc.), if a gelatin can be selected which resembles previous stock without alteration of the additions, it is far better. The use of chrome alum, for example, is cumulative, and plates or films coated with an emulsion containing it will go on hardening for several months, during all of which time the rate of penetration of the developer will be progressively retarded, with a consequent alteration in the apparent speed unless carefully checked.

It is very desirable in all tests of the physical characteristics of gelatins to submit the sample to the same initial treatment. Thus any change in pH will be responsible for wide variations in the swelling capacity. The ions of many salts have a profound effect on physical properties. As an example of laboratory practice, in making a five per cent solution, 5 grams should be weighed out and placed in small pieces in 90 cc of distilled water (or tap water if the test demands), and allowed to swell for one hour at room temperature, 70° F. The water is then warmed, the gelatin dissolved by stirring, and the volume brought up to 100 cc. The temperature should not be allowed to exceed 160° F. It should then be stood on the bench and allowed to cool until it attains the temperature that is required for the test, for which a suitable temperature would be 105° F.

An example of a commercial test is tabulated on the next page.

GELATIN TEST. Lot No. 117.

Grease	None
Clarity	Complete
Engler viscosity at 10%, temp. 35° C.	3.3
Setting point of 10% solution	27.8° C.
Melting point of 10% solution, after two hours.....	31.9° C.
Reduction by ammonia-silver nitrate	None
Copper, lead, zinc	None
Iron salts	Traces
pH	5.6
No. of cc of 5% chrome alum required to precipitate 10 cc of a 10% solution at 50° C.	5.9

For more detailed information on gelatin, the reader is referred to Dr. S. E. Sheppard's monograph " Gelatin," Vol. 1; Kissling's " Leim und Gelatin " (Stuttgart, 1923); and the textbooks of Alexander, Bogue, and others.

The brands of gelatin largely used in emulsion making are Nelson's No. 2 and Nelson's X-opaque and S. E. emulsion leaf, (made at Warwick, England), Simeon's Winterthur (Swiss), Heinrich's and D.G.F. (German), Bertrand's (France), and last, but not least, the excellent products of the Atlantic Gelatin Co. and American Agricultural Co. Most makers are generous in the extreme with regard to supplying samples, but it is a useful guide to them when ordering to specify the approximate viscosity and hardness desired, if possible to send samples of those brands in use, and to state the type of emulsion for which the gelatin is wanted — fast negative, slow positive, bromide or chloride paper, and so on. Prices average about 85 cents to $1.25 per pound, and as an example of likely quantities for commercial work on a moderate scale, about twenty-five to thirty pounds may be estimated for each day's run of 3,000 feet of sensitized material forty-two inches wide. Gelatin will keep almost indefinitely if stored in a cool and dry place, and it is the experience of many firms that if kept for

six months before use it gives the best results. As already stated, bulk gelatins are best made up of mixtures of two or three batches or makes, which are arranged to run out at different times. A couple of weeks should be allowed to make a thorough test of a new sample. In making the test, a word of caution may be given. In packaging leaf gelatin it is the manufacturers' usual practice to draw from two or three bins, so that a one-pound packet may contain three or more different varieties. If fifty grams are required from a pound packet, a cross section of sufficient thickness should be cut on the cutter so that a piece of each sheet is included in the test solution.

The reader may wonder why gelatin remains the only colloid which is successfully employed as a vehicle for sensitive silver salts. Its sensitizing properties are sufficient reason, but its vehicular power, porosity and protective powers combine to make it unique. Collodion is still used in process work, and for special types of emulsion of a slow speed. Silver halides can be precipitated in a solution of pyroxylin in alcohol-ether, and collodio-bromide and collodio-chloride papers have long been in commercial use. They possess one advantage, that if coated on a base first coated with gelatin, the developed image in collodion can be removed or stripped off the support by treating the print with hot water, which dissolves the gelatin interleaf but does not affect the collodion. An example of this is the Defender Chromatone bromide paper. The image, after toning, can be floated off the support and mounted in layers for the production of a three-color print. Stripping papers can be similarly made for a variety of purposes, although it is a doubtful point whether a coating of hardened gelatin emulsion on top of a gum dammar or wax coating of the support does not yield a better material.

We have seen in Chapter I how excessively small need be the proportions of ingredients or impurities in gelatin to be

responsible for important changes in emulsion quality. It is therefore easy to understand that all chemicals used in emulsion making should be of a high order of purity. There are three types of chemicals generally available. One is the standard type sold for amateur and professional photography. Another is the so-called chemically pure or C.P. variety, and a third type is sold for the laboratory for more exact work, described by the term analytical reagent or A.R. For emulsion making in small quantities, A.R. chemicals are worth the extra cost. At least silver nitrate and ammonium bromide should be A.R. quality. In general, other chemicals may be of the C.P. type. In all formulas given in the following pages, water may be taken to mean distilled water unless otherwise stated. Emulsions are usually washed to best advantage in tap water, or supplies from artesian wells.

Of the ordinary emulsion-making ingredients, ammonium bromide is one of the most important. For extreme speed emulsions this should not contain more than 0.2 per cent of chloride. The finest quality is probably made by combining purified bromine, free from chlorine or hydrobromic acid, with pure ammonia liquor. Less pure samples can be improved by re-crystallization. The chloride content can be checked by boiling a weighed sample with concentrated pure nitric acid, driving out the bromine, and titrating the residue with centi-normal silver nitrate solution.

Silver nitrate is made by dissolving silver metal free from copper and lead in nitric acid. The carefully re-crystallized product is usually sold at a price calculated on the ruling price of silver at the time of order. It must be free from nitrite. Its formula is $AgNO_3$; that is, it is a salt without water of crystallization; molecular weight 170. For convenience, it may be kept in the form of a concentrated solution, such as $2N$ or $2\frac{1}{2}N$, in stone jars. In the following text, however, many

formulas will be found in which the silver nitrate is " wetted " with a small quantity only of water in order to convert it into a highly concentrated solution of the ammonio-nitrate. Here the dry salt will in most cases be found more convenient.

There is much to be said in favor of keeping chemical stocks in liquid form. It is probably more accurate and definitely more convenient. In the case of silver nitrate, if a 2N solution containing 340 grams per liter is made up, the ammonium bromide may conveniently be made up also as 2N, having 196 grams per liter. Equal quantities then react completely. On the other hand, such a reagent as ammonium bromide, which is used in slight excess of the equivalent weight of silver, may be found more convenient to handle in the form of a ten per cent solution.

Ammonia must be free from iron and pyridine compounds. There is an advantage in breaking down the concentrated ammonia to 0.920 specific gravity, as at this strength each cubic centimeter will almost exactly re-dissolve one gram of silver nitrate or be equivalent to one gram of $AgNO_3$. It will be found a great convenience to have it delivered in this form, although the gravity must be checked from time to time. Ammonium and potassium iodides are best made up in the form of solutions and kept in the dark when not in use. A discoloration on keeping, due to the liberation of some free iodine, need not be feared. Indeed, some emulsion makers think that the solution in this form is preferable. Chrome alum should be selected free from contamination by small orange crystals of dichromate, and should be made up with water not above 100° F., as otherwise it may decompose and lose its hardening properties. It should not be neutralized. Chrome alum is most usually handled in the form of a five or ten per cent solution, which should be re-filtered if at any time, on keeping, it shows a deposit.

It is assumed that a reasonably accurate balance or pair of scales is available, and a larger balance where works-scale quantities are to be weighed. A balance sensitive to one or two milligrams is needed, since in many emulsion formulas the reacting compounds are used in proportions closely approximating to their combining weights. The type of chemical balance which
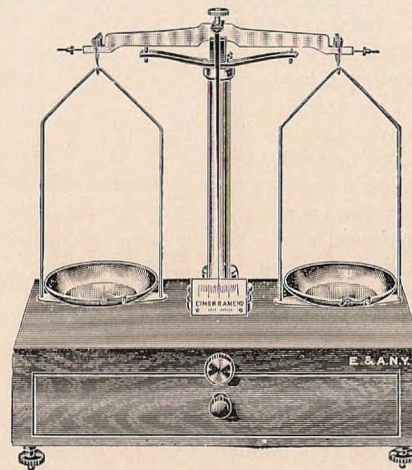
FIG. 7

depends on a moving weight sliding over a scaled bar is not recommended, but a balance of the laboratory type shown in Fig. 7. A set of weights ranging from one gram to five hundred grams with fractions to ten milligrams is suggested.

The following is a list of the chief chemicals which will be needed in the course of the work described in this book:

> Acetone
> Acid, acetic, glacial
> Acid, citric
> Acid, hydrobromic
> Acid, hydrochloric

Acid, nitric
Acid, phosphoric
Acid, sulphuric
Alcohol, denatured, photographic quality
Alcohol, pure
Alum, chrome
Ammonia, concentrated
Ammonium bromide
Ammonium chloride
Ammonium iodide
Barium chloride
Calcium chloride
Carbitol acetate
Cupric chloride
Dextrin
Distilled water
Formalin, 40%
Gelatins, various
Glycerin
Litmus paper
Methyl alcohol
pH indicators
Nessler reagent
Phenol crystals
Phenolphthalein
Potassium bromide
Potassium chloride
Potassium citrate
Potassium dichromate
Potassium iodide
Potassium thiocyanate
Rochelle salt (sodium potassium tartrate)
Sodium chloride
Sodium citrate
Sodium oleate (glycerin substitute)

It is assumed that the usual photographic chemicals are available. Calcium chloride or sulphuric acid will be required for the desiccator.

A word may be said here about alcohol. Denatured spirit to be used in emulsions must be free from mineral oil, aldehydes, pyridine or any coloring matter. A special type of industrial spirit is made for the photographic industry which consists of ethyl alcohol (C_2H_5OH), with a small percentage of wood spirit or methyl alcohol (CH_3OH). This, however, can only be obtained with a permit. A form of denatured alcohol containing about one per cent of gasoline which has been used by the author with most types of emulsion with success, can be obtained without a permit in any quantity. This is Synasol, supplied by Carbide and Carbon Chemicals Corporation, 30 E. 42nd Street, New York City. Where emulsions are to be used for commercial purposes it would not be recommended, but for experimental work it may be found a great convenience. Where only small quantities of spirit are likely to be used for laboratory scale experiments and cost is of no object, the reader is advised to use pure grain alcohol or ninety per cent alcohol, both of which are available in most laboratories. In works practice, a permit will be required for the necessary amount of industrial spirit, which will run into considerable quantities. Spirit is used in commercial emulsions in proportions varying from five to ten per cent of the total volume. In factory routine, frequent checking up of the spirit is necessary to look out for the presence of aldehydes or other deleterious impurities.

While a still for the preparation of sufficient quantities of pure water is an essential on any works-scale production, what is more important in selecting a site for an emulsion laboratory is to determine whether or not the available water supply is suited to the work.

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CHAPTER III

LABORATORY EQUIPMENT

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Layout for Experimental Work — Commercial Production and Its Requirements — Ventilation — Safelights — Digesting Apparatus — Thermostatic Control — Washing and Filtering of Emulsions — Making up — Cold Storage

THE accommodation required for emulsion making depends primarily on the quantities involved and type or types of product to be made. As already hinted, one of the first things to be ascertained in contemplating commercial production is the suitability of the water supply or the provision of good water, and freedom from atmospheric contamination. While modern air-conditioning plants make it possible to work in towns and cities, a new plant is generally started in a vicinity where the air is clean and fresh and space is plentiful.

We shall endeavor in this chapter to discuss plant and apparatus both for the experimentalist and for the production of commercial quantities. In many instances, of course, the larger plant is a multiplication of the smaller unit. But where the coating is to be done by any type of machine, conditions are necessarily very different from experimental work where the coating is by hand. The laboratory type of work will be dealt with first, but it will be understood that much of what is said applies to both cases.

While small quantities of emulsion of excellent quality can be made in the laboratory, even in speedy varieties, the emulsion maker must have the right tools to work with, light-tight accommodation, reasonably good ventilation, an ample water supply, and above all, a room free from dust for coating, where heat up to 70° or 75° F. can be more or less controlled. Very

small scale work can be done in one room, used alternatively for mixing, washing, coating and testing. In many instances of experimental work this is the only condition under which it can be carried on. The ideal accommodation for small-scale work, however, is to have at least four rooms or subdivisions of a large room, where (*a*) the solutions can be weighed out and prepared, (*b*) the emulsification, ripening, washing and digesting can be carried out, (*c*) the finished emulsion can be coated and dried, and (*d*) the final product can be tested or used for photographic work. The latter is obviously the average photographer's darkroom.

The coating and drying room should be as free from dust as possible, with sufficient and suitable ventilation which involves no light leaks. Cleanliness and order are above all things to be desired, the utmost care being taken to keep all graduates, crocks, stirring rods, beakers, dishes, thermometers, etc. scrupulously clean. Cupboards are better than shelves for storing chemicals and apparatus, bottles and glassware being first class dust catchers and requiring frequent rinsing and wiping with a clean damp cloth.

Any room to be used for coating and drying sensitive material must be thoroughly light-tight, this usually involving rather more investigation than would suffice in ordinary darkroom work. By shutting oneself in the room in complete " darkness " for ten or fifteen minutes, it is often astonishing to find how much stray light there is in a room previously thought to be absolutely dark. Black or dark brown paper and paste or glue is generally a sufficient remedy, or the filling up of cracks with mortar or plaster of Paris. A strip of felt or rubber beading along the bottom of doors is often a help, or a wooden lath screwed to the floor to cover the clearance space. Benches about three feet high are more convenient than tables, as practically all work must be done standing and not sitting. This does not
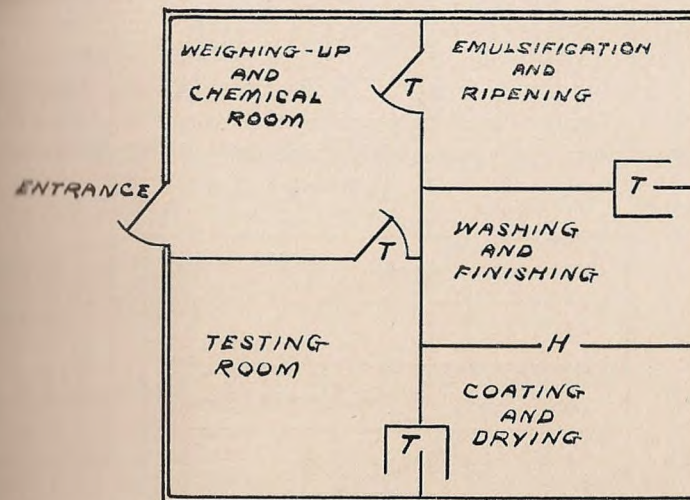
FIG. 8

apply to benches with sinks for washing jars and crocks, where a more convenient height is two feet to two feet, three inches. Sinks should be of ample size, and if of porcelain or enamelled iron and not of wood, wooden slats should be placed over the bottom to prevent breakage.

A small layout is shown in Fig. 8, in diagrammatic form. The general idea, as is often suggested for commercial laboratories, is that the work should take place in a cycle, one operation following another in the ordinary sequence, so that chemicals and solutions are prepared at one end, and the testing of the finished product can be carried out at the other. It is a great convenience to have a light trap between the coating room and the emulsioning room, as shown at *T* in Fig. 8, as one can then go freely from " light " to " dark " at will. If two people are doing the work, a small hatch *H* with sliding panel is useful for han-

dling crocks, solutions, etc., from the making-up room to the coating room.

A word may well be said here about illumination. It is a common idea to have black walls in the darkrooms. This is bad practice. If the source of light is properly filtered, the walls and ceilings may be *white,* when they will reflect a maximum

SLOW BROMIDE RESPONSE

TRANSMISSION OF YELLOW SAFELIGHT

FAST NEGATIVE RESPONSE

TRANSMISSION OF RED SAFELIGHT

ORTHOCHROMATIC RESPONSE

TRANSM'S'N OF RUBY SAFELIGHT

UPPER: PANCHROMATIC RESPONSE
LOWER: GREEN SAFELIGHT TRANSM'S'N

400   500   600   700 $m\mu$

FIG. 9

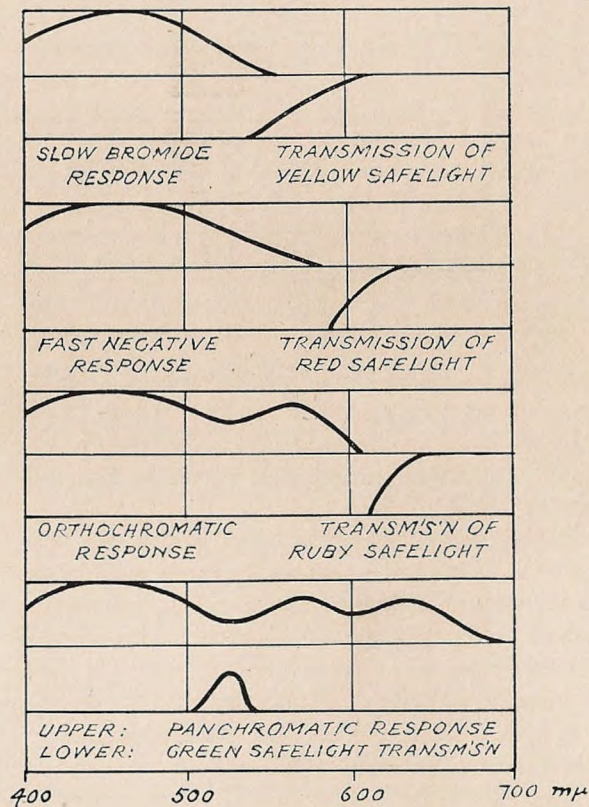amount of diffused light from all parts and greatly increase comfort in working. Inverted ceiling lamps throwing the light upwards so that no direct rays fall on the bench or table are the best to use for general illumination. The ordinary vertical type of lamp will be needed on the benches themselves. Electric torches provided with a piece of " safe " gelatin or glass fitted in the top should be provided for reading thermometers in the darkroom.

Type of emulsion	Color of safelight	Type
Chloride and chlorobromide	Yellow	Wratten OO
		Agfa 105
Bromide paper or transparency ...	Orange	Wratten O or OA
		Agfa 104
Non-color-sensitized	Red or yellow-green	Wratten Series 1 or Series VIa
Orthochromatic	Deep red	Wratten Series 2 or Agfa 107
Panchromatic	Narrow-cut green	Wratten Series 3 or Agfa 108
Infrared	Same as for panchromatic	

The spectral transmission of these various types of safelight is shown in Fig. 9, with the average spectral response of types of emulsions for which they are recommended shown immediately above them. Ground-glass bulbs are to be preferred to plain glass as they diffuse the light better, unless the safelight glasses themselves are of the diffusing type. Ten-watt bulbs are obtainable from most photographic dealers and should be used in the bench lamps.

As white light must also be provided in all rooms, it is a good plan to place the switches for them high up at the side of the doors, so that a physical effort must be made to reach them. This simple arrangement almost entirely prevents turning on the white light by accident. In any works operations the need

for proper light traps between darkrooms is imperative, and automatic switches are usually provided for making it impossible for anyone to turn on the white light when the safelight is being used. The white lights in the emulsion and coating rooms should be of low candle power in order to keep the eyesight for dark operations. It is customary in modern coating and cutting rooms for operatives to spend a few minutes in a preparatory room of very low illumination before starting work, and to rest there for a short time after work to accustom the eyes to the change of level.

As regards apparatus, we shall again consider the experimental requirements first, discussing the commercial plant later. It is hardly necessary to say that for what apparatus may not be available, simple substitutes can usually be found. On the other hand, it is more likely that additional apparatus will be added if any serious work is undertaken, such as an accurate balance, filter pump, viscosimeter, proper temperature control, some means of pH determination, etc. In connection with thermometers, the advice is given to spend liberally on good quality ones that can be easily read. Except with " boiled " emulsions, temperatures above 140° F. (60° C.) are rarely needed, and if a short-scale type be used, the readings will be correspondingly clearer in the darkroom. Eimer and Amend (New York) make a student's type 30 cm long, reading from +10° to +110° C. and +20° to 220° F., marked either on the glass stem or on a paper scale inside the outer glass. Both types can be obtained with a short scale reading from 0° F. to 130° F., which is a great convenience. Note that chemical thermometers scaled for total immersion are not suitable for general work. Thermometers of the clinical type, with a broken thread of mercury so that a temperature taken will remain recorded until the mercury is shaken down, are very useful. These can be obtained with any temperature range if specially ordered through a maker or scien-

tific apparatus dealer. It is often recommended that the bulb should be protected by a perforated gauze of some non-reacting metal, but probably the best way to safeguard thermometers in emulsion work is not to use them as stirring rods!

Emulsions are ordinarily made in stoneware or earthenware crocks, and these are not easy to obtain in small sizes except from scientific apparatus makers and some of the larger department stores. Glazed stoneware jars, sometimes used as " waste jars " in laboratories, can be obtained from Eimer and Amend in sizes from 1 gallon capacity upwards, this size being $7\frac{1}{2}$ inches high and $7\frac{3}{4}$ inches outside diameter, and costing, with loose stoneware cover, just over a dollar. The experimenter will, however, require smaller sizes, and such crocks, with covers, of one pint, one quart, and half-gallon capacity should be obtained. For very small mixings there is nothing so convenient as a small well-glazed earthenware casserole pot of the tall, not squat, type. These can be had on searching diligently enough at some of the hardware and department stores. At least one large stoneware jar with hole or " tubulure " at bottom must be available for washing emulsions (see p. 70). A one-gallon jar will suffice for washing any negative emulsion that is to finish up not more than one liter (35 oz.); a two-gallon jar will suffice for lots of two to three liters. Rubber corks should be used for the bungs, but they should be washed with hot soda water before use.

Glass stirring rods should be twelve inches long and at least one-half inch in diameter. A stout stirrer that can be gripped firmly so that good wrist action can be applied, which is stout enough to beat up the emulsion thoroughly, is quite an important item. Stirring rods with rubber guards should *not* be used.

Scales and weights must be reasonably accurate, as such small quantities as fractions of a gram have frequently to be weighed. Some sixteen-ounce and thirty-two-ounce bottles are

useful for stock solutions. Graduates ranging from ten cc to 500 cc should be available, and some Pyrex or glass beakers of 100 and 250 cc capacity. Pyrex beakers, student's pattern, graduated in clear figures, can now be obtained which are almost unbreakable, cheap, and approximately accurate for general work. One or two plain filters, thirteen to fifteen cm outside diameter (250 to 500 ml capacity) will be needed, and a couple of separatory funnels if mixed jet emulsions (p. 100) are to be made.

As most solutions are used hot, it is important to have sufficient heating facilities for getting the various items ready for emulsification. Depending on the size of the operation, anything from a large aluminum saucepan to a steam-heated rectangular wooden or stainless steel tub with heavy service immersion heater can be used. A metal heating pan about sixteen by twenty inches and about eight inches deep is a very convenient size for experimental work, with either an immersion heater or a small gas ring underneath. Either can be easily thermostatically controlled. For small single lots of emulsion, an aluminum saucepan standing on an ordinary domestic type of electric heater will answer quite well. In many laboratories, existing equipment will meet the case, provided it can be kept sufficiently free from contaminating influences.

A good laboratory stop-watch is invaluable if any serious work is intended. As important as the watch is a really good darkroom clock, which can be depended on to ring the alarm bell when a pre-set time has expired. A little extra money allocated to the clock will be found a good investment. In preference to the use of luminous hands and dials, it is recommended to place the clock on a small box fitted to the wall, a strip of dark green safelight being inserted in the top (Fig. 10) through which light from a ten-watt lamp at the bottom of the box passes upwards on to the dial and makes it just sufficiently visible. A

small projecting piece, P, will prevent any light spreading to the room. A metronome is exceedingly useful for counting seconds when working in complete darkness or very feeble panchromatic light.
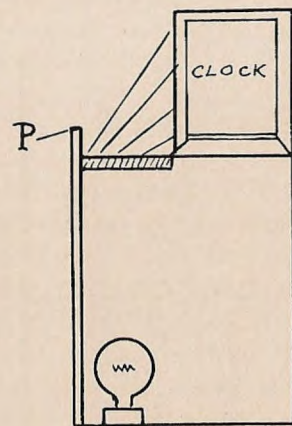
FIG. 10

If the student of emulsion technique wishes to study grain growth and morphology, a first-class microscope outfit will be required. A low power is useful for studying mechanical defects and large developed grains and grain aggregates, but for any examination of silver halide crystals a $\frac{1}{21}$-inch oil immersion objective is needed. Photomicrography of silver bromide crystals can be done with surprising success without the use of any photomicrographic apparatus except a ninety-degree prism on the eyepiece. This simple technique has many advantages over elaborate equipment. The microscope, with its mirror removed, is placed on top of a light-tight box, with an aperture about an inch and a half in diameter, H, (Fig. 11) cut out in the top. A lamp L (Pointolite or concentrated filament

type) is placed underneath, in the box. The rays thus pass directly upwards to the Abbe condenser. The small eyepiece prism, *P*, deflects the rays at right angles on to the wall, where a plate, *AB*, is stood on a suitable ledge or support, and receives the image. Final focusing of the crystals is thus done actually

FIG. 11

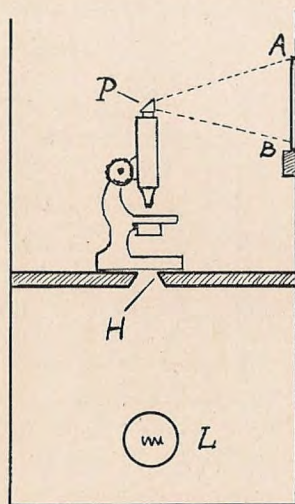on the plate, and all that has then to be done is to switch off the lamp (or insert a filter in the light path), replace the plate *AB* by an unexposed one, and make the exposure. When the eyes get accustomed to the complete darkness in which this work must be carried out, exact focusing can be done quite easily. A bit of dead-blacked brass or a cardboard tube between the aperture in the top of the box and the Abbe condenser will prevent any extraneous light from fogging the plates. As with high power an image of the light source should cover the whole field, a good alternative to the Pointolite is one of the flat strip in-

candescent lamps used in sound recording, which runs from a six-volt storage battery taking about thirty amperes. These lamps are obtainable from the General Electric Company.

While, for cooking or digesting purposes, Thermos or Dewar flasks are most convenient for small lots of emulsion, a thermostatically controlled pan is more or less a necessity if work on any serious scale is to be undertaken. A metal pan similar to that already described for heating solutions will be convenient, but as it will be required at a lower temperature it should be a separate piece of apparatus. A deepish pan sixteen by twenty inches and twelve inches high is a convenient size. This can be kept filled with water to a height of five or six inches, or within an inch and a half or two inches of the top of the smallest crock used. For uniformity of work, standard-sized lots of emulsion should be made as far as is possible, so that the water level in its relation to the amount of emulsion is kept fairly constant. In other words it would be bad practice to have a half-gallon crock eight inches high standing in only three inches of water, even if the contents were kept well stirred.

Such a metal pan can be fitted with a hinged lid unless the emulsions are to be stirred during digestion. In some commercial plants, where very long digestions are given at a low temperature, it has been found best to digest or finish without stirring, the whole of the bulk gelatin having been added and dissolved beforehand so that sedimentation is reduced to a minimum. Any coarse grains which do settle can be largely eliminated by careful decantation or suitable filtering. On the other hand, Carroll and Hubbard state [1] that in their experiments all emulsions were stirred continuously during digestion to prevent sedimentation. Similarly Trivelli and Sheppard state [2] that " the object being to obtain a uniform, relatively fine-grained material, silver halide emulsions are continuously and thoroughly stirred." With short-timed finishing of very high-speed

emulsions having a long scale of gradation, it is the author's experience that the crock should be left unstirred in the digesting pan, but every formula has its own particular optimum conditions and no fixed rule can be even suggested.

The apparatus needed for washing small lots of emulsion will depend entirely on the bulk that is to be handled. In a number of the formulas given in this book, a small unit of about one liter is set out, which can be multiplied as required for commercial bulks. The bulks used in manufacture, as elsewhere stated, may run up to fifty or sixty gallons in the case of paper emulsions, while fast emulsions are generally made in smaller units which are blended for better uniformity. It may be pertinent to refer here to what appears to be a very indiscriminate mixture of grams and ounces, liters and gallons, centimeters and inches, Fahrenheit and Centigrade. The metric and avoirdupois systems have become inextricably mixed in the industry, and any reference to photographic literature indicates that the two systems are so much in use that alternative figures have to be given. The gelatin manufacturer sells his gelatin by the pound, rarely by the kilo, even in Europe; dyes are sold by the pound and in ten-gram or one-hundred-gram lots; silver nitrate is bought largely in 1000-ounce parcels in England, but is meticulously dissolved up in the factory in the form of bi-normal or tri-normal solutions which are measured by metric system for use. And so it goes on. In most cases temperatures have been given in this book in both Centigrade and Fahrenheit figures.

To return to the washing apparatus. The stoneware jars referred to on page 43 will be found ideal for washing small lots, but as explained later tanks are used for commercial batches. As good washing depends on getting the noodles in as intimate contact with the water as possible, their gentle agitation in each change is necessary. The agitation can best be done by gentle stirring with a glass rod or spoon, keeping the shreds well sepa-

rated without breaking them. At the end of each change, the water is run off, provision being made that no shreds escape through the outlet. A false bottom of suitable textile material may be used, so that when the wash water is run off the noodles can be thoroughly drained. When washing is complete, draining should be made as complete as possible. It sometimes happens in washing that the gelatin takes up so much water that on remelting the volume is greater than the desired amount. This will lead to thinness of image and frequently to fog. The remedy is to use colder washing water, to use a less absorbent gelatin, or to decrease slightly the bulk of the reacting solutions in mixing. It is good practice in the laboratory in hot weather to throw in a few ice cubes with each change of water if the temperature of the darkroom cannot be controlled.

It will be noted in the formulas which follow that about five per cent of alcohol is included in the " finals." It will be found good practice to pour this alcohol on the washed noodles after they have been transferred to the crock, and before starting to melt up. This accelerates melting, which is good practice, as it confines the final digestion or finishing within stricter control. The crock should therefore be stood in really hot water, 160° or 180° F. and the emulsion kept well stirred, so that the shreds nearest the outside of the jar do not get raised to a higher temperature than those in the middle. When the emulsion temperature has reached 105° F. (40° C.), it should be removed from the water, because the jar itself will be hotter, and a further rise in temperature of the contents will take place. Great care must be taken, in fact, that the temperature of the emulsion is not allowed to exceed that of the final digestion temperature, and that as soon as this has been reached, the crock is transferred immediately to the digesting pan. When the digestion is finished, the emulsion should be poured into a cold crock and the finals added. These are usually chrome alum solution to

harden the film, free ammonium or potassium bromide to prevent edge-fog in plates and fog on keeping (in the case of films and papers), a preservative such as carbolic acid, thymol, sodium salicylate, etc., and any such gelatin-plasticizer as glycerin.

The made-up emulsion is now filtered, and for laboratory scale operations nothing better can be recommended than two to four thicknesses of good quality cambric or linen which has been boiled in order to remove any sizing. A fine quality men's handkerchief is excellent for the purpose. Filter paper is useless; chamois leather is not advisable, as it is usually uneven in thickness and the emulsion merely runs through the thinnest part. If suction is available, such as that from a good filter pump attached to a faucet having a good head of water, a Buchner funnel will be found very useful. It may be questioned why, when chemicals of the highest purity are employed, any filtration should be needed. Leaf gelatin contains a good deal of string fiber, unless dried on wire nets; if ground, it will contain a surprising amount of dust and dirt. Even re-crystallized chemicals contain some dirt, and an examination of the filter cloth, after the emulsion has run through it, will reveal the need for filtration. In addition to mechanical dirt, filtration goes a long way towards breaking up *clumps* or aggregates of silver halide grains, which are always formed to a more or less extent in the process of making.

If the cambric or linen is laid over the top of a clean crock, it should be attached by a piece of twine or tape tied tightly around the top edge. The linen is gently pressed downwards to form a bag, and the emulsion is poured into the bag, and filtering helped with a glass stirring rod. If the emulsion is obdurate, a vacuum can be created in the crock by pulling the linen tight with the hands; this has the effect of drawing the emulsion through. It is the usual practice to coat a test plate

at this stage, and then to set the emulsion off in ice water, remelting it again a day or so later when required for coating. Emulsions will usually keep for several days, or even weeks, if stored in a room kept below 45° F.

We can now give some attention to work on a larger scale, where somewhat different handling of the emulsion will be required. While the " unit " lots described in subsequent chapters may be increased by simple multiplication, as the bulk grows larger various modifications must be made in order to prevent overheating. One of the most successful pioneer dry-plate manufacturers always claimed that it is possible to produce in one liter (35 oz.) all the qualities and speed of a works-size batch of emulsion, and this is correct provided that works batches are made in moderate units, such as two to three gallons and not in bulks of fifty to a hundred gallons. When planning works-scale operations, it is advisable to decide on the policy to be adopted; that is, whether to make in comparatively small lots of two or three gallons and mix these at a later stage for coating, or to manufacture in bulks of five or ten times this size. The difference in sheer mechanical handling that is involved must be obvious. Convenience in handling is much greater if moderate quantities are made at the time of emulsification, and blended after washing. The shreds can be mixed after washing, and remelted as a blend, or each small unit can be carried through to the end and tested *before* blending, which is a surer way of obtaining perfect uniformity of product.

In the commercial manufacture of films, plates, and papers, two things of first importance stand out — freedom from dust, already discussed, and adequate control of humidity and temperature. It unfortunately happens in many cases that a building designed for some other purpose is adapted for the making of sensitized products. Such a building is rarely as efficient or satisfactory as one which has been specially designed. On the

other hand, many factories which the author has visited in Europe show signs of continual additions due to trade expansion, where compromises have clearly had to be made. One noteworthy difference between a plate factory and one for film or paper coating, is in the length of building required. While plates will set in half a minute on a thirty-foot machine, and can be lifted off and stacked in cupboards to dry, both film and paper have ordinarily to be run from the coating head to a drying tunnel where the material hangs in loops or festoons and travels slowly along the track for anything from three hundred to six hundred feet. Being dry by the time it reaches the far end, it can be immediately re-reeled, thus making the process a continuous one, which is frequently carried on three eight-hour shifts a day for days at a time. Koebig's catalogue [3] gives particulars of a film coating machine which winds the coated stock in the manner of a spiral, thus greatly conserving space.

Whatever the product may be, we are concerned in this chapter more especially with the emulsion-making department. Here the importance of cleanliness must be again emphasized. Ample space is most desirable. Temperature control is indispensable. The layout already discussed for small-scale operations needs merely to be amplified and elaborated. In many factories, the work is distributed among several buildings, each complete in itself. Each one has then its own emulsion-making laboratory to feed the particular coating room. This system, by the way, has the great advantage that if, as occasionally happens, some chemical or other trouble arises, it hampers work in only one section of the factory.

If the whole laboratory layout can be on one floor, so much the better, as then the various rooms can be arranged in definite sequence, so that stores and weighing rooms are the commencement, and the finished emulsion comes out at the end. The store for chemicals and gelatin should be arranged so as to be conven-
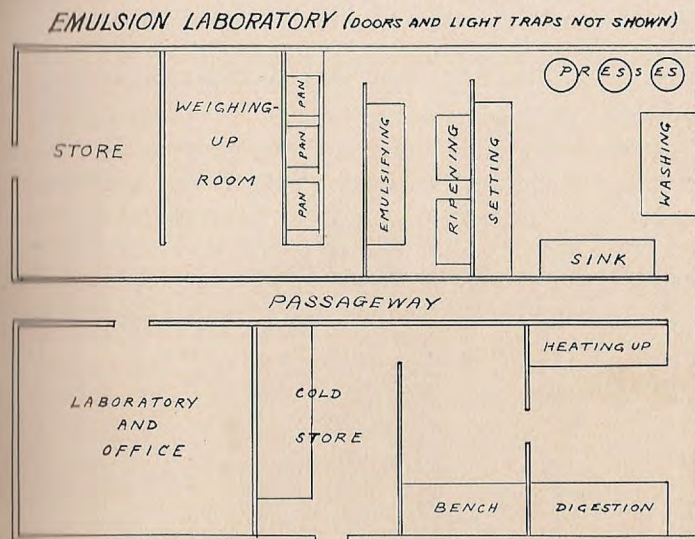
FIG. 12

iently situated for unloading goods. The finished emulsion can be wheeled in small light-tight trucks from the making-up room to the building where the coating is done. A suggested plan is seen in Fig. 12, where the store leads into the weighing room, and the crocks and silvers are heated for mixing in a small compartment next to it. The emulsification is then carried out on the bench in the next compartment, the emulsion placed in the warm water pans to ripen, and then set in the cold tanks in the end room. It will be noticed that in the emulsifying room two ripening pans are shown. In many emulsions of the " all-ammonia " type, emulsification is carried out at a low temperature and when the bulk gelatin is added, the emulsion must be raised to about $105°$ F. as quickly as possible, in order that it may be properly dissolved. It is often necessary, therefore, to

have one pan for ripening at the lower temperature and a hot pan for heating the jar after the gelatin addition. With large batches of emulsion, some form of mechanical stirrer is a convenience in the latter operation.

The term " ice water," used in the setting troughs, is very common in emulsion parlance, but is unfortunately a somewhat slipshod one. It may be taken to mean, however, that the temperature is around 36° F., and that some ice is always kept floating in the water. The cold pan water can of course be cooled by a refrigerator coil and thermostatically controlled.
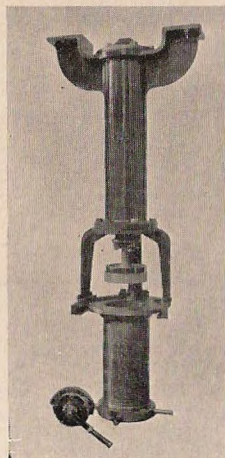
FIG. 13

The set emulsion, which may in some cases be washed in from three to five hours, though more generally the next day, is pressed into noodles or shreds in the setting-off room by the presses indicated. The noodles are most conveniently washed in the same department. As considerable quantities of water must be handled in the washing process, a cement or composition

floor and walls which can be hosed down, with good gutters running to an ample waste, should be provided. Large faucets are needed to expedite the refilling of the washing troughs, and a suitable water main with ample pressure will be needed to insure the necessary hydraulic pressure for the shredding machines.

FIG. 14.   FLOOR PRESS SHOWING EMULSION CONTAINER SWUNG OUT FOR LOADING WITH JELLY

These presses may be attached to a wall fitted in a strong steel frame for suspension from the roof (Fig. 13) or can be fixed in wooden frames on the floor. The emulsion container is usually made so that it can be swung clear of the pressure cylinder for charging, as shown in Fig. 14. This represents a

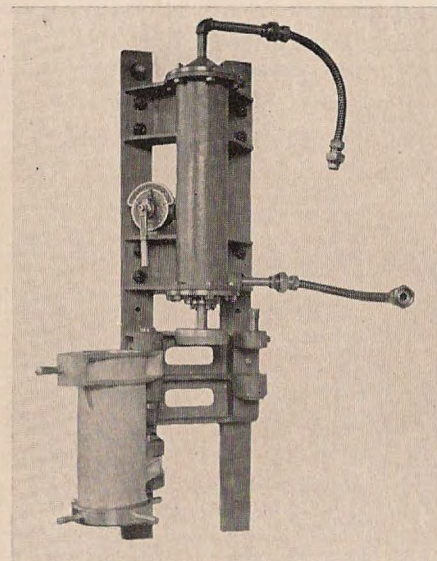Dixon [4] press, which is constructed of gun metal, with a piston rod of stainless steel, and a plunger cap of nickel fitted with a wooden face. The emulsion container (seen swung out for charging in the figure), is lined with pure nickel, and the perforated shredder plate, which drops into the bottom of the container, may be made of pure nickel also. This plate, having perforations three-sixteenths or one-fourth inch in diameter, must be very stout so as to stand up to the force of the cold jelly when squeezed through it. A sterling silver shredder plate is strongly recommended by the author.

The washing tubs, which receive the noodles as they fall from the press, may be of wood or stoneware. If the latter, they
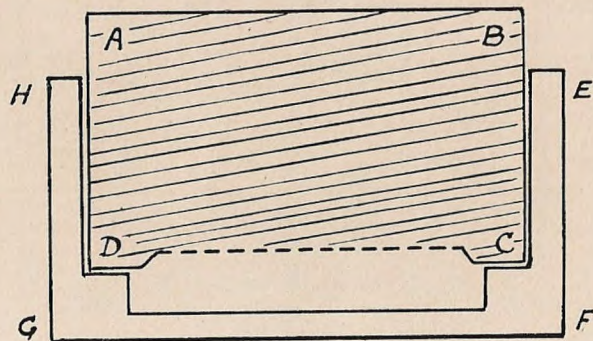

FIG. 15

should be provided with wooden trestles which can be wheeled easily to the part of the room where washing takes place. Considerable divergence of opinion exists as to the best method of washing. If four volumes of water are allowed for each volume of emulsion (before shredding) and the noodles are kept sufficiently separated by wooden paddles or some simple and gentle agitating device, and the wash water is thoroughly drained off after each change, it will be found that twelve changes of five

minutes each, with three minutes draining, will adequately wash practically any type of emulsion. Three or four hours are recommended by some writers, but this tends to over-swell the emulsion and affect its character.

One form of washing trough is shown diagrammatically in Fig. 15. Here an inner wooden tub, ABCD, with gauze or canvas bottom drops into an outer trough, EFGH. The inner vessel is about one-third filled with noodles, and water is fed into it until it well covers them. In draining, a small loss of emulsion is inevitable, as, in mechanically keeping the shreds separated, small bits are bound to be broken off and pass through the screen at the bottom of the tub. The loss in washing should not exceed one to one and one-half per cent. Cold water, never above 55° F., should be used.

The washed shreds, as explained later, are remelted and subjected to a process of digestion during which the speed increases very greatly, and while in most cases the temperature used lies between 120° and 125° F. (about 49° to 52° C.), it may be considerably more in the case of slow emulsions, or of course of "boiled" emulsions (p. 6). A type of digesting pan which can be made on a small laboratory scale or on a works scale is seen in Fig. 16. The emulsions crocks stand in an inner rectangular pan of metal which in turn stands in an outer one. Both contain water. A thermostat shown in the inner pan controls a fairly heavy heating element, via a suitable relay, which is fixed at the bottom or at one side of the outer pan. If no stirring is to be given, the crocks may be covered with loose lids, but in many cases vertical stirrers are fitted to a loose cover on top of the pan, as shown in the diagram. These are motor driven, and turn only fast enough to prevent sedimentation.

Some ingenuity must be used to take care of condensation water dropping from the bearings of the stirrers or elsewhere into the crocks, which could easily fog the emulsion by chemical
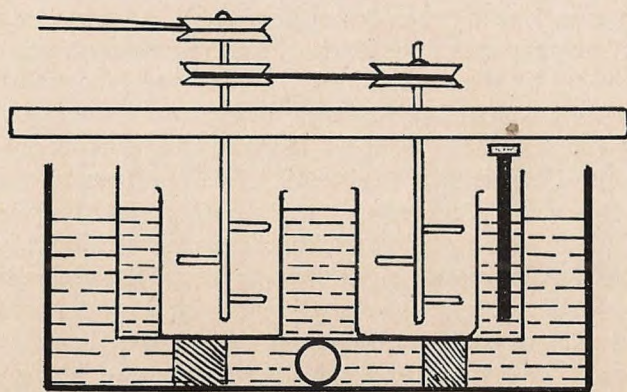
FIG. 16

contamination. Some form of loose cover for the crocks themselves as well as an overhead guard will combine to give the necessary protection. Needless to say, the apparatus can be simplified by having one pan only of water, the thermostat and heating element being contained in it along with the emulsion. It is then an advantage to have the outer water itself stirred to insure an even temperature.

The thermo-regulator should be capable of a range of control of between 110° and 140° F. (45° and 60° C.). An immersion electric thermostat consists usually of a thin metal tube hermetically sealed at the bottom, which contains a sensitive bimetallic bar that extends from the bottom about half-way up the tube. The contact points are protected by a condenser to prevent sparking. The control temperature is often regulated by a removable key so that, once set, it cannot be tampered with or altered accidentally. Care must be taken that the thermostat is capable of handling the load required, which will of course depend on the bulk of water involved.

Reference has been made in an earlier part of this chapter to Thermos flasks. For test lots of emulsion in the factory,

these are very handy and deserve some further notice. The flask should be filled with hot water several minutes before it is needed, at a temperature two or three degrees higher than the digestion temperature. If the emulsion when put into the flask is also a couple of degrees higher in temperature (Fahrenheit), it will probably drop to the desired point or a trifle below during digestion, the figure over the total time averaging out very nicely. A practical point that should be emphasized is that thermostatically controlled apparatus will operate most satisfactorily in a room where the temperature does not undergo drastic variations. Where the laboratory is maintained throughout the year at about 70° F., very little difficulty will be found in controlling water baths and pans.

FIG. 17

The digested emulsion must be made up as quickly as possible, and this is done by (a) lowering the temperature to 105° F. or below, and (b) adding such final additions as chrome
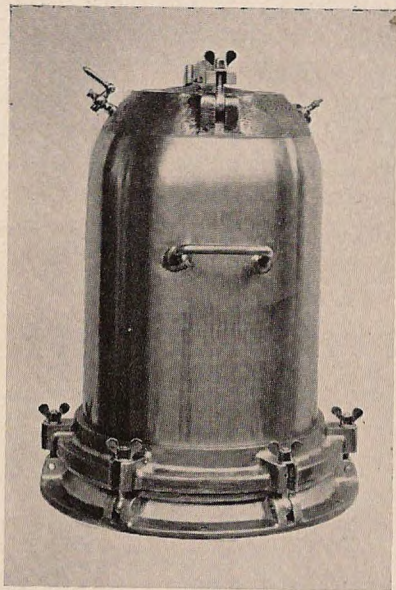

FIG. 18

alum, alcohol (if this has not been already added), potassium or ammonium bromide, and any other chemicals. The speed then stays put more or less, and the emulsion can be filtered and sent to the coating room or reset and put into cold storage until required.

Filtering can be done by gravity, or with the help of either pressure or suction. A typical example of a pressure filter is the Dixon model,[4] which is an enclosed cylindrical vessel of 960 ounces capacity, fitted with a perforated metal plate for

the support of the filtering medium, and an air valve for connection to a pressure pump. It is designed for use upon a metal or wooden table support, under which the emulsion jar or receiver can be placed. It is seen opened out in Fig. 17 and closed for use in Fig. 18. Two forms of suction filtering plant are seen in Fig. 19 and Fig. 20. In the first of these an inverted funnel, over the top of which is tied the filter material, is placed near the bottom of the receiving jar. The tube of the funnel, and a bent glass tube leading to a suction pump, fit tightly into a rubber cork in the neck of the receiver. Moderate suction is applied to the bent tube. The other type is made by a well-known firm of earthenware manufacturers.[5] This is a jar with outlet pipe for suction apparatus to be connected; a heavy perforated stoneware disc sits on top of the flange of the jar, and above this is a stoneware top. The filtering medium is placed between the disc and the top, and suction provides the seal. Another type of suction filter, made by Koebig,[8] is seen in Fig. 21.

When filtering by gravity only, a larger apparatus of the type described on p. 50 is used. The chief difficulty in all filtering of emulsions is the choice of material. Filter-cloth makers
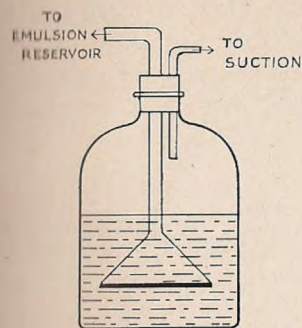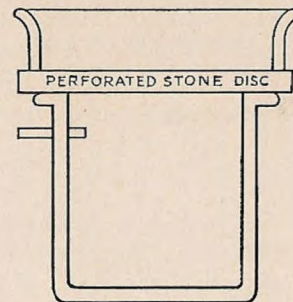

FIG. 19

FIG. 20

have a wide variety to choose from, but it will be difficult to improve on the four thicknesses of fine linen or cambric already suggested.
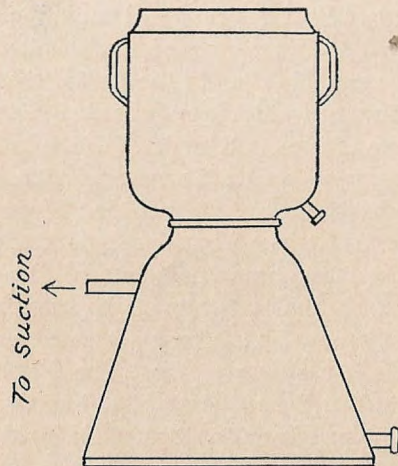

To suction ←

FIG. 21

The filtered emulsion is quickly set, and for this purpose it can be returned to the setting tanks in the washing room, or preferably to a separate cold room, where the temperature can be automatically maintained at somewhere below 45° F., or the jars can be stored in ice water or cool cupboards. The time that made-up emulsion can be safely stored, depends entirely upon its previous history.

Chapter References

1. Carroll and Hubbard, *Bureau of Stands. Journ. of Research,* 7, 226, 1931.
2. Trivelli and Sheppard, The Silver Grain of Bromide Emulsions, p. 32.
3. August Koebig, Radebeul, Germany.
4. Thomas Dixon and Sons, Ltd., Letchworth, England.
5. Doulton and Co., Ltd., Lambeth, London, Eng.

CHAPTER IV

NEGATIVE EMULSIONS

Their Structure and Composition — Types of Formula — Preparation of the Reacting Solutions — Emulsification — Ripening — Setting — Washing — Final Digestion or Finishing — Making up — Anti-halation Methods — Reversal Emulsions

A NEGATIVE type of emulsion of moderate speed is probably the most suitable to select for a first consideration of emulsion making. The speed and average grain size and some other properties of the slower types of emulsion are as follows:

Type	Relative Contrast γ	Resolving Power	Latitude *	Speed H & D	Average Grain Size microns
Transparency or lantern	3.2	100	25	5	1
Process	3.0	90	25	20	1.5
Photogravure	2.8	80	40	40	1.0–2
Commercial	2.2	65	75	90	1.5–2
Motion picture positive	2.7	80	50	150	1–2

* Ratio of exposure at limits of the straight line portion of the characteristic curve for development to gamma infinity. In many cases this portion is measured between the points where gamma is 0.5 at the toe and shoulder.

In so-called grainless emulsions of the type described on page 136, the mean diameter of the grains (AgBr crystals) is of the order of 0.0002 mm, or 0.2 μ. While speed and grain size do not necessarily increase side by side, the grains of fast emulsions are generally larger than those of slower ones, reaching 3 to 4 μ, although the diameters are invariably mixed. Thus

Clerc [1] states that in a particular emulsion the distribution between the different sizes has been found to be as follows:

Less than 1μ .... 61 per cent
From 1μ to 2μ .... 32 per cent
From 2μ to 3μ .... 6 per cent
Above 3μ .... 1 per cent

In a slow emulsion for reproduction purposes the extreme ratio of diameters was found to be not more than one to five.

A number of rapid emulsions dried in air (containing an equilibrium amount of moisture of not more than 15 per cent) showed on analysis to average:

Water 10   parts by weight
Gelatin 55   parts by weight
Silver bromide .... 32.5 parts by weight
Silver iodide .... 2.5 parts by weight
                         100 parts

Traces of silver chloride were found. Weigert and Luhr state that they found as much as 2 mg per square meter of free silver metal. Silver chloride is almost impossible to exclude, as samples of ammonium bromide may contain as much as two per cent of chloride. A good sample of NH_4Br for negative emulsions should not contain more than 0.2 per cent. The slower types of emulsion being considered in this chapter would ordinarily contain about half the above proportion of silver iodide, or less. As chemical analysis (p. 231) of a slow film indicates a coating weight of some 60 to 90 mg of silver halide per square decimeter, the skeleton of the emulsion may be built up somewhat as follows, it being assumed that a liter of emulsion would be distributed over, say, 150 plates of 5 by 7 inches size, or a twenty-foot run of film base forty-two inches wide. For convenience, the amounts of alkaline halides required to convert one gram or part of silver nitrate are given in the table which follows on the next page.

Reacting proportions of halides to combine with one part of silver nitrate,
$AgNO_3$ *(molecular weight 170)*

Ammonium bromide, NH_4Br ...... mol. wt. 98   reacting amt. 0.576
Potassium bromide, KBr .... mol. wt. 119   reacting amt. 0.700
Ammonium chloride, NH_4Cl ...... mol. wt. 53.5 reacting amt. 0.373
Potassium chloride, KCl .... mol. wt. 74.5 reacting amt. 0.431
Sodium chloride, NaCl .... mol. wt. 58.5 reacting amt. 0.408
Ammonium iodide, NH_4I .... mol. wt. 143   reacting amt. 0.617
Potassium iodide, KI .... mol. wt. 166   reacting amt. 0.638

Bearing in mind that the emulsion must be washed, during which process the jelly takes up almost its own bulk of water, the final volume of emulsion desired must be about halved in the making.

Formula for 1 liter of emulsion (1000 cc)

A. Water .... 350 cc
   Ammonium bromide .... 32.5 g
   Potassium iodide .... 0.5 g
   Gelatin .... 10.5 g

B. Silver nitrate 25   g
   Distilled water .... 5 cc
   Ammonia (conc.) a sufficient quantity to redissolve the precipitate of silver hydroxide first formed (this will require about 25 cc of ammonia of 0.920 s.g.)

C. Silver nitrate 25   g
   Distilled water .... 110 cc

Here we see that about 500 cc of water is divided between the salts and silvers in the rough proportion of 35 to 15. The bromide is used in about 8.5 per cent excess of the combining quantity. The iodide is present in the proportion of one per cent of the weight of silver nitrate. The gelatin in this case is three per cent of the water in which the salts are dissolved. The silver nitrate is divided into two equal parts, one of which is highly concentrated and redissolved with ammonia; the second half is

used plain, and is dissolved in just over four times its weight of water. Plain silvers should not as a general rule be used in a higher concentration than one to four of water.

The excess of bromide used over the weight needed to combine with a given quantity of silver nitrate varies over wide limits. Wall [2] quotes cases where the excess varies from 1.9 parts per 100 of silver nitrate (Burton) to 92.4 parts per 100 (Eder). Eder is also quoted as using in different emulsions 8.4, 67.4, and 75.4 parts respectively per 100 above the combining quantities of $AgNo_3$, indicating at least that there is a very great tolerance. He states that the explanation usually accepted for the favorable action of the excess bromide is that the finer particles of silver halide are dissolved by the excess and in the course of ripening are deposited on the larger grains (cf. Ostwald ripening), thus giving increasing sensitivity. It will be found, however, on studying the earlier literature that a larger excess of bromide was used in cases where all or a large proportion of silver nitrate was redissolved, and this indeed appears to be necessary in order to prevent fog. Only a very small excess is actually needed where the silver nitrate is divided into three or even four parts and added to the salts piecemeal, with very little ammonia, allowing fairly long intervals between additions; or where the iodide is added separately after the first emulsification with silver and bromide only, with or without ammonia, when it appears to act as a peptizer.

The three solutions in the above formula are heated, A and C to 110° F. (43° C.), and B to 70° F. (21° C.). B is poured in a steady stream into the crock containing the salts A, stirring fairly briskly, the precipitation taking about five seconds. C is then at once poured in, this time through a funnel with a three or four millimeter outlet, stirring briskly. After ripening for fifteen minutes, without stirring, or at least giving only an occasional gentle stir, the bulk gelatin is added, dry, about 70 g

being used, which will bring the concentration up to approximately eight per cent of the final bulk of 1000 cc. A little gelatin, together with a small amount of the silver halides, is inevitably lost in washing. Fifteen minutes should be allowed for the gelatin to dissolve completely, even if powder be used, the crock being gently stirred the whole time. The temperature must not be allowed to rise above 105° F. (40.5° C.) during this operation, but if the same emulsion be made on several occasions, the same temperature conditions should be repeated as far as is possible. When the gelatin is dissolved, the emulsion is set off by placing the crock in ice water, and giving the contents an occasional stir until gelling takes place.

The above way is a convenient one for expressing the formula, but only one of many. Another, frequently met with in European literature, would be as follows:

(a) 180 cc gelatin solution 5%
(b) 162.5 cc ammonium bromide solution 20%
(c) 5 cc potassium iodide solution 10%
(d) 25 cc silver nitrate solution 1:1
(e) 100 cc silver nitrate solution 25%
(f) 70 g gelatin, dry

This is very approximately the formula already given. It is of course a great convenience to use reacting substances in the form of solutions, especially silver nitrate. In some factories these are made up in the form of multi-normal solutions of which equal volumes are equivalents. In several of the formulas given in this book, where highly concentrated silvers are employed, it will be found more practical to weigh the silver nitrate out.

A further method of setting out a formula is used by Carroll and Hubbard [3] in the case of an " all-ammonia " emulsion, and we find that they have expressed it in more academic fashion as follows:

Water .... ml 250   Water .... ml 500
AgNO$_3$ (0.353 mol) ... g 60   NH$_4$Br (0.409 mol) ... g 40
NH$_4$OH conc. (0.71 mol)   KI (0.0035 mol) ...... g 0.58
         to redissolve   Gelatin .... g 30

Excess bromide is seventeen per cent. The halide-gelatin solution was kept at 45° C. ± 0.5° during mixing, which took four and one-half minutes, and during ripening. After ripening for twenty-five minutes, 70 g of gelatin previously swelled in cold water was added, taking seven to ten minutes, and the emulsion was chilled. (The *mol* figures given are obtained by dividing the molecular weight of the substance into the weight used.)

Another distinctive type of emulsion is that recommended by Heyne [4] for negative motion-picture film. Three solutions are prepared as follows:

> A. Gelatin .... 250 g
>   Water .... 3500 cc
>   Potassium bromide .... 400 g
>   Potassium iodide .... 10 g
>
> B. Silver nitrate .... 500 g
>   Distilled water .... 1500 cc
>   Ammonia (s.g. 0.910) .... about 475 cc
>
> C. Gelatin .... 500 g
>   Distilled water .... 2500 cc

The gelatins in solution A and C are allowed to swell in the water. The salts are then added to A and both solutions are raised to 122° F. (50° C.). The silver nitrate is dissolved in water, and ammonia added as usual, sufficient to redissolve the silver hydroxide. This is used at room temperature and is added slowly to the crock with good stirring.

The emulsion is maintained at 112° — 122° F. (45° — 50° C.) for thirty minutes, when the gelatin solution C is added to it at the same temperature. The emulsion is then digested

for a further fifteen minutes, and is set off in ice water. It is stated to attain its highest sensitivity during the digestion after washing or finishing. A temperature of 112° — 132° F. (45° — 55° C.) is recommended for the finishing. In this process a small trace of ammonia may be added. (This addition is *not* recommended by the author unless a second washing be given, when the bulks will require modification throughout, or the pH be lowered to just above normal by suitable treatment with the finals.) During the final digestion, small hand-tests are made at short intervals, and when the maximum useful speed and gamma have been obtained, the usual additions of chrome alum, bromide, spirit, etc., are made. In the case of film coating, one to one and one-half per cent of glycerin may be needed.

Let us assume that the emulsion has been given its correct ripening time, and that the bulk gelatin has been added. It is important that this be very thoroughly dissolved. Powdered gelatin should be " poured " slowly into the emulsion with good stirring; this will avoid its annoying tendency to form into gluey lumps which are troublesome to dissolve. In making small lots of emulsion it will be found a convenience to cut up *sheet* gelatin beforehand into small pieces with a clean pair of scissors. The gelatin melted, the crock or jar is stood in ice water and the emulsion allowed to set. It should always be given an occasional stir until it begins to gel, especially in the case of large batches. These, if of any fast variety, are best distributed over a number of small one and one-half or two-gallon cold crocks to expedite setting. In the case of emulsions where the whole of the silver has been treated with ammonia, washing is usually given within from three to five hours, otherwise ripening goes on in the cold, and fog may result. With emulsions where less than fifty per cent of the silver has been converted, it is customary to leave the emulsion in the cold room until next day. In factory practice it is of course important to have some system

by which the time between emulsifying and washing is kept
more or less constant for each type of emulsion. Thus if all-
ammonia and part-ammonia types are being made, the all-
ammonias can be mixed in the morning and washed in the after-
noon, while the others are mixed in the afternoon and washed
the following morning. It will be found a convenience to take
the set emulsion from cold storage and leave it at room tempera-
ture for two or three hours before washing, otherwise it may
be unmanageably stiff for shredding. This applies more par-
ticularly to small lots or types containing a high concentration
of gelatin.

Small lots of emulsion can be broken up with the hand, and
pieces of the size of an orange wrapped in a piece of coarse net-
ting (about one-eighth-inch mesh) and squeezed through the
material. The netting is such as is used for embroidery work,
and must be very thoroughly washed before use, as the sizing
will otherwise cause trouble in the way of fogging or desensitiza-
tion. Various devices used in cooking which can be bought at
the hardware stores or department stores have been recom-
mended from time to time for breaking up the emulsion, but the
danger here is that the zinc from any galvanized parts will fog
it, and although a textile material of sufficiently large mesh is
more trouble to use, it is definitely recommended. The jelly
comes through the netting in the form of broken shreds an
inch or two long, and if the emulsion be held under the water
while squeezing it through, the bits or noodles will keep nicely
separated. They can then be transferred to the washing jar.
A piece of muslin or cheesecloth (also previously washed out)
is tied over a jar with a bottom outlet as shown in Fig. 22, the
shreds put into the bag formed by the material, and the jar
filled with water.

At the end of five minutes the plug is removed and the water
run out, and three minutes is allowed for the shreds to drain.

The draining may be made more thorough by teasing the shreds
with a glass rod or spoon. The washing procedure is then re-
peated, and after about eight such changes a test of the wash
water with Nessler's reagent will usually reveal that the am-
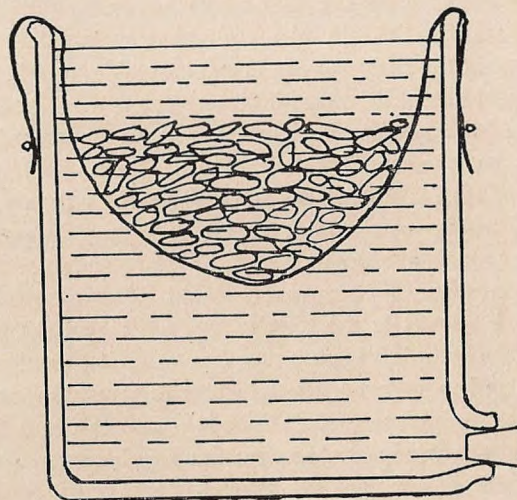
FIG. 22

monia has been eliminated. If not, one or two further changes
should be given. The same procedure applies to works-scale
washing, but here it is most important to insure that the swell-
ing of the noodles has not been too much, so that on remelting
and addition of the finals, the bulk is too large. The best prac-
tice is to use tared crocks or nickel or stainless steel pans, and
to weigh the emulsions rather than measure them with a stick
or any form of graduation.

Considerable difference of opinion exists as to the best length
of time for washing. Bogue found [5] that the swelling and vis-
cosity of a gelatin, which are their minimum at a pH of 4.7, in-

crease regularly with a rise in pH up to about 8.5, but that above that value they decline slightly, due to an increasing solubility. As washing proceeds, and the pH becomes lowered, the swelling is probably reduced, and it is advisable to get rid of the great bulk of ammonia in the first stage of washing by quicker changes, making the later changes of longer duration. It was customary in the early days of emulsion-making to give several hours; more recent literature indicates two and one-half to four hours. If the noodles be kept thoroughly separated during washing, and are carefully drained in the intervals between the water changes, sixty to eighty minutes should suffice, except in cases of highly ammoniacal or of color-sensitive emulsions where any excess of bromide may retard sensitization. The final wash water should give no reaction with silver nitrate as compared with a control; the Nessler test will reveal the presence of residual ammonia. Here it may be stated that distilled water for washing has not proved satisfactory in general practice. In most cases poorer speed and slight fog seem to result from its use. That the character of an emulsion can, however, depend in a remarkable degree upon the characteristics of the local water used for washing is well proven. Wash water has in certain cases been prepared by adding to distilled water the ingredients found by analysis in a natural water which has proven satisfactory. But as a general rule the town supply, or supplies from artesian wells, will be found perfectly good. The presence of mineral salts affects to some extent the swelling of gelatin. Patents have been granted for the buffering of emulsions, maintaining the hydrogen ion concentration within a range of pH 5 to 10 by various additions, as disclosed in recent Kodak patents.[6] The pH of the washed negative emulsion may vary between 7 and 8.5, though acid emulsions will of course have a lower pH.

A method adopted by Carroll and Hubbard [7] for shredding

small lots was to set the ripened emulsion by pouring it in a layer of one cm to two cm thickness into a clean enameled tray floated on water at 5° to 8° C., and leaving it overnight. The jelly was then pressed through a sieve built up from sharpened metal strips set on edge, which cut the emulsion into clean shreds five to six mm in cross section. The shreds were placed in silver-plated cans with twenty-per-inch mesh screens of pure nickel at the bottom. The washing was stated to be very thorough, lasting six to eight hours, with frequent hand stirring of the shreds. In the absence of ammonia in the emulsion, the pH after washing was 7 ± 0.5; if made with ammoniacal silver oxide the pH might be as high as 8.5.

The emulsion shreds having now been washed so that they consist of merely insoluble silver halides in gelatin, they are remelted in a water bath, and any final additions made. In re-melting, a good bulk of really hot water is desirable, so that the noodles melt as quickly as possible. The temperature must nevertheless be kept within a degree or two of that at which the digestion is to be carried out, especially in the case of fast emulsions. The remelting is an essential part of the process of making, and it is highly important in routine work to control the temperature employed, and the overall time taken. As already indicated, an alternative to remelting a number of small batches is to blend the washings from a number of crocks and remelt in bulk.

The final digestion or finishing is carried out in thermostatically controlled water baths such as have been described in the previous chapter. Although there is actually no specific connecting link between final speed and

$$Time \times Temperature$$

of cooking, it is certain that above 120° F. (49° C.) some critical stage is reached where sensitivity very rapidly increases.

The temperature of the finishing is another matter on which some divergence of opinion exists, but this is rather because the critical point depends so much on the particular formula. One might hazard the generalization that fast negative emulsions made with ammonia are best digested at a temperature not above 125° F. (52° C.), while slow emulsions, and particularly those prepared with acid, are best treated at 160° F. (71° C.) or somewhat under. The finishing time may be as short as half an hour in the former type, or it may run into three or four hours in the latter. This can only be a very rough comparison, and the extent to which the time may be shortened by raising the temperature is a matter that must be found entirely by experiment for each individual emulsion formula. Probably less sedimentation takes place at the higher temperature and less time, in spite of a lowered viscosity of the gelatin.

An interesting example of the effect of the final digestion upon speed is shown by the curves given in Fig. 23. The fact that washing was in this case done by centrifuge does not interfere. Four lots of one particular emulsion, ripened initially for (a) 5 minutes, (b) 30 minutes, (c) 60 minutes, and (d) 120 minutes, were digested after washing for periods up to two hours. It is seen that while in all cases there is a tendency for the speed to rise to a maximum and then to fall off, the highest speed is obtained when the ripening has been longest. With increase in ripening time, however, the regression of the speed after the maximum has been reached is more pronounced.

In discussing the effect of grain size on the finishing of emulsions, Trivelli and Smith [8] state that before starting the finishing operation, which was done at 60° C. (140° F.), the emulsions, with the addition of gelatin and water, were brought up to a fixed weight and to the same temperature, 40° C. (104° F.). " In this condition," they say, " the emulsion is in its lowest state of sensitivity." They further state that the increase in
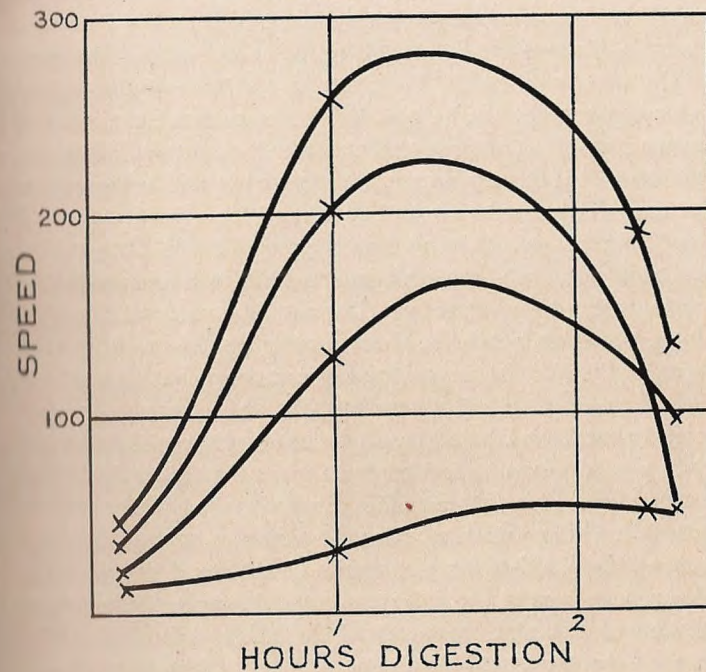
FIG. 23. SPEED OF CENTIFUGED AMMONIA-PROCESS EMULSIONS AT FOUR TIMES EACH OF RIPENING AND DIGESTION. Ripening time (reading up from bottom) curve (a), approximately 5 minutes; curve (b), 0.5 hour; curve (c), 1 hour; curve (d), 2 hours. (Carroll and Hubbard)

speed can be expressed by the ratio between the H and D speed obtained after digestion at 60° C. and the speed measured at 40° C. Similarly the increase in gamma can be expressed by the ratio between the gamma obtained after digestion and the gamma measured at 40° C. *before* digestion.

It may be said, by and large, that the time required for finishing or final digestion must be found by trial and error for every individual emulsion. One method suggested is to make " wet

tests " at frequent periods during the cooking. Suppose, for example, that we are finishing a washed emulsion by digestion in the water bath at 60° C. Every five or ten minutes, a few cubic centimeters can be pipetted from the crock and coated upon a small sheet of glass and set on the ice-cold levelling table. As soon as it is thoroughly set, it is exposed behind a step-wedge (p. 210) for a fixed time and developed for a fixed time at a fixed temperature. The necessary apparatus will of course be available. If the step-wedge be mounted in a deep printing frame, with a thin fillet of wood or aluminum around the edge about a quarter-inch wide, the wet plate can be carefully laid down on the fillet frame and the exposure made without soiling the wedge. Such a test frame should be part of the equipment in every emulsion laboratory. A series of wet tests of this type gives a good visual indication as to when the climax has been reached, by showing more and more steps as the cooking time is extended. After x minutes, when the maximum useful speed has been attained, either fog will step in or the speed will actually diminish, as seen in the series of curves shown in Fig. 23. On future makings, check wet-tests of the emulsion at short intervals when approaching the optimum time of digestion will control the result, though they should not normally be necessary in works practice.

The reader is advised, when making his first negative emulsions, to give the final cooking at 125° to 130° F., and to coat plates at intervals of ten minutes or so, using a measured amount filtered through one thickness of muslin in a beaker; and to dry these plates in the cupboard, and make strict comparative tests as to speed, gamma, and fog, on the lines discussed in Chapter XII. A suitable coating weight must be made, as otherwise the measure of the fog will be badly out. These tests will furnish information for the guidance of future makings, and provide the best means for investigating any formula, or for checking up a

new sample of gelatin with a known formula. In such tests it is inadvisable to add any finals such as free bromide, alum, preservative or spirit.

It has already been stated that an emulsion comprising grains of a large number of diameters gives the best gradation. It has been frequently recommended that to obtain this quality a mixture of coarse-grained and fine-grained emulsions should be used. If, for example, a very rapid emulsion be made in which a long ripening has brought about the growth of a high proportion of coarse grains having high sensitivity, the admixture of a slower but more contrasty emulsion having finer grain would help to build up highlight density without affecting the shadows appreciably. Jahr [9] states that highly sensitive but flat emulsions can be mixed in various proportions with contrasty emulsions of medium or even low sensitivity. The addition of a very fine-grain emulsion of high gamma infinity not only helps to increase highlight density, but adds opacity to the mixed emulsion and makes possible a more economical coating weight. On the other hand, it must be borne in mind that when mixing emulsions having a different iodide content, the powerful affinity of iodine for silver may cause some reaction of one emulsion on the other; it is not therefore entirely possible to predict from the characteristic curves of two emulsions that are mixed, exactly what the characteristic curve of the mixture will be.

It is a more reasonable procedure to provide for the precipitation of grains of the various sizes required in one single emulsion, and this can be done by bearing in mind the points which have already been discussed in connection with emulsification. We know, for example, that a concentrated solution of silver nitrate, re-dissolved and " flopped " wholesale into the crock, will give a more or less homogeneous mixing of equal-sized grains producing high contrast with heavy maximum blacks and low

latitude. We know also, that inasmuch as grain size increases with ripening time, the silver could be added in small quantities, spread over a period, so that when the ripening was cut short by the addition of the bulk gelatin, the various precipitates of silver halide would have grown to respectively different sizes. The grain-size frequency curve of an emulsion is an important guide to its characteristics. Owing further to Ostwald ripening, prolonged heating tends to give a maximum of coarse grains, these having grown at the expense of the smaller ones. Hence, by dividing the silver into two, three, or even more parts, and adding them one at a time, it is possible to make an almost unlimited variety of precipitable mixtures providing equally an unlimited variety of characteristics in the finished emulsions.

A further alternative is to add the first silver in the form of a plain, moderately dilute solution (say 1:4 concentration) and after an interval of a minute or two to add the iodide. The remainder of the silver is then added. This tends to increase the time required for ripening, and there is some evidence that the effect of the iodide so added is that of a peptizer, dispersing the initial silver halide precipitate. A variation, therefore, of any formula in which the silver is added in stages, is to add the first silver plain (though some ammonia should be present in the salts solution), then to add the iodide, preferably with a small quantity of ammonia, and finally to add the remainder of the silver in one or more additions. A small quantity of ammonia should always be present in *either* the salts or the first silver solutions, otherwise clots or agglomerates of precipitates may be formed, which will cause black spots on development without exposure, owing to insufficient colloid protection. Silver bromide without a clothing of gelatin will be spontaneously reduced to black metallic silver on treatment with an alkaline developing solution.

Although, with a proper choice of gelatin and a good formula,

maximum speed should be obtainable without fog, several substances have a useful effect in keeping away fog, which really means in destroying the developability of over-ripened or over-digested grains. Thus in his well-known book, *Ausführliches Handbuch der Photographie,* Dr. J. M. Eder gives as substances that destroy latent chemical fog, tincture of iodine, bromine, chlorine, and minute quantities of a dichromate acidulated with mineral acids. Against this, sensitivity is considerably lowered by additions to an emulsion of bromine or iodine, or the metallic perchlorides. The most useful anti-fogging addition is probably a trace of hydrobromic acid, which is frequently made to an orthochromatic emulsion which requires to be fog-free but need not yield any shadow detail, such as for example the so-called document type of emulsion. A few cubic centimeters of a 1:1000 solution of hydrobromic acid may be added to one liter of the emulsion, but its effect should be carefully tested on speed and on the foot of the characteristic curve before such treatment is adopted. A trace of cupric chloride is sometimes used in collodio-bromide emulsions for the same purpose. More recently, anti-fogging substances have been found for use in making extremely high speed emulsions, and thereby making possible some of the newer family of films which have so changed the complexion of modern instantaneous photography; reference to these will be found in Chapter XIV, to which the reader is referred.

The phenomenon of halation, as such, needs little explanation here. While irradiation or reflection of light from the emulsion particles within the film can cause a spreading of the image, the chief trouble is met with in glass plates, where rays of light meeting the film obliquely from the lens strike the far side of the glass support, and are reflected back therefrom, reaching the emulsion again at an appreciable distance from the original point of the image. The application to the back of the support

of an absorbent layer having a refractive index as nearly as possible that of glass, was originally suggested by M. Carey Lea. A later method was to interpose a light-absorbent substratum between the emulsion and the glass or film base. This substratum could be colored with a dye that could be destroyed by an acid fixing bath, or discharged by the use of any one of several other similar treatments which do not at all affect the image.

The idea of employing a light-absorbing film of gelatin containing, for example, curcuma or fuschin, was suggested in 1878. An acid dye would be used, being more readily washed out of the gelatin. As a substitute for a dye, a 0.6 per cent gelatinous solution of potassium permanganate has been suggested by Oakley.[10] The permanganate is reduced during development to more or less colloidal manganese hydroxide which is readily soluble in the average acid fixing bath, or it may be removed by the use of a two per cent solution of sodium bisulphite. Various types of anti-halation treatments are now applied to high speed panchromatic films, for particulars of which the reader is referred to the patent literature. In the case of films, the Eastman Kodak Company has used a magenta dye in the noncurling layer applied to the back of orthochromatic film, and a green layer with certain panchromatic materials. The chemical composition in each case is such that they bleach out completely in a " properly compounded developer and fixing bath." In the case of thirty-five millimeter film, a blue-gray dye is actually incorporated in the base. Light transmitted by the emulsion must thus pass twice through the dye in order to get back to the emulsion and cause halation.[11] The blue-gray dye is therefore twice as effective as it would at first appear. It does not bleach out in the processing operation, but its presence has no ill effect on the printing quality.

A further type of fast emulsion which may be dealt with in

this chapter is the reversal film used with many kinds of natural color material. The Autochrome plate, introduced in 1905 by the Lumière Company, gave a positive image in natural colors by means of such an emulsion. The color matrix consists of starch grains colored blue-violet, green, and orange, in predetermined proportions, and on top of this is coated a very thin layer of reversal type emulsion. The plate (or film) is exposed through the back, hence the silver halide grains must be appreciably smaller than the elements of the color matrix. The first development gives a negative image, which is converted by reversal into a positive. The reduced silver is soluble in an acid solution of potassium permanganate or in chromic acid, while the unexposed and therefore unreduced silver bromide is *not*. Hence after " bleaching," the original negative image will disappear, leaving transparent gelatin, while the unexposed silver bromide remains. If, therefore, this be now exposed and developed, it will be in turn reduced and will obviously give black where there was white in the negative image. The negative " blacks " being dissolved out and showing *white* when viewed by transmitted white light, a positive of the original subject is obtained. In the old Agfa color process (The *New* Agfa film is a triple-coated continuous image type, and does not depend upon a matrix. See p. 122) the color matrix, and the matrix and the " reseau " used in Dufaycolor film, are similarly coated with these reversing emulsions. Reversal of this type must not be confounded here with the reversal that occurs in any negative emulsion on gross overexposure, represented in the characteristic curve by the turn of the shoulder where density decreases after a certain maximum of progressive exposure. An exposure of something like one thousand times normal is needed to give a reversed image by straight exposure and development, but such a method is entirely useless for color-screen plates and films.

Owing to the fact that the colored elements of a good matrix for a direct natural-color process must be exceedingly small, the need for an extremely fine-grained emulsion is self-evident; yet it must be fast enough to make snapshot exposures practical. The potato starch grains of the Autochrome matrix, separated out by levigation, vary in diameter between 8 μ and 20 μ, about four million going to the square inch. The Dufaycolor matrix or reseau has a geometrical formation of alternate lines 500 to the inch, which are dyed red, and lines made up of alternate green and blue rectangles about one-two hundred and fifty thousandths of an inch each in area. The function of the reduced silver grains in any such process is to block out any unwanted color element when the whole image is viewed by transmitted light, or projected. Thus in the case of a green leaf, the image must be transparent only over the green elements, and the blue and red elements must be blocked out by opaque silver deposits. To get this effect as perfectly as possible, the requisite number of grains must be packed into the unwanted area. Yet if the film be too thick or too deep, we may get scatter effects as well as parallax. The desideratum is therefore to have a fast, very finely grained emulsion with such density-giving powers that the thinnest possible coating may be adequate, giving an image as nearly as possible in optical contact with the color matrix. A coating weight determination (p. 231) of an average color-screen film will indicate something between 35 and 65 mg of silver halide per square decimeter — about half that of an average negative film. Even then a developer containing a silver bromide solvent such as a thiocyanate must be used in the first developer in order to get an image of sufficient clarity.

It is by no means certain that we have heard the last of color-matrix types of natural color film. The immense amount of work done by Powrie and others indicates possible success of a highly commercial character, in spite of the success of triple-

coated subtractive films. A very full description of the many lines of attack on the color matrix problem is given in E. J. Wall's " History of Color Photography." [12] Where an emulsion is required for experimental work of this kind, the reader is advised to confine his first attempts to a speed of 200 to 250 H and D. Reference to the hypersensitized emulsions of very high speed will be found in Chapter XIV. An emulsion of the speed named can be super- or hypersensitized after coating by bathing the dry plate or film in a solution of ammonia and alcohol in the proportions:

Distilled water	1000 cc
Stronger ammonia water	3 cc
Alcohol	250 cc

A 0.2 per cent solution of triethanolamine or borax will act similarly, or even soaking in distilled water for three minutes and drying in a warm current of air. Bathed material may be one and one-half to two and one-half times the speed of the original emulsion, but it keeps in good condition for only three or four days, so it must be prepared only slightly in advance of the time when it will actually be needed.

A method of combining initial high speed with fine grain in the reversed image was referred to by the author in 1932.[13] By using the most sensitive, larger, grains for the exposure of the negative image, and having in the emulsion a sufficiency of small diameter and relatively insensitive grains left over, the latter will, on adequate exposure and development after bleaching out of the initial image, give a reversed image of good resolving power and adequate blocking-out power. Such an emulsion can be made by dividing the silver into two parts, one being re-dissolved and the emulsion ripened, after its addition, in considerable excess of alkaline halide, the other silver being added plain with no ripening time allowed:

A. Water .... 2500 cc
    Ammonium bromide .... 380 g
    Ammonium iodide .... 5 g
    Soft gelatin .... 80 g

B. Silver nitrate .... 300 g
    Water .... 100 cc
    Ammonia (s.g. 0.910) .... *q.s.* to redissolve

C. Silver nitrate .... 300 g
    Water to make .... 1200 cc

Solution *B* is added at 85° F. to the crock containing *A,* which should be at 100° F. After fifteen minutes initial ripening, solution *C* is added through a three to four millimeter nozzle with brisk stirring. The bulk gelatin of 720 g is immediately after added dry, and the whole stirred for fifteen minutes, bringing the temperature up to 105° F. When dissolved, it is set in ice water. After very thorough washing, it is digested for an hour at 125° F. and the color-sensitizing dyes are then added in the usual way. It is finally made up to ten liters with the additions below:

Spirit (less the amount already added in the
    form of dye solutions) .... 500 cc
5 per cent chrome alum solution .... 100 cc
10 per cent phenol solution .... 100 cc
1 per cent ammonium bromide solution ..... 50 cc

The emulsion is richer in silver than is usual with negative emulsions which are to be used for ordinary photography, but in order to keep the film compact and very thin, only about half the usual coating volume is applied. The gelatin may advantageously be still further reduced if suitable coating facilities exist.

Reversal emulsions are steadily becoming of greater importance. Quite apart from color work, practically all substandard motion-picture work is of the reversal type, and im-

mense quantities of 8 mm, 9.5 mm and 16 mm black-and-white reversal films are manufactured. Reversal emulsions are also necessary for triple-layer subtractive color films, and their application is being extended to other purposes where the production of a direct positive image is of advantage. In sub-standard motion-picture work, it is to be remembered that great enlargment of image is involved in projection, so that extremely fine grain is of the utmost importance, always provided that it can be coupled with adequate speed.

Chapter References

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4. W. Heyne, Handbuch der Wiss. und Angew. Phot., p. 268.
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Chapter V

SLOW EMULSIONS

Sensitive Material for Copying, Commercial Work and Transparencies — Methods of Producing High Resolution and Fine Grain — Chloro-bromide Emulsions — Chloride Emulsions — Mixed-jet Emulsification — Development of Warm Tones.

IT has been seen in a previous chapter that a fast negative emulsion can be made by " boiling " a suspension of silver bromo-iodide in gelatin until the grains are sufficiently ripened and digested. In this type of emulsion it is probable that sensitization takes place as much in the ripening as in the finishing stage. It has been seen also that by the use of ammonia the temperature and time needed for arriving at a similar speed and character may be greatly modified. It is doubtful whether the extreme speeds attained in recent years can be produced by the boiled method.

We come now to the problem of making comparatively slow emulsions, of 25 to 150 H and D. Such emulsions play a very important part in industry. They are indispensable for copying work, for recording purposes, for the making of transparencies, and for various branches of photo-mechanical reproduction. The coating of positive emulsions on film stock of course runs into enormous figures in the motion-picture industry. Some six thousand million feet of thirty-five millimeter film were used in 1933.[1]

In what way, may we ask, do these slow emulsions differ from rapid ones? The answer is that a slow emulsion is made with substantially finer grain, which is not allowed to grow to any extent in ripening. This is controlled by the concentrations of the solutions employed in precipitation, by temperature, and

largely by pH. A slow emulsion may easily be made to develop a gamma of 3.0 or 4.0 and may indeed be required to do so, but it has a fine grain and a high resolution coefficient. The fast emulsion will probably develop a gamma of no higher than 1.0 to 1.8. Apart from improved resolution, irradiation is reduced;
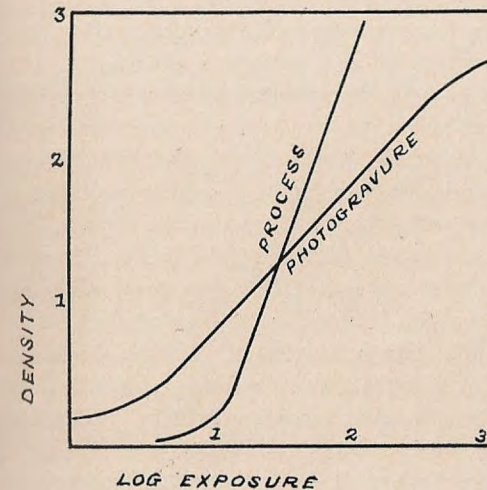

LOG EXPOSURE

FIG. 24

In other words spreading of fine line images is minimized, and there is a less tendency to halation.

The production of slow, fine-grained emulsions must be divided into two classes, (a) the photo-mechanical type, where we need either blacks or whites with no intermediate tones, and a high inertia is of no consequence but rather an advantage, and (b) brilliant and contrasty emulsions where the density range is long and latitude is of a high order, but with which high maximum blacks can nevertheless be obtained where desired. The type having a high inertia, and giving intense blacks

on heavy exposures but insignificant densities on low exposures, is seen in characteristic form in Fig. 24, as compared with a transparency type of emulsion having low fog, fairly high maximum density, but a long even scale of gradation. Both types should be made with a high concentration of silver in order that the actual film coating may be as thin as possible.

The first type is made most easily by precipitating the silver halides as far as possible in a uniform grain size. In practice, it is found best to pour concentrated silver nitrate rapidly into the salts solution and to add the bulk gelatin immediately after precipitation so as to inhibit ripening, which is synonymous with grain growth, and also leads to the formation of grains of different diameters, which in turn gives a milder slope to the characteristic curve. Against this, we need brilliant images, low densities and absolute freedom from fog, good gradation and an attainable gamma of 2.0 to 3.0 to provide a first-class transparency emulsion. Our knowledge of the laws of precipitation indicates that pouring the silver in a fine stream with rapid stirring and the use of more viscous solutions, should give the physical result. The production of fine grain needed for photogravure or diapositive work demands not only a more viscous solution for the salts, but reduced silver bromide solvents such as excess alkali halides and ammonia in the ripening. The addition of silver at a moderate concentration or only partially redissolved through a nozzle at a slower rate, with mechanical stirring of the crock, or the pouring of the silver and salts solutions simultaneously through two jets or nozzles into a solution of plain gelatin, gives the " process " character with the longer scale of gradation. Mixed jet emulsions of this type with the whole of the silver redissolved will yield very great contrast, especially if the bulk gelatin be added immediately after precipitation. In very slow emulsions, such as chloro-bromide and chloride types, the substitution of hydrochloric or citric acid

for ammonia is customary, the citric acid often being divided between the salts and the silver.

The following characteristics may be taken as representative of the slower types:

Emulsion	Speed, H & D	Density range	Gamma infinity
Photogravure	60–100	1.5	1.8
Process	25–60	2–3.5	3–5
Lantern	6–10	2.5	3
Chloro-bromide	1–2	2.5	2
Chloride	0.1–1	4	4

It has already been pointed out that the characteristic curve is steepened and latitude shortened by having more or less homogeneous grains of similar diameter. This condition is obtained in the formula given below by adding a concentrated redissolved silver at a low temperature to the salts, adding the gelatin at once and setting as quickly as possible. Alternatively the salts and silver can each be dissolved in the same bulk of water and poured into the crock simultaneously with the apparatus described on p. 100. The gelatin solution may be made alkaline with ammonia, or acid with a mineral acid to neutralize the ammonia set free by reaction of the silver nitrate with the alkaline halides. This helps control the tendency for rise in speed.

Bearing in mind that a process emulsion when coated requires about sixty to eighty milligrams of silver halide per square decimeter, and that the gelatin-silver ratio should be kept low, we may formulate the emulsion somewhat as follows:

A. Ammonium bromide	230 g
Ammonium iodide	5 g
Gelatin	200 g
Water	4000 cc
B. Silver nitrate	350 g
Water	50 cc
Stronger ammonia water	q.s. to redissolve

The gelatin is soaked for thirty minutes in the salts solution A, which is then heated and the gelatin dissolved. It is then cooled to 95° F. (35° C.). Solution B is used at room temperature, 70° F. (21° C.), and is poured on quickly out of a stoneware jug, taking two or three seconds only. The crock should be vigorously stirred, if possible by mechanical means. Immediately after emulsification, 550 g of powder or broken gelatin is added, the jar being stood in water at about 160° F. (70° C.) to facilitate quick melting, but the temperature of the emulsion itself must not be allowed to rise above 105° F. (40.5° C.). The gelatin will take ten to fifteen minutes to dissolve completely. The emulsion should then be transferred to an ice-cold crock or a number of smaller ones and stood in ice water, stirring until gelling begins. Not more than three to four hours should be allowed between setting and washing. The final wash water should give a clean Nessler test. When washed, 250 cc of spirit is poured over the shreds, which are then remelted in the usual way, and the emulsion is digested for about two hours at 125° F. (52° C.). One or two cubic centimeters of ten per cent glacial acetic acid solution is added and well stirred in, sufficient to bring the pH to just below 7. The remainder of the alcohol, 250 cc, is then added, together with 100 cc of chrome alum solution and 50 cc of ten per cent potassium bromide solution. The emulsion is next filtered and set off, being remelted next day or when required for use. Such an emulsion will keep in the cold room for several days, but should always be checked for fog by a wet test before being sent to the coating room. The total bulk of the above emulsion should be ten liters.

The wet test for fog is made by coating about twelve cubic centimeters of the emulsion on a 5 by 7 inch plate, setting it on the cold slab, and placing it in a plateholder with the slide half drawn. It is exposed about eight feet from a 25-watt in-

candescent lamp for a few seconds, and then washed under the tap and developed in total darkness for about three minutes in any ordinary M.Q. developer. The exposed portion will develop up jet black, and the unexposed part should appear by comparison dead white in the Mazda light.

E. J. Wall gives the following formula for a process emulsion:

A. Potassium bromide	....	450 g
Potassium iodide	....	5 g
Gelatin	....	625 g
Water	....	4800 cc
B. Silver nitrate	....	500 g
Water	....	1250 cc
Ammonia to redissolve		

Solution B is run into the salts solution through a very fine jet, taking fifteen minutes. A is at 68° F. (20° C.), and B at 113° F. (45° C.). The mixed emulsion is then digested for fifteen to thirty minutes, cooled, set and washed, and finished in the usual way. Note that the viscosity of the salts solution is quite high. Jahr suggests at least doubling the gelatin used in emulsifying an ordinary type emulsion and increasing the iodide by fifty per cent. It is the author's experience that an iodide content of not more than 1.5 per cent of the silver nitrate equivalent, a considerably lower concentration of the gelatin in the jar (about four per cent), and a very concentrated silver solution, give the best grain and contrast for photo-mechanical emulsions, provided always that the addition of the bulk gelatin and the setting be *very quick*.

When we come to plates or films suitable for photogravure, where a density range of not more than 1.5 is required, and a maximum density of say 1.8 (the lowest tones having a density of 0.3), a somewhat modified type of emulsion is needed, involving a longer scale of gradation and lower gamma infinity. This may be obtained in two ways. Either fifty per cent only

of the silver may be redissolved and the remainder added plain to the salts five to ten minutes after the first precipitation, and ten to twenty minutes allowed for ripening, or a portion of the silver nitrate solution, say one third, may be first added dilute to the salts, with the iodide omitted. Instead of redissolving this first silver nitrate, about one third only of the amount of ammonia that would be required to redissolve it, should be added. This will, of course, give a dirty brownish black solution containing undissolved silver hydroxide, but this will not disturb the result. On emulsification it will yield a perfect silver bromide precipitate. After an interval of, say, three minutes, the iodide is added in about ten times its weight of water, rendered alkaline by ammonia to about five per cent of the total weight of silver; immediately afterwards the balance of silver is added plain, at a temperature of 115° to 120° F. Ten to fifteen minutes further ripening may then be given, and the bulk gelatin added. The formula would thus appear as follows:

A. Ammonium bromide .... 230 g
   Gelatin .... 160 g
   Water .... 2600 cc
           Temperature 110° F.

B. Silver nitrate .... 120 g
   Water to .... 440 cc
   Stronger ammonia water .... 40 cc
           Temperature 70° F.

C. Ammonium iodide .... 6 g
   Water .... 60 cc
   Ammonia .... 18 cc
           Temperature 70° F.

D. Silver nitrate .... 240 g
   Water to .... 960 cc
           Temperature 120° F.

E. Dry gelatin .... 640 g

In coating emulsions for photo-mechanical work, it must be borne in mind that the thinnest possible film should be made which is sufficiently robust. A considerable amount of handling takes place in processing, and while the film must exhibit no tendency to frilling and must be abrasion-proof, it must be thin enough to make the various operations such as cutting with ferricyanide, intensifying, washing, etc., as quick as possible. The addition of a yellow dye such as Brilliant Yellow, Tartrazin, or Naphthol Orange, will assist in preventing spreading of the image by irradiation. Some form of backing is, however, the most satisfactory means of preventing halation.

The slow photo-mechanical emulsions above described range in speed from 25 to 150 H and D. A still slower type is used for black tone diapositive and lantern plates. A speed of 5 H and D is very suitable for lantern emulsions, and here again absolute freedom from fog is most important, as it greatly enhances brilliance on projection on the lantern screen.

The formula below is stated to yield excellent slow iodobromide emulsions for transparencies:

A. Potassium bromide .... 150 g
   Potassium iodide .... 4 g
   Gelatin .... 250 g
   Water .... 2500 cc

B. Silver nitrate .... 375 g
   Water to .... 2500 cc

One cubic centimeter of five per cent pure hydrochloric acid is added to A. Both silver and crock are heated to 130° F. (55° C.) and emulsified. The crock is stirred and maintained at 140° F. (60° C.) for thirty minutes. Then add 300 g of dry gelatin and dissolve with stirring. The emulsion is then set off in ice water. While the addition of a little ammonia to the emulsion is suggested just before setting, such procedure is *not* recommended by the author. The washed emulsion, after the

addition and solution of another 250 g of dry gelatin, must be digested at 120° F. (49° C.) for a time varying from an hour and one-half to three hours. This time depends largely on the brand of gelatin used, and can be decided only by actual test. The usual procedure is to take samples periodically from the crock as it stands in the digesting pan, and coat sample plates, making sensitometric tests of the series of plates when *dry* under identical conditions of exposure and development. Finals are:

Spirit	500 cc
5 per cent chrome alum solution	50 cc
10 per cent potassium bromide solution	50 cc

As a preservative in this or any slow emulsion, there is little to beat carbolic acid (phenol), of which about three grams to the gallon may safely be used. This may be dissolved in the spirit, except where the spirit is poured on the shreds in re-melting them after washing. The final bulk of the above emulsion prior to filtering should be 12,500 cc.

Reference to the literature will disclose many formulas in which the gelatin is divided equally between the salts and the silver, thus mixing two viscous solutions in the precipitation. While an extremely fine grain can be obtained in this way, it is not easy to avoid grain aggregates, which give black " pepper " spots in the developed image. Preferable to the divided-gelatin method is the double-jet method of precipitation described later.

A slow emulsion made with a mixture of the chloride and bromide of silver has the property of yielding warm black, sepia, or reddish-brown tones, on straight development, and has therefore been much used for transparency and lantern slide work. Similar emulsions applied to paper give warm black tones which have been much in vogue. These tones are to be distinguished from the tinted images obtained by the use of motion picture positive stock coated on slightly tinted nitrate base.

The ratio of bromide to chloride is capable of infinite variation, affecting both contrast and color, although the physical formation of the halide grains can equally influence both the tone formed on straight development and the effect on tone of restrained or diluted developers. Just as the higher affinity of iodine for silver over that of bromine will cause an iodide to turn out some of the bromine of silver bromide, so a bromide will convert some of the chloride of silver into bromide or bromo-chloride. If the bromide be much in excess of the chloride in an emulsion in which both halides are present, the tone will be colder but the gradation will usually have a longer scale; an excess of the chloride will tend towards higher contrast and a shorter scale, but will more readily yield color on suitable development.

A point noticeable in the study of published formulas is that in these emulsions a very small excess only of soluble halide over the combining weight is employed, and that free acid, often in considerable quantities, is used. This will be seen from the two following formulas, due respectively to J. B. B. Wellington and E. Valenta:

	Wellington	*Valenta*	
A. Ammonium bromide	20 g	2.0 g	
Ammonium chloride	—	11.6 g	
Sodium chloride	10 g	—	
Citric acid	50 g	—	
10% nitric acid	—	4	cc
Gelatin	70 g	65	g
Water	500 cc	500	cc
B. Silver nitrate	50 g	50	g
Citric acid	50 g	—	
Water	500 cc	500	cc

The method of mixing varies. In Wellington's formula, the silver solution is introduced in a fine stream at room temperature to the salts solution, which has been heated to 160° F.

(70° C.). The emulsion is allowed to stand for ten minutes and is then set and washed. Valenta on the other hand recommends heating both salts and silver solutions to 140° F. (60° C.) and adding silver to salts in the usual way.

Another formula, due to Valenta, and suggested for transparency work, is quoted by Jahr: [2]

A. Ammonium bromide .... 15.2 g
   Sodium chloride .... 1.5 g
   Gelatin .... 50 g
   Water .... 400 cc

B. Silver nitrate .... 30 g
   Water .... 400 cc

Both solutions are heated to 140° F. for emulsification, and after mixing, the jar is maintained for an hour at 140° F., being mechanically stirred during this time. It is then set and washed.

It will be noted that after washing, these emulsions have a rather low gelatin concentration. Chloro-bromide and chloride plates should have a very thin film of emulsion and a coating weight of not more than twenty-five to forty milligrams of silver halide per square decimeter. If difficulty is experienced in coating in the laboratory, a little fresh gelatin may be added to the washed emulsion on remelting, bringing the gelatin up to about six per cent of the total weight of liquid. It must be very thoroughly dissolved by stirring, solution being complete before adding the alcohol and chrome alum. It is usual to reset the emulsion after making up and to remelt just before filtering, prior to coating. Little if any free bromide should be added; a small excess of chloride may be beneficial, although it may impart a greenish tint to the blacks, or be prejudicial to warm brown tones by imparting to them a greenish tinge. This green tinge is particularly difficult to eliminate in chloro-bromide papers. If there is a tendency to fog, or if the image is too flat, a little potassium chloride solution may be used, together with

a little citric acid, not potassium citrate. Better still is a change of gelatin. Most manufacturers are aware of the particular types of gelatin which suit these slow emulsions, and will provide likely samples if asked.

Potassium chloride is suggested rather than sodium or ammonium chloride, as it is not hygroscopic, and hence can be used even with an unwashed emulsion. It will be noted that the chlorides and bromides of various alkali metals are used in different formulas, but experience has proven that provided the respective combining weights are employed they all work much alike. This does not apply to metallic salts such as cupric chloride and thallium chloride. The use of one to three per cent of cupric chloride (compared with the silver) can perceptibly increase the brilliance, tending to give improved whites and better contrast in projected screen images. Cupric chloride solution is added to the finished emulsion when making up.

The gelatin being at high concentration in emulsifying and there being practically no excess of soluble halides and a low pH, little ripening takes place, hence the grains remain small and any tendency toward speed is inhibited. According to Jones,[3] redness of the image, i.e., its departure from *black*, is dependent on the size of the developed grains. This was well illustrated by the work of L. F. Davidson and T. T. Baker on the photomicrography of developed chloro-bromide images using a $\frac{1}{20}$-inch oil immersion lens (Beck) and dark ground illumination, with Agfa color plates. The color of the grains by transmitted light was excellently recorded. Warmth of tone is best regulated by length of time of reduction coupled with the presence in the developer of a small trace of silver halide solvent. The particular type of fine-grained emulsion containing chloride in conjunction with bromide of silver seems to lend itself to the production by direct development of colloidal silver of ultra-microscopic size, yellow, red, or purple grains being re-

duced with a proportion of black grains of microscopic size. The presence in the developer of ammonium chloride or ammonium carbonate definitely helps the formation of color, but these compounds can only help when the grain size is of a suitable fineness. Apart from the actual *size* of the silver halide precipitate, the use of more concentrated gelatin in emulsification gives a more solid clothing of the particles, which again appears to assist in the production of color. In the case of pure chloride emulsions (*q.v.*) it is noteworthy that a plain hydroquinone-caustic soda solution, or a developer such as the Gevaert G-251, will yield most easily a series of tones from warm black to red merely by *dilution,* giving longer development time with exposure remaining more or less constant. Several hours' development with extremely dilute hydroquinone-soda can be made to yield purple and bright magenta tones.

Silver chloride darkens in the light, but will yield only a flat, grayish image on prolonged exposure.* Given an exposure under a negative of the order of 25,000 meter-candle-seconds, which may or may not give rise to a faint visible image, the emulsion can be developed to an intense blue-black in any suitable solution such as amidol or metol-hydroquinone. Silver chloride is, in general, emulsified with gelatin by adding silver nitrate to the solution of chloride, though the pouring of the gelatin-salts solution on to the silver solution has been advocated. The gelatin is sometimes dissolved in the salts solution, sometimes divided between the silver solution and the salts solution. Another favorite method is to run solutions of silver nitrate and sodium, potassium, or ammonium chloride through

* If a small quantity of potassium or sodium nitrite be added to a silver chloride emulsion, it will " print out " in sunlight and give an image of sufficient depth to be toned with gold and fixed. Exposure-meter paper is usually prepared with a nitrite to induce visible darkening of the silver halide.

two matched jets into a plain solution of gelatin, the salts being always very slightly in excess. This method has the advantage that the silver chloride is not formed initially in a large excess of soluble chloride, which excess diminishes progressively as the precipitation proceeds, but the conditions of colloidal precipitation are maintained constant through the entire emulsification.

One essential of a chloride transparency or development paper is that the whites must remain absolutely clean, that is, that the fog density on normal development does not exceed about 0.02. Another is that the blacks are bluish black or warm black, but are not greenish in tone. These features are mentioned because it is by no means easy to insure them. Also, as with all slow emulsions, it is not always easy to obtain sufficient contrast. A gamma of 4.00 or thereabouts should be one of the features of a chloride emulsion. One difficulty in the making of the emulsion is the avoidance of coarse precipitates, which develop spontaneously owing to insufficient colloidal protection; these cause the black spots or flocks previously referred to as pepper, and may easily spoil an otherwise good emulsion.* Their formation appears to be quite independent of the concentration of gelatin or rate of stirring, but it is always a liability where the chloride of silver is concerned. A suitable coating weight is twenty to twenty-five grams of silver chloride per liter, one liter being allotted to a twenty-foot run of paper forty-two inches wide or the equivalent of four hundred lantern plates 3 by $4\frac{1}{4}$ inches.

Many formulas have been published for fine-grain, slow emulsions, particularly chloride and chloro-bromide, in which the

* A certain amount of small flocks has been found an actual advantage in emulsions for photogravure. Their formation appears to rob the blacks of some of their density, thereby making them more transparent and assisting shadow detail, while not interfering perceptibly with highlight detail.

salts and silver solutions are poured simultaneously into the crock containing plain gelatin solution. The silver halide is then formed throughout the precipitation with a constant excess of salts, which can be adjusted to be extremely small, and can be controlled by the time of lead given. Thus in Fig. 25
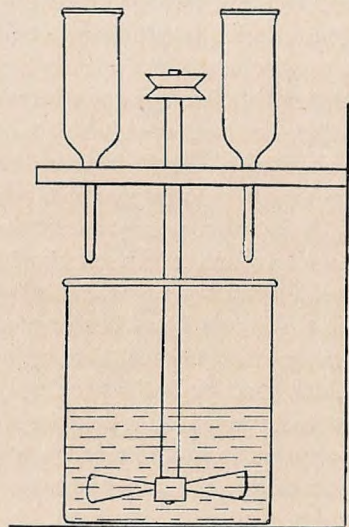

FIG. 25

the two solutions are poured into two cylindrical funnels the ends of which have been drawn out in the flame into fine jets. By making the drawn-out part long enough.(Fig. 26) small bits can be filed and broken off in different positions as indicated by the arrows until the cylinders empty at the same rate. Another method is to connect a short length of barometer tubing, say one inch long, to the outlet of the funnel by a piece of rubber tubing; in this way tubes of the same bore can be assured, and the salts merely started, with a pinchcock, so many seconds be-

fore the silver. Any timing must of course be made with samples of the actual solutions to be used, each at its respective temperature. It is not advisable to use funnels with glass taps. If, say, 2000 cc each of silver and salts are to be poured into
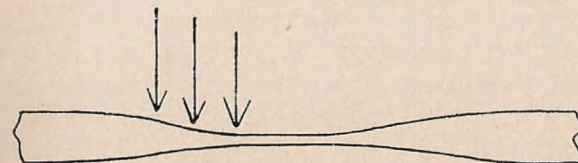
FIG. 26

5000 cc of ten per cent gelatin solution, 25 to 50 cc of the salts solution would be run in before the silver was started. This would insure a lead of halide and prevent free silver nitrate from coming into contact with the gelatin, which might give rise to dichroic fog or veiling.

Mixing of this type, as a rule requires vigorous stirring. This may be done by means of a glass, wooden, nickel, or chromium-plated propeller, or a pair of propellers running in opposite directions. Small variable laboratory stirrers are supplied by Eimer and Amend and Central Scientific Company; these are fitted with induction motors so that no sparking takes place. It will be found, however, that for quantities of two liters upwards, with viscous solutions of gelatin, considerable power is required to insure efficient continuous stirring. With sufficient practice the hand and wrist and a one-half or three-quarter inch stirring rod are difficult to beat for experimental lots of a liter or two. But where a series of strictly comparative tests is being made, proper control and uniformity of mixing is naturally essential. In works practice a one-half-h.p. motor would have sufficient power for stirring a crock of three gallons capacity or more.

It must be borne in mind that starting with 5000 cc of ten per cent gelatin solution, the gelatin concentration in the crock at the end of mixing will have dropped to 5.5 per cent. If uniform concentration is to be maintained, then if x per cent of gelatin be used in the water in the crock, the silver and salts solutions must each contain x per cent of gelatin also; in this case the gelatin concentration of each of the three solutions would be reduced to 5.5 per cent in the above example. Further reference to this type of emulsification will be found in Chapter VIII.

Care must be taken in the drying of transparency plates, as owing to the thinness of coating, drying marks at the edges are apt to appear. The rate of drying is limited by the rate of diffusion of water in the gelatin layer to the evaporating surface; [4] it thus progresses more rapidly at corners and edges and proceeds by a gradual regression of the moist area to the center of the plate or film. It would appear that the extra tension due to the more rapid drying renders the sensitive salts liable to darken on development without exposure (*cf.* pressure marks), and to prevent the trouble with thinly coated slow plates, it will be found advisable not to turn the heat on in the drying cupboards as soon as in the case of thicker-coated bromide plates. An addition of one-quarter per cent of glycerin to the emulsion may be found helpful.

Chapter References

1. Twentieth Century Fox Film Report, 1933.
2. R. Jahr, Handbuch der Wiss. und Angew. Phot., p. 240.
3. Chapman Jones, Phot. J. *51*, pp. 159–174.
4. Photography as a Scientific Implement, p. 139.

CHAPTER VI

COLOR–SENSITIVE EMULSIONS

Action of Color-Sensitizers — Orthochromatic and Panchromatic Plates and Films — Self-filtering Emulsions — Hyper-sensitizers — Bipacks and Tripacks — Three-layer Color Films — Dye-couplers and Color Formers

A PLAIN silver iodo-bromide emulsion is not sensitive to color as is the human eye. The maximum response is to light of wavelengths ranging from 430 to 470 mμ in the blue-violet, the sensitivity ending at about 520 mμ in the green region of the spectrum. Ordinary emulsions are sensitive to the extreme violet and ultra-violet, response to the latter being terminated by the ultra-violet absorption of gelatin. By reducing the gelatin to a minimum, the response can be lengthened to about 180 mμ. Silver bromide emulsions are also sensitive to the shorter radiations having wavelengths varying from 10^{-9} to 10^{-7} cm, and even to the gamma rays, which are of the order of 10^{-8} mm.

The response of a gelatino-bromide emulsion to the spectrum of white (incandescent) light is seen in E in Fig. 27; the visual activity V is shown in comparison with it. It is seen that while the most active color visually is situated at about 555 mμ, the bromide emulsion has a maximum response at a much shorter wavelength. The relative sensitivity of average " ordinary " or " color-blind " emulsions, orthochromatic (green-sensitive), and panchromatic (fully color-sensitized) types is seen compared in Fig. 28, the green-sensitive type (B) having a characteristic hump at 540 to 550 mμ, and the panchromatic (C) having — usually — two less clearly defined maxima at 540 and 640 mμ, indicating the use of two color-sensitizers. Combina-
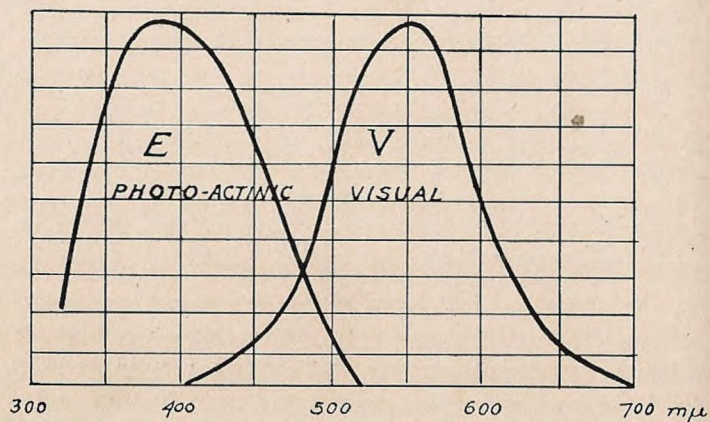
FIG. 27

tions of color-sensitizers have been found which together pro-
duce an almost continuous response without appreciable max-
ima from the violet to the middle red of the spectrum.

Color-sensitizers are dyes which when added to the emulsion
actually color the silver halide grains or their sensitive nuclei
or spots so that they absorb additional radiations, the energy
of which can be converted into chemical energy and thus render
the grains reducible in the developer after exposure. As the
photo-chemical reaction when light impresses the film can only
take place if the radiations are absorbed by the system, it can
be understood that the dye used must be complementary in
color to the rays for which it " sensitizes." The maximum of
sensitivity conferred does not, however, coincide exactly with
the absorption maximum of the dye, but in the case of iodo-
bromide emulsions is generally shifted 15 to 20 mμ towards the
red end of the spectrum. This shift is complicated by the fact
that the dye may impart to the grains a different color from its
own in aqueous solution, and that it may color silver bromide,

silver chloride, and silver iodide, differently among themselves.
An important desideratum in color-sensitizing is to provide as
far as possible that no excess of dye is used over and above that
actually needed to give the optimum result in any particular
emulsion.

For many years after the possibility of color-sensitizing had
been discovered, only greenish-yellow sensitivity could be added
to the normal blue-violet response. This was done by adding
the dye *eosin* to the emulsion, first suggested by Waterhouse
and afterwards used successfully with collodion by Vogel.
Tailfer later used eosin and erythrosin in conjunction with am-
monia in making gelatino-bromide plates. Erythrosin is one of
the finest green sensitizers available even today, and is an alkali
salt of fluorescein (potassium or sodium tetra-iododofluorescein-
ate). It stains the grains pink or magenta, so that they absorb
light of the complementary color *green;* the dyed emulsion is
thus sensitive to violet, blue and green. The increased truthful-
ness of the monochrome rendering of colored objects with these
plates caused them to be named orthochromatic or isochromatic.
Wall states [1] that from 0.07 to 0.10 gram of the potassium
salt is generally used to one hundred grams of silver nitrate.

In the first years of the present century, fairly powerful yel-
low and red sensitizers were discovered, and thus it became pos-
sible to render an emulsion sensitive to the entire range of the
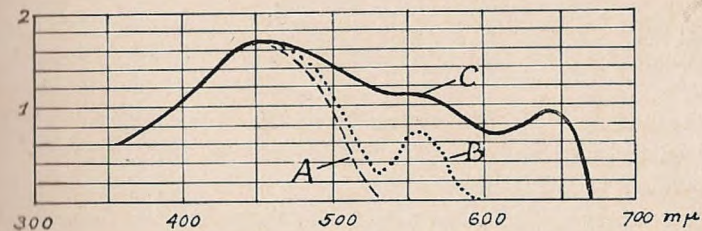

FIG. 28

visible spectrum. Such emulsions were termed *panchromatic*. It must be noted, however, that comparatively few dyes will act as color-sensitizers, and that these require to be used in the highest possible state of purity if consistent results are to be obtained.

Two things will be noticed from a consideration of Figs. 27 and 28. The visual and photographic curves of Fig. 27 are similar in shape but considerably displaced as to wavelength, Fig. 28 shows that while the blue-violet sensitivity A remains in each type of emulsion, neither the ortho B nor the panchromatic variety C has anything like the response of the human eye to the other colors. Color-sensitive plates, from the emulsion maker's standpoint, must therefore be divided into three distinct classes:

(a) The orthochromatic type, suitable for general landscape and flower photography, document work, etc., when used with a yellow filter on the lens to depress the predominant blue-violet sensitiveness.

(b) The panchromatic type, more or less evenly sensitized to all visible colors from 400 to about 650 mμ, required for black-and-white reproduction of colored objects fully corrected, or for color photography where the spectrum is divided into three more or less equal parts, blue-violet, green and orange-red.

(c) Locally sensitized types, with sharp peaks of color-sensitiveness, of special value in conjunction with contrast filters for photomicrography or for regional spectrography and other scientific purposes; in this category infrared plates would be included.

In class (a) the predominant sensitivity to blue-violet may be reduced by the inclusion in the emulsion of a yellow " filtering " dye. Such a dye should not have any desensitizing effect on the intrinsic speed of the silver bromide grains. Naphthol yellow, tartrazin and thiazol yellow have been recommended; [2] brilliant yellow is another suitable dye. The filter-dye method can also be made to depress the blue-violet in a panchromatic emulsion to make it have a color response similar to curve V

in Fig. 27, but by some curious mischance this has never been offered to the public by manufacturers, who appear to find the panchromatic film plus compensating filter more practical. An emulsion which gave remarkably good monochrome rendering of colored objects without a filter was that in which F. F. Renwick used auramin,[3] which he claimed not only acted as a blue sensitizer but increased the range of sensitivity in the red obtained with pinacyanol; the auramin actually depressed violet and made a partial self-screening, though this is not claimed.

The green sensitizer used in the most popular orthochromatic emulsions is undoubtedly erythrosin (Fig. 29). It is largely
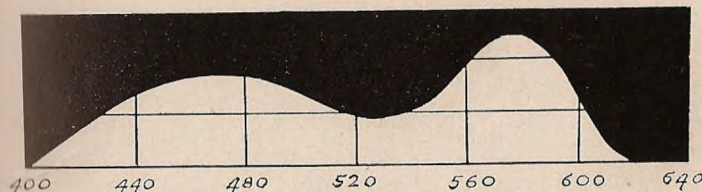

FIG. 29

employed in the industry for plates, films, and document papers, and is used in many rollfilm emulsions where it confers mild green sensitivity and increases brilliance. It gives little color correction in daylight unless used with a yellow filter. Erythrosin can be added to a finished emulsion or it may be mixed with the silver solution just before emulsification. Eder's early formula, which has never been greatly improved, involved the addition of a solution of erythrosin to the ammonia-redissolved silver; this procedure probably gives the highest peak of green sensitivity that can be obtained. The addition to a finished emulsion of a solution of erythrosin containing a small quantity of ammoniacal silver hydroxide or a weak solution of silver chloride in ammonia, may give extremely pronounced green

sensitivity, but is likely to cause fog, poor keeping, and black spots, and is only advised where a very pronounced peak is desired for special work.

The following emulsion, based on Eder's lines, will be found very satisfactory:

A. Water .... 3500 cc
   Ammonium bromide .... 350 g
   Ammonium iodide .... 8 g
   Soft gelatin .... 150 g

B. Silver nitrate .... 500 g
   Water .... 250 cc
   Ammonia, concentrated .... to re-dissolve
   Just before mixing, add two per cent erythrosin, dissolved in equal parts of alcohol and water 25 cc.

Using the salts solution at 90° F. and the silver at 70° F., the silver is " flopped " into the crock without stirring. When added, it is stirred gently for one minute. Six hundred and fifty grams of dry gelatin is then added and stirred in for fifteen minutes, bringing the temperature of the crock up to 105° F. It is then set quickly in ice water, very thoroughly washed after about five hours, and digested as usual. Final volume to be ten liters, inclusive of:

5 per cent chrome alum solution .... 100 cc
5 per cent phenol in alcohol .... 500 cc
1 per cent ammonium bromide solution ...... 50 cc

If the emulsion is to be made self-screening, there should be introduced *before* the finals sufficient of the yellow dye in a watery solution of about two per cent strength to impart a pale yellow color to the emulsion when tried out on glass coated with about the normal thickness, 10 or 12 cc to a 5 by 7 plate. A number of trials must of course be made, and tried out when dry by photographing a color chart in daylight or daylight-filtered Mazda without a compensating filter. Loss of speed

may be due to the presence of a " filler " in the dye, or to the use of too large a quantity of dye, or to insufficient green sensitivity to admit of the use of the filtering dye. Pure dyes must be used for this purpose.

Erythrosin for emulsion-making purposes is made of exceptional purity by Meister, Lucius and Brüning of Hoechest am Main, Germany. A pure grade is also supplied by Eastman Kodak Company (product of National Anilin Company). Commercial erythrosin may be purified, according to Wall,[4] by dissolving three parts of the dye in one hundred parts of water, and adding dilute sulphuric acid gradually until the whole of the tetra-iodo compound is precipitated, the solution being then colorless. The precipitated dye is filtered off and washed repeatedly with distilled water. It may then be conveniently made up as a two per cent solution, dissolving it in a mixture of equal parts of distilled water and alcohol, to which a few drops of ammonia have been added. Instead of adding the erythrosin to the ammoniacal silver solution, this dye solution may be added, as stated, to the finished emulsion, in which case the quantity employed would be the equivalent of about one part of solid dye to one thousand parts of silver halide. It is best added five or ten minutes before the end of the final digestion. It must be remembered that any emulsion sensitized for greenish-yellow must be handled in deep red light. Both emulsion and coated plates should be shielded from direct rays, and the safelights should be re-tested from time to time.

While there may be nothing to replace the old erythrosin as an all-round green sensitizer, Meister, Lucius and Brüning have produced *pinaflavol*, which confers extraordinary sensitivity in the blue-green, continuing through to the beginning of the yellow. It appears to show a tendency with some emulsions to give fog, and a somewhat low gamma. It is a basic dye, and the fact that it produces a response to the most obstinate part

of the spectrum, the blue-green region around 520 mμ, makes it of particular interest. The pinaflavol maximum is, in fact, at about 527 to 530 mμ. For adding to a finished emulsion, the makers recommend the use of about 20 cc of a 1:1000 solution to the liter. Both Orthochrom T and pinaverdol are recommended, but while excellent green sensitizers, they confer such high orange and red sensitiveness that they should be considered along with the panchromatic dyes.

The use of too much dye is liable to cause fog, does *not* increase color-sensitivity, and may slow the emulsion by deeply coloring the grains and the surrounding gelatin, thereby acting as a light-filter rather than as a sensitizer. This point is well illustrated by the increase in sensitivity which can be produced by merely bathing commercial panchromatic plates in plain water.

The next type of dyes to be considered comprises the derivatives of quinoline, such as cyanin itself, the iso-cyanins introduced by Miethe, and the carbo-cyanins more recently applied by König. An immense number of these sensitizers has been produced and investigated in recent years. It is beyond the scope of this book to enter into the chemistry of these compounds, and for their study the reader is referred to the last few years' issues of " Photographic Abstracts," published quarterly by the Royal Photographic Society of Great Britain, and the library of the U. S. Patent Office, where a vast and constantly growing number of patents are available. Practically every important manufacturer of films and plates today possesses his own organic laboratory for the manufacture of his sensitizers. A few of these have been placed on the market, but the firms concerned have not been over generous, and the cream of such products are not only reserved for factory production, but their use is hedged around by the patent position.

The great increase in speed of panchromatic emulsions wit-

nessed in recent years has been largely due to the new technique of " super-sensitization." That it is possible to attain sensitization by the addition of such super-sensitizers higher than the sum total of the individual sensitizers, is claimed by Dr. C. E. K. Mees.[5] An alcoholic solution of the sensitizer and super-sensitizer is diluted with water and added to the emulsion. As a given instance, ten parts of pinacyanol may be super-sensitized with one part of pinaflavol, the region of response induced by each, overlapping. The net effect is to obtain greater speed in the sensitized region than the sum of the two sensitivities conferred by each separately. Another example is that of a thiacarbocyanin, super-sensitized by the addition of 8-alkyl-diabenzthiacarbocyanin.

The amount of these color-sensitizers added to an emulsion is small as compared with fluorescein salts. About 0.05 per cent of the weight of silver bromide would be used in the case of pinacyanol; 0.07 per cent in the case of pinachrome, Orthochrom T or pinaverdol. These dyes are all rapidly decolorized on exposure to light in the form of aqueous solutions or thin films. The color-sensitiveness they impart is retarded by the presence of free bromide in the emulsion, which appears to oppose the dyeing of the halide grains. This is probably the reason why the addition of a trace of silver nitrate to the sensitizing bath often increases the effect, but such addition is dangerous practice unless the washing of the emulsion is made under the strictest possible control.

Some of the modern red-sensitizers give the best results if added to the emulsion before it is completely digested, this seeming to assist in the adsorption of the dye on the halide grains or their nuclei. Whether the emulsion is digested with the dye in, or the dye is added at the final stage, it is important that it should be absolutely free from fog — one for example which will give on normal development without exposure, a fog read-

ing of not more than 0.02. For the reason already noted, the smallest possible quantity of free bromide should be added as a final, and extra careful washing should be given to insure that the excess bromide used in emulsification is thoroughly removed. Lithium bromide is sometimes recommended as giving cleaner results than the potassium salt. An emulsion having a low iodide content, say two per cent only of the silver bromide, also reacts in general more favorably to the sensitizers. Owing to their fugitive character the isocyanins and analogous dyes should be made up in artificial light and stored in dark bottles. A warm mixture of ethyl and methyl alcohol is generally used to dissolve the dye, which is as a rule soluble only about one part in a thousand (1:5000 in the case of Sensitol Violet), and when dissolved the solution is broken down to strength by further addition of alcohol. Where two or more sensitizers are used, it is advisable to add each one separately, with a short interval between additions.

Different sensitizers must be used in different quantities to produce the best results. In the majority of cases the spectral band or bands for which the dye sensitizes is not interfered with by the next dye added. Thus it is claimed that pinaflavol, used to sensitize up to 590 mμ with a maximum at 527 mμ, can be used with pinacyanol, which will continue the sensitivity along the spectrum up to about 640 mμ. By a combination of dyes the peaks of which, as measured on a wedge spectrograph (p. 210), add up to a more or less uniform level, it is possible to produce a panchromatic emulsion having almost equal sensitivity throughout the visible spectrum.

For many cases of scientific work, it is of advantage to use plates or films locally sensitized; thus eosin, erythrosin, rhodamin, etc., give a pronounced green maximum and can be used with good results in conjunction with a green contrast filter in the photomicrography of specimens stained with carbol fuch-
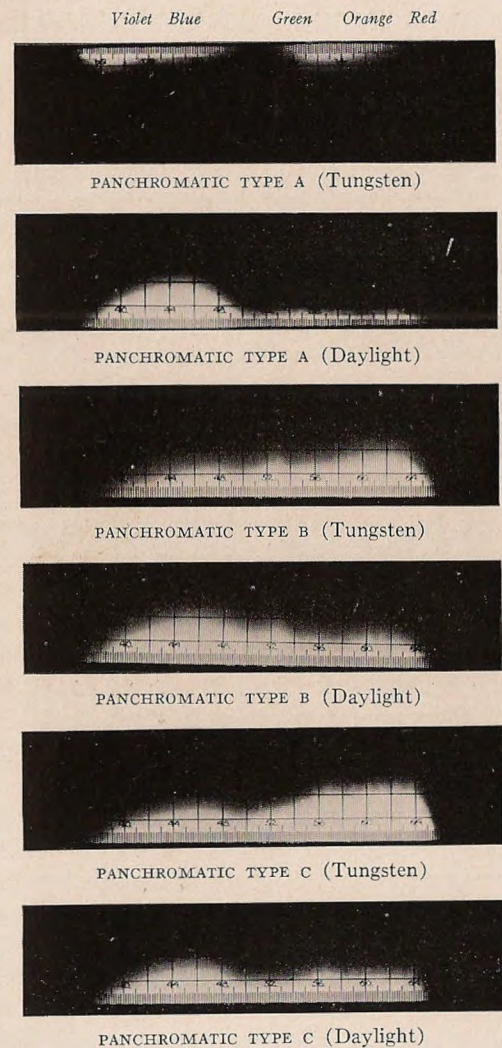

Violet Blue   Green   Orange Red

PANCHROMATIC TYPE A (Tungsten)

PANCHROMATIC TYPE A (Daylight)

PANCHROMATIC TYPE B (Tungsten)

PANCHROMATIC TYPE B (Daylight)

PANCHROMATIC TYPE C (Tungsten)

PANCHROMATIC TYPE C (Daylight)

FIG. 30. TYPES OF PANCHROMATIC EMULSION, A, B, AND C. (*Courtesy Eastman Kodak Co.*) Visible violet begins just before 400 mμ (40 on the scale), highest visible green is at 550 mμ, and red sensitivity ends at about 650 mμ, although the eye responds up to 700 or beyond.

sin, etc. On the other hand, dicyanin is a good sensitizer for deep red, leaving an insensitive gap in the green; such an emulsion is useful for work with a red or orange contrast filter for photography of designs, wood grain, photography through mist, and so on. Where work is required mostly in the orange region, and deep red sensitivity is not required, Orthochrom T, pinachrome and pinaverdol (Ilford Sensitol Green), can be recommended. Newer dyes, especially for the infrared region, are to be found in dicyanin, above mentioned, kryptocyanin and neocyanin.

The sensitivity of some panchromatic plates as manufactured by the Eastman Kodak Company is seen in Fig. 30; these represent the A, B, and C types of material. It will be seen that all of them exhibit the inherent sensitivity from the ultra-violet up to 500 mμ, but that the ratio this region bears to the region of longer wavelength varies. The upper spectrogram in each case represents the response to incandescent electric light, the lower one to daylight. Incidentally, these pairs give an excellent idea of the difference between daylight and artificial light as regards spectral distribution. It may be noted, too, that the red-sensitivity appears to extend further into the red in the case of incandescent light, but this, of course, is due to the greatly increased energy of the latter in the red region. As explained in the chapter dealing with sensitometry, the spectral character of the light must be taken into strict consideration in making any measurements of either the speed or the color-sensitivity of panchromatic emulsions. Many of the spectrograms published in the early literature are entirely misleading at first sight, because they were made with artificial light, often incandescent gas, and for the same reason any speed measurements of color-sensitive materials can be accurate only if the light sources by which they were obtained are specified. The undyed emulsion is sensitive up to 500 mμ, let us say. We then

add a new band of 500 to 600 mμ by means of a color-sensitizer to the response. Assuming the useful region in each case to begin in the near ultra-violet at 350 mμ, we have a response in the plain emulsion of 350 to 500 mμ, and of 350 to 600 mμ in the other; hence the area of response in the spectrum is five-thirds as great in the case of the sensitized emulsion as in the plain one, and its speed will appear proportionately greater if it be exposed in light which is rich in the added wavelengths.

The speed of a color-sensitive emulsion can thus only be estimated fairly by taking into account the spectral quality of the light. The speed numbers given by some manufacturers have in past decades been very misleading, because if correct color rendition of the blue-violet in monochrome is required in the studio, and the necessary filter be used on the lens to obtain it, the effective speed will be reduced again to what it would have been had the speed measurement been made by daylight or properly filtered tungsten light.

We now come to the infrared region of the spectrum, invisible radiation of wavelength extending from about 760 mμ onwards to 10^6 mμ. The early infrared region has recently become of considerable importance in aerial photography and in much industrial work, both of which are making rapid advance owing to the excellence of the infrared material that has become available. A plain silver bromide emulsion of the boiled type was prepared by Abney, and was claimed to be so red-sensitive that a kettle of boiling water was photographed by its own radiation. The author found that a collodio-bromide emulsion could be sensitized for the early infrared with Benzo Green. Sensitivity up to 800 mμ has also been obtained by bathing an ordinary plate for ten minutes in a five per cent solution of sodium bisulphite, washing in water for a few minutes, and then bathing again in a one and one-half per cent solution of sodium carbonate. Infrared sensitizing is now obtained by the

addition of dyes to the emulsion. Dicyanin was used in 1919, being discovered during the researches carried out during the 1914–1918 war to produce sensitizers that had previously been made only in Germany. Kryptocyanin was produced later, sensitizing for the region between 700 and 800 mμ, with a max-
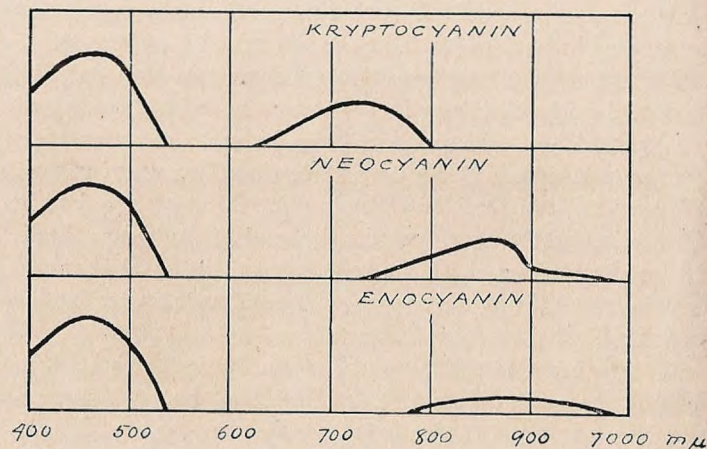

FIG. 31

imum near 750 mμ. It is a particularly interesting dye for experimental work because it can be used with little fear of fog, and will yield plates of good keeping quality. Later, in 1925, neocyanin was discovered, which extended the sensitive region to 950 mμ. One of the carbocyanins, xenocyanin, gives a maximum at 960 mμ and extends right up to about 1,200 mμ. Certain emulsions sensitized with it have a response up to 1,350 mμ. Some of the responses of infrared sensitive emulsions are seen in Fig. 31. Tetracarbocyanins have been prepared by Dieterle and Reister [6] which are claimed to sensitize two or three times as highly as the corresponding acetoxy-substituted dyes. A

method of preparing nonacarbo cyanins for infrared photography beyond 11,000 mμ is described by these authors. According to Clark,[7] plates which are to be used for spectrographic work beyond 900 mμ must be hypersensitized in order to obtain practically useful speeds. These later infrared sensitizers are not at present commercially supplied, but are prepared by manufacturers for their own use. Dicyanin, kryptocyanin and neocyanin, however, can be obtained.

In Fig. 32 is seen the most recent infrared introduction of the Eastman Kodak Company, which is applied to plates and films

Courtesy Kodak Limited, England

FIG. 32. WEDGE SPECTROGRAM OF INFRARED PLATE AND FILM FOR AERIAL PHOTOGRAPHY

for aero work. It has a wide band of sensitivity, but when this is restricted by the use of an infrared filter, the emulsion is stated to be many times faster than previously existing materials.

FILM PACK EMULSIONS. — Where separate emulsions are used in color-photography for the three primary images, plates may be used in a split-beam or one-shot camera, or films may be laid one over the other in the form of a sandwich and the rays from the lens made to pass through the top film to the one beneath it for the green impression, and thence to a third film which receives the red impression. In such a sandwich, the top film is an un-color-sensitized emulsion, sensitive merely to blue-violet.

For readier separation in a one-shot camera, three distinct emulsions are frequently used. One of these is panchromatic or red-sensitive, one orthochromatic or green-sensitive, and the third normal or " color-blind." When three films are used in

the form of a tripack, three *similar* emulsions are usually employed. The most obvious order is an upper ordinary or blue-violet sensitive film facing the lens with a green-sensitive film next, screened with a yellow filter which may be incorporated in the top emulsion or coated as a yellow filter layer on the base of the upper film or used as a thin sheet of dyed gelatin between the two films. This yellow filter also suffices to suppress the
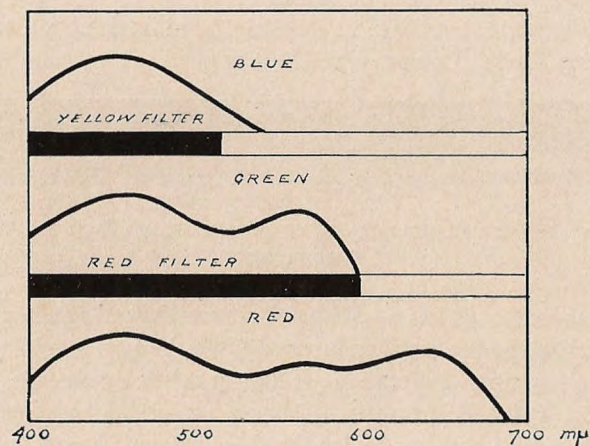

Fig. 33

blue-violet in the back (red response) film if the latter is made red-sensitive only and not fully panchromatic, as, for example, if sensitized with dicyanin. If it be panchromatic, then a red filter must be used. As there is already a yellow one screening the green-sensitive emulsion, the second filter may be magenta, since magenta + yellow = red.

Naphthol yellow or brilliant yellow serves as a good first filter dye; azo rubine, crocein scarlet or rhodamin G will then serve for the red screening component. The general scheme is

seen in Fig. 33. The filtered responses of a commercial tripack (Defender) are shown in Fig. 34. In any attempt to experiment with tripack emulsions, it must be remembered that as the three elements are exposed simultaneously, the relative *filtered* speeds of the three members must be equalized. The
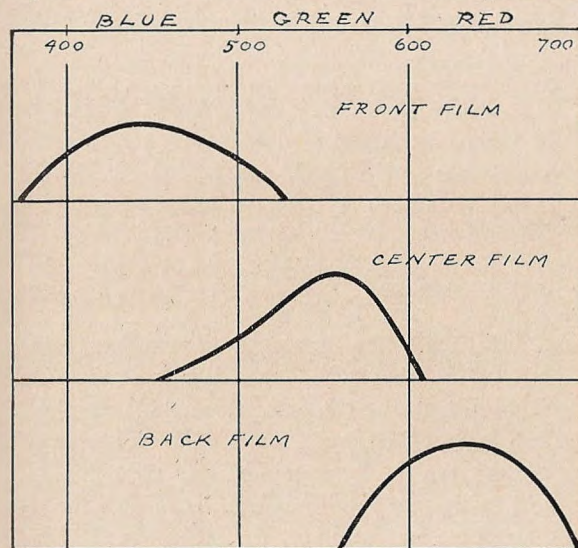
Fig. 34

light is considerably diminished by its passage through the front film, which must therefore have the highest possible transmission, but the lowest sensitivity. The intermediate or green-sensitive film must also be sufficiently transparent to admit of the necessary amount of light reaching the back (red) member. The Defender tripack utilizes more heavily coated emulsions for the blue- and green-sensitive components, so that higher contrasts may be obtained; this is of course the equivalent of allowing a longer time of development for the yellow

printer in three-color work. Alternatively, different types of emulsion may be selected, the aim being that the three images obtained on development are of equal gamma and as far as possible of similar density range.

The following typical specification is made up from data obtained from a number of published patents dealing with tripacks:

Front emulsion. Coating weight 40–50 mg per dm². Average grain size 1.2–1.8 μ. Speed 80–120 H and D. Percentage transmission to yellow light, 35–40%.

Middle emulsion. Coating weight 60–70 mg per dm². Average grain size 2 μ. Speed 250–300 H and D. Percentage transmission to red light, 30–35%.

Back film. Coating weight 110–130 mg per dm². Average grain size 2.5 μ. Speed 1000–1500 H and D.

In assembling the Defender tripack, the two front films, blue- and green-sensitive, are placed face to face, with the base of the blue-sensitive film facing the lens. The third member of the combination is faced lensward, shielded by a red coating on the base of the green-sensitive middle film. Experimental packs can be most easily made up by using glass plates for the front and back members and a film for the middle one. This fact is mentioned on account of the difficulty which may be experienced in coating film base in the laboratory with sufficient accuracy.

The filtering of the blue-violet rays from the green recording film, if not effected by the use of a self-screened emulsion, can be done with a very thin layer of gelatin stained with tartrazin or naphthol yellow between the two emulsions. As tartrazin transmits some ultra-violet, and aesculin or ultra-violet filter should be used on the camera lens. If the red filter takes the form of an actual coating on the back of the green-sensitive middle member, a dye such as Congo red, which is easily decolorized by an acid fixing bath, should be used. Carmine L,

lanafuchsin SB, and tolan red are also mentioned by Wall for this purpose.[8]

The use of a bipack is involved in *two*-color photography. Here the factor of the filter dyes and the speed of the emulsions must again be adjusted so that equal exposure is required in each member for a white object. For two-color work in daylight the Eastman Kodak Company recommends Wratten filters No. 28 and No. 40A, or No. 28 and No. 40 for incandescent tungsten light. Similar color analysis can be obtained by the use of two films as follows:

Front. A fully green-sensitized emulsion, using a Wratten Aero No. 1 or a K-2 filter on the lens.

Back. A panchromatic emulsion.

Interleaf. An orange filter between the two, or an orange coating on the base of the orthochromatic film, both emulsion surfaces facing the lens.

The performance of experimental two-color packs can be properly checked only by tests with the spectrograph (See Chapter XII).

The term monopack is used for a plate or film that comprises a series of non-separable emulsion layers coated one on top of the other, the emulsions being self-screened to effect separation, or dyed material being coated between the sensitive layers. Selective sensitization alone is not adequate. The idea dates back to 1891, when an English patent was granted to H. Kuhn. By straightforward development, the appropriate colors are obtained as silver deposits in each layer. These three black-and-white separation negatives are then converted into the respective color images either by the production of a dyestuff in the parts occupied by the silver, or by *destroying* dyes already incorporated in the emulsion layers, or by dissolving out the negative images and color-developing the remaining (unexposed) silver bromide.

In 1905, K. Schinzel, then a clerk but seventeen years old, coated a plate with three layers of emulsion, each layer being sensitized for one of the three primary colors, but dyed with the color complementary to it. Thus the red-sensitive layer would be dyed cyan, the green-sensitive layer magenta, and the blue-violet-sensitive layer yellow. It was Schinzel's idea, after developing and fixing the exposed monopack, to treat it with a weak solution of hydrogen peroxide. The dyes to be used were such that through the catalyzing action of the reduced silver they would be decolorized to an extent proportional to the different densities. *Color formers* instead of actual dyes were shortly afterwards suggested by this inventor.[9]

The first Mannes and Godowsky patent [10] described an upper self-screened emulsion layer on top of a rapid red-sensitive emulsion. This two-color monopack was developed and fixed in the usual way, the reduced images being afterwards converted into silver ferrocyanide, one for use as a mordant for a basic orange dye; this was done by means of a solution *the diffusion of which could be controlled*. The other (ferrocyanide) image was then toned with a blue-green toning bath. From this brief description, the beginning of the modern monopack can be appreciated.

A three-layer process was meantime worked out by Dr. Bela Gaspar, whose prolific patents date from about 1930. Using black-and-white separation negatives obtained with a split-beam camera, and making from them separation positives, he employed for motion-picture printing in color, nitrate film stock which was coated on one side with a blue-dyed emulsion and on the other side with first a yellow-dyed, and then a magenta-dyed emulsion. The dyes were destroyed on development in proportion to the presence of developed silver; the image was then bleached and the residual silver bromide converted into chloride, on which the sound track was developed. The whole film was then fixed in hypo and all remaining traces of silver

removed, leaving a dye image of great brilliance. Such film was of course applicable to printing only.

In a subsequent process,[11] a monopack for exposure in the camera is described. A blue-sensitive layer is coated on the support first, and this receives the lens image. On top of this are coated the green and red layers. A distinguishing feature is that, to speed up the material, dye generators, rather than actual dyestuffs, are used. The blue-violet emulsion, it is suggested, may contain about fourteen grams each of gelatin and silver halide per square meter; the yellow (complementary) dye generator being 0.85 gram per square meter of 1-phenyl-3-methyl-pyrazolone-5. The green emulsion layer is color-sensitized with 2-methyl-1-ethyl-pseudocyanin iodide, and contains a dye developer of one gram per square meter of 1-amino-8-naphthol-3:6-disulphonic acid, which is rendered insoluble through precipitation within the emulsion by triphenylguanidin acetate. This layer is made self-filtering by the addition of 0.75 gram per square meter of tartrazin. The top layer is color-sensitized with pinacyanol, using one gram per square meter of diphenylguanidin acetate, and colored by a suitable red dye. The film is developed, fixed, and washed, and the dyes in the two lower layers generated by treatment with a nearly neutral solution of:

Water 100   cc
Sodium acetate 10   g
Diazosulphanilic acid .... 0.5 g
This is used at a temperature of between 3° and 8° C.

The film, after being washed and dried, is treated with a blue dye solution, the dye being precipitated in the top layer. The dyes are then destroyed in proportion to the silver deposits of the images by treatment with an acid solution of thiocarbamide.

In the Kodachrome process, after straight development of the three primary images, the reduced silver is dissolved out and

the residual silver bromide is exposed and treated with a blue-green developer. An acid bleach is allowed to diffuse through the two upper layers, the lowest remaining blue-green. In the two upper layers the metallic silver is converted into silver chloride. This is next exposed and developed with a magenta-forming developer. Then follows the next bleach which is confined by controlled diffusion to the top layer only, where once again the dye is destroyed (magenta) and the silver converted into silver chloride. This is exposed and color-developed yellow, after which all that remains is to dissolve out the silver with a solution such as Farmer's reducer (ferricyanide and hypo).

It had been known at the time of the early experiments that many developers produced more or less insoluble dyes by interaction with the silver deposit. Pyrogallol, the oldest known, gives orange, amidol yellowish-red, while blue dye images are given by leuco-indophenols and leuco-indamines and indoxyl. Red images are given by the leuco-azomethines and thio-indoxyl. However, in alkaline (carbonate) solution they are readily re-oxidized by atmospheric oxygen with the production of colored fog. The chemical story of the investigations which led to modern solutions of the problem is well told by Karl and Ludwig Schinzel in their various articles in *Das Lichtbild*.

In any experimental work on monopacks, where dye generators which are either insoluble or not diffusible, are mixed in the emulsion layers, the remaining unused generator must be easily washed out; for example, with caustic alkali. The above authors [12] state that for color photography by simultaneous color development, coupling components which give the appropriate dye in each layer with the oxidation products of a suitable developing agent or by simultaneous oxidation by the silver halide, must be mixed in the three layers.

The insoluble salts of the naphthols or their derivatives and

analogues, the arylsulphonamines, pyrazalones and acidic methylene compounds can be added to the layers. Calcium or barium hydroxide, guanidin or sodium glycocollate may be added to maintain stability. The carboxyl or sulphonic acids of couplers may be added to the layers in the form of insoluble or barely diffusible salts with inorganic or preferably colloidal organic bases. The coupling component is used in quantity equal to about one-half of that of the silver halide present. A developer containing one per cent of p-amino-dimethylanilin hydrochloride and five per cent of sodium carbonate is recommended.

One of the difficulties in tripack manufacture is the thinness of the emulsion layers, which is indispensable in order to avoid scatter. Present day precision coating machines are capable of coating layers which when dry are as low in thickness as 3 to 4 μ. Optical contact, *i.e.*, the actual coating of each layer on top of the other, is necessary and the three coatings of a monopack must provide definition which it is impossible to obtain with any form of tripack in which three separate films, however thin, are employed.

The chemistry of direct and indirect dye couplers and of color formers has already given rise to a literature of its own, and it is impossible to do more than touch on some of the aspects of the monopack and its problems, in these pages. Recourse to the patent literature is necessary to any form of study, though an immense amount of information will be found in the articles of the Schinzel brothers already mentioned.

For the purposes of experiment, when two (or three) layers of emulsion have to be processed, an addition of alcohol and glycerin to the bleaching solution will help to prevent penetration to the lower layers. The actual emulsion used can be made to assist in this direction also; thus the lower emulsion, first coated, may be made with a gelatin having a low water absorp-

tion coefficient, which is in turn hardened to the maximum extent, while the upper emulsion is made with a soft gelatin which swells readily and to which a small proportion of sorbitol is added. It should be pointed out, however, that only comparatively crude experiments can be envisaged with monopacks without refined facilities for both coating and processing.

Although it is beyond the scope of this book to enter into the manufacture of emulsions containing color formers, the following formulas for producing colored images by direct development of silver bromide emulsions may be given. A basic developer is used as follows:

Sodium carbonate	40	g
Sodium sulphite	20	g
2-amino-5-diethyl aminotoluene hydrochloride	0.5	g
2 per cent potassium bromide	30	cc
Water	1000	cc

The blue-green coupler is:

2-4-dichloro-1-naphthol	1	g
Acetone	5	cc
Basic developer	250	cc

The magenta coupler is:

p-nitrophenylacetonitrile	0.05	g
Acetone	5	cc
Basic developer	250	cc

The yellow coupler is:

Aceto acetanilide	0.5	g
Acetone	5	cc
Basic developer	250	cc

The image is formed in color on development with the above solutions, and is afterwards fixed in plain hypo solution. The reduced silver is then removed by treatment with hypo-

ferricyanide when the clear dye images are left. In triple-coated film it is conceivable that the dye couplers could be incorporated in the respective emulsions, the one basic developer then producing simultaneously the three colored images. In the formation of such a monopack it would facilitate production if a very thin layer of 3 to 4 μ of gelatin were coated between each emulsion layer as is done in the case of Kodachrome film.

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CHAPTER VII

X–RAY AND ULTRAVIOLET

X-ray Emulsions — Intensifying Screens — Lippmann Emulsions — Ultraviolet Plates.

IN the first few years following Roentgen's discovery of the X-rays, it was found by empirical experiment that plates coated with a slow silver bromide emulsion containing the least possible quantity of silver iodide, gave the fastest response. High speed to visible light had very little to do with the matter. It must be remembered that at this time X-rays were produced with very crude tubes, excited by Ruhmkorff coils fitted with the old hammer type of interrupter, capable of giving a spark in air of only a few inches. Exposures of as much as thirty *minutes* were quite common for thick parts of the body, and it was not at first understood that short-wave radiation had a greater penetrative power, without which the longer waves could not produce a result, no matter what *quantity* of energy was used. Fig. 35 shows how the penetrative power increases with decrease in wavelength in the case of aluminum.[1]

While the action of X-rays on photographic emulsion films is very similar to that of visible light, examination of microscopic sections through the developed film shows that the rays produce an equal distribution of grains of reduced silver throughout its whole thickness. It is thus evident that greater density can be obtained by increasing the thickness of the layer of sensitive silver salts, or alternatively its silver halide content. As stated, however, X-rays of different frequencies do not have an equal quantitative effect, and while the shorter wavelengths

are needed for penetration of deep or thick parts of the body or for metallographic work, the shorter or " soft " rays produce the greatest blackening. For study of the sensitometry of X-ray photography the reader is referred to the work of Wilsey and Pritchard.[2]

In medical practice, the peak voltage used, which is a direct measure of the penetrative power, varies between 35 and 90
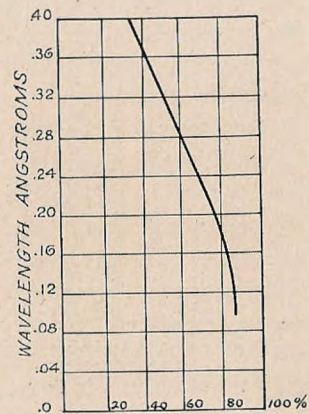
FIG. 35

kilovolts. This is ordinarily obtained from a transformer, and after rectification is applied to the tube. The modern X-ray tube has a cathode which is heated by a local circuit, and as the heat is increased, so the electrons emitted by it lower the resistance of the path between it and the *anode*, and so control the hardness of the radiation generated at the anode surface. Over this range the one type of X-ray emulsion functions so satisfactorily that different emulsions have never been made for work in different parts of the X-ray spectrum.

According to Charlesby,[3] the response of a photographic emulsion to incident X-radiation is appreciably affected by the

absorption of the beam within the film layer, a fact that must be taken into consideration in X-ray sensitometry. This point is mentioned, inasmuch as X-ray plates are used to some extent in the measurement of radiation, which is determined by their photographic blackening powers under controlled development.

During the first years of X-ray photography, numerous substitutes for silver *bromide* were investigated, the trend of thought being that heavy salts of silver (such as silver tungstate, for example), or perhaps salts of heavy metals themselves, having a high molecular weight, would absorb more of the radiation and convert it into chemical energy. An alternative thought was that the addition of heavy, inert metallic salts incorporated in the emulsion might add to the effect of the exposure by secondary or scattered radiation. The results of countless experiments in these directions ended in a verdict for straight silver bromide; but as the rays were only partially absorbed by their passage through an ordinary emulsion layer, it became obvious that the plates should be coated as richly as possible. Hence coating weight was increased from, say, 120 milligrams per square decimeter to 180 or more milligrams, in some cases by giving a double coating. Too thick a film has, however, many disadvantages.

Plates of excellent service were produced along these lines, reducing exposure to a fraction of what had previously been necessary, and at the same time immense advance was made in the construction of apparatus for producing the high tension supply and in the tubes themselves. A very important advance was next made by the introduction of so-called intensifying screens. A piece of card or celluloid coated with a layer of artificial Scheelite (calcium tungstate), glows a brilliant blue to bluish-white under the influence of X-rays, and the fluorescence excited provided photo-actinic light about five times as

effective on a silver bromide emulsion as the original rays. Hence by placing the active surface of such a screen in close contact with the emulsion film during exposure, the latter was so greatly reduced that the great bulk of radiographic work quickly came to be done with intensifying screens. In so doing, the problem of the emulsion maker was somewhat changed in complexion, for now emulsions were needed which were sufficiently sensitive to X-rays themselves, but had also an optimum response to the blue rays fluoresced by calcium tungstate.

The fact that only a low proportion of the incident rays is absorbed by both intensifying screen *and* emulsion, led to the idea of coating film base with emulsion on both sides, when two intensifying screens could be used, one on either side of the double-coated film. An English patent was applied for by the author in 1916 for the use of two intensifying screens in this manner with thin glass plates (X-ray film had barely made its appearance at this time), but the diffusion of the image on the far side owing to its separation by the glass, led to its abandonment. Later, a double-coated film of magnificent quality, made by the Eastman Kodak Company, overcame this problem of definition, and double-screen technique became standard practice, except where the finest possible definition was required, or for " thin " subjects such as hands, wrists, etc. The grain of the calcium tungstate crystals not only tends to give a slight granularity to the image, but each tiny crystal acts as a source of secondary radiation which throws off rays of the same wavelength as the original beam in all directions, and so causes diffusion. The general use of intensifying screens naturally led to some attempts to modify the emulsions, as at least eighty per cent of the exposure reaction is probably that obtained from *visible* (fluorescent) light. At one time plates were even specially manufactured having a maximum response to that part of the spectrum and having a normal coating weight. Present-

day emulsions, however, are composed chiefly of silver bromide and can be used equally well with or without screens.

Yet another change is now affecting the position. Inasmuch as a full exposure for a deep part of the body involves gross overexposure of the soft tissues, detail in the latter is necessarily lost. To overcome this drawback, a plain X-ray film is being used in many cases on top of the sandwich of intensifying screen — double-coated film — lower intensifying screen, so that it receives relatively only about one-tenth of the effective exposure of the double-coated film. The un-intensified film thus gives the detail in the soft parts, while the screened film is correctly exposed for the main subject. A method was patented by Dr. Leonard Levy and the author [4] for incorporating the calcium tungstate in cellulose acetate base when casting the latter, so that the film would be automatically self-screening.

A general emulsion for X-ray work, providing the necessary density and gradation, and suitable for use with or without screens, may be made as follows:

A. Water .... 3000 cc
   Nelson's X-opaque gelatin .... 360 g
   Ammonium bromide .... 520 g
   Potassium iodide .... 6 g

B. Silver nitrate .... 600 g
   Water .... 150 cc
   Stronger ammonia water .... to redissolve

C. Silver nitrate .... 200 g
   Water .... 800 cc
   10 per cent nitric acid .... 10 cc

Weigh out the salts and gelatin in *A* and allow them to stand in the water for four hours. Raise to 110° F. (43.3° C.) and cool back to 90° F. (32° C.). Add *B* rapidly from a jug at room temperature with gentle stirring. After an interval of three minutes, add *C* at 120° F. (49° C.) through a four milli-

meter nozzle, with rapid stirring. Then immediately add 800 grams of American Agricultural Co.'s high viscosity gelatin, and stir until dissolved. The crock is stirred while pouring in the gelatin powder. Take to 105° F. (40.5° C.). Then set quickly in cold small crocks in ice water. Wash after twenty-four hours until free from ammonia, then digest from one to two hours at 120° F. (49° C.).

Final additions are:

   2 per cent solution of phenol in spirit .... 600 cc
   5 per cent chrome alum solution .... 50 cc
   10 per cent potassium bromide solution ...... 100 cc

Total bulk is 12,000 cc. Recommended coating weight, 200 to 220 milligrams per square decigram.

A practical reason for keeping the iodide low is that in fixing tanks such as are generally used, a high percentage of silver iodide will accumulate in the hypo solution and will convert part of the silver bromide in films subsequently immersed into silver iodide, which takes very much longer than silver bromide to fix.

Before leaving the subject of X-ray emulsions, it should be stated that investigations in recent years have indicated that fluorescent screens glowing a color other than that of calcium tungstate, for example green or orange, might be usefully employed in conjunction with a highly color-sensitized film. A zinc sulphide screen, for example, fluoresces bright green or bluish-green according to the method of manufacture, and with an orthochromatic emulsion will admit of excessively short exposures. Levy and West [5] have done much work in this direction, and have evolved a special screen for this technique. Whereas the fluorescence spectrum of calcium tungstate extends roughly from 370 to 470 mμ, that of their " fluorazure " screen is compressed into a sharply defined spectral band extending from 390 to 490 mμ.

ULTRAVIOLET SENSITIVE EMULSIONS. — While silver grains are sensitive to light of practically all wavelengths shorter than the visible violet, the ordinary emulsion shows a distinct slackening off in response at 280 mμ. This is primarily due to the natural opacity of gelatin to the ultraviolet. The response of the emulsion decreases steadily as wavelength decreases, showing a marked drop at 240 mμ, and ending altogether at about 200 mμ. Some attempts have been made to sensitize emulsions to ultraviolet by the addition of a sufficiently concentrated solution of sodium salicylate (Tien-Kin). Application is also made to the surface of the emulsion of oil or vaseline, which absorbs ultraviolet energy and converts part of it into fluorescent light of longer and more photographically active wavelengths. Diminution of the gelatin vehicle, with a consequent exposure of the silver bromide filtered with a minimum of colloid, still remains the best practice, as originally suggested by Schumann,[6] whose name is usually associated with this type of plate.

Schumann's technique is as follows: a plain silver emulsion is prepared, rather weak in gelatin. A five per cent concentration of gelatin is suitable. The quality of the gelatin is stated to play an important part, and Nelson's No. 1 is particularly recommended. The emulsion is ripened and digested at one operation by heating to 140° F. (60° C.) for a sufficient time, and is then set in ice water and washed. Very pure ingredients should be selected and, as a small trace of organic matter appears to be prejudicial, freshly distilled water should be used throughout. By keeping the washing water cold (42° to 45° F.), swelling of the gelatin will be minimized. The washed emulsion is next diluted with a large volume of hot distilled water, breaking it down to a fraction of the usual concentration, and this very dilute emulsion is poured into a scrupulously clean tank on the bottom of which has been placed the glass plate that is to be coated.

The temperature should not be above 65° F. for this sedimentation operation, otherwise there will be a tendency towards halation. The silver bromide, with just enough associated gelatin to make it adhere to the glass in a good continuous film, deposits gradually, and when the coating is sufficient the supernatant liquor is very carefully drained off and the plate allowed to dry in a flat position. Using a fluorite prism, and plates prepared in the above-indicated manner, the whole apparatus being in vacuo, Schumann is stated to have photographed the spectrum of hydrogen to 120 mμ.[7]

The individual worker will find by experience the best procedure with his own working conditions and apparatus. Plates so prepared are insensitive to light of longer wavelength than about 300 mμ. While Schumann worked largely with a pyrogallol-soda developer, Lyman[8] recommends an ortol-potash formula. Any free bromide in the developer appears to increase the grain size of the image, and for that reason should be avoided.

An alternative method of treating plates coated with a slow or medium speed emulsion such as an X-ray type has been given by Duclaux and Janet.[9] The plates are placed horizontally in a dish or tank filled with ten per cent (by volume) of concentrated sulphuric acid in water, and are kept for four hours at about 77° F. They are then carefully removed and washed in a very gentle current of water, and then dried. The treatment has the effect of removing both gelatin and silver, except for a very thin layer. This is stated to give plates two hundred times faster than commercial Schumann plates.

LIPPMANN TYPE EMULSIONS. — This type of emulsion yields a color-sensitive, fine-grained plate suitable for experiments with the well-known Lippmann process of natural-color photography. The process depends on the interference of light waves traversing the emulsion before and after reflection from the

back of the plate, which is in contact with a mercury mirror. It thus necessitates an exceedingly fine grain; Lippmann emulsions are usually referred to, in fact, as *grainless*. A method described by Lehmann is as follows:

A solution of gelatin is first prepared:

A. Hard gelatin	20 g
Water	390 cc

This is dissolved and filtered through spun glass (glass wool) or cotton batting (wadding) and used at 95° F. (35° C.).

To 80 cc of the *A* solution add

Distilled water	10 cc
Silver nitrate	4 g

To the balance of solution *A*, add and dissolve 3.2 g of potassium bromide. Taking care that there is no froth on this, it is slowly poured into the gelatin-silver solution at the same temperature, stirring fairly gently during the precipitation and for three and one-half minutes afterwards.

The following sensitizing dyes are then added immediately:

Pinacyanol (1:1000 alcoholic solution)	4 cc
Orthochrom T (1:1000 alcoholic solution)	4 cc
Acridin Orange (1:500 alcoholic solution)	4 cc

This mixture of dyes must have been previously warmed to 86° F. (30° C.). It is added slowly with gentle stirring, not more than forty-five seconds being taken. Under no circumstances must the emulsion be subjected to any further heating, the object being to avoid grain growth and fog formation.

A very thin coating is applied to glass which has been so perfectly cleaned that, if breathed upon, the condensation is even all over and clears quickly. The coated plates are laid on a cold slab to set, and are then washed in a trough with gently running water. Ten minutes should suffice to remove the potas-

sium nitrate. The washed plates are best dried in a horizontal position; this is stated to give the most brilliant colors.

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Chapter VIII

COATING EMULSIONS ON GLASS

Preparation and Cleaning of the Glass — Substratums — Drying Cupboards and Drying Problems — Coating Heads — Ventilation and Heating

THE coating of negative and positive emulsions on glass, at one time the only support available, suffered a severe setback when rollfilm, and later cut film, came into such general use. Plate coating has nevertheless been continuously maintained on a large scale, particularly for the South American markets, and in recent years certain advantages over film base possessed by glass, especially in the photo-mechanical industries, have brought about a decided return to the dry plate. The study of silver halide emulsions necessarily involves coating and testing them upon a suitable base, and for laboratory and investigation work glass is definitely, except where matters specifically relating to film technique are involved, the most satisfactory medium, especially as it lends itself so well to hand coating.

Carefully filtered emulsion of suitable viscosity is coated upon sheets of chemically cleaned glass. A known quantity is poured on and distributed evenly over the surface while warm, any excess over the desired amount having been previously poured *off*. The coated glass is laid on a cold levelling table, where the emulsion sets to a firm jelly within thirty to sixty seconds. The set plates are placed in a dust-free dark cupboard to dry, where they may remain for from four to twelve hours, according to the temperature and humidity of the cupboard and efficiency of the ventilation.

In commercial practice, the glass sheets are washed by a machine in which they are made to pass between reciprocating

brushes and rollers. A cleansing solution such as soda is sprayed on them during their passage through the first part of the machine. They next pass through water sprays, then between rubber rollers which squeeze off the superficial water, and are finally sprayed with a weak solution of chrome alum or sodium silicate, which leaves the surface with a *substratum* or " tooth " which serves to anchor the emulsion to the glass surface and to prevent the danger of frilling or blistering during the processing of the plates.

The chief commercial sizes of plates in use in the United States are 4 by 5, 5 by 7, 8 by 10, 11 by 14 and 14 by 17 inches. Larger sizes are used in photo-engraving work and commercial photography. Four by five plates are coated as 8 by 10 and cut, when dry, into quarters; 5 by 7 would be coated as 7 by 10 and cut into two. The most popular English sizes are $3\frac{1}{2}$ by $2\frac{1}{2}$ (the higher figure is quoted first), $4\frac{1}{4}$ by $3\frac{1}{4}$ (quarter-plates), $6\frac{1}{2}$ by $4\frac{3}{4}$ (half-plates), $8\frac{1}{2}$ by $6\frac{1}{2}$ (whole-plates), 10 by 8, 12 by 10 and 15 by 12 inches. The gauge of the glass increases with the larger sizes; the sheets themselves run about one-sixteenth inch short of the nominal size in either direction to insure easy fitting in plateholders.

The sheets of glass are delivered in crates, and require a certain amount of sorting. The glass must be fairly flat, uniform in thickness, and as colorless as possible. It must also be free from bubbles and flaws. Drawn glass, which has come into use recently, may have slight channelings, the worst of which must be rejected, but " flat " negative glass is ordinarily slightly curved, and the concave side is placed uppermost on the coating machine. The plates, after washing and drying, must be inspected to make sure they are all concave side to one direction so that no delay is caused in feeding them to the machine.

It is never advisable to use old negative glass from which the

developed film has been removed. The original image is liable to appear as a " ghost " in the newly exposed picture, and is probably the explanation of the only genuine " spirit " photographs which have puzzled laymen. Clerc states [1] that it may be supposed that the presence of ultra-microscopic particles, probably of metallic silver in solid solution in the glass, are the cause. Suitable glass in small quantities, known as negative glass, can be obtained for experimental purposes from suppliers of photo-engraving materials, such as Geo. Murphy, Inc., of New York, etc., or of course from any firm of glass merchants.

A solution of potassium dichromate of two ounces to the pint, to which two ounces of sulphuric acid has been very cautiously added slowly, with stirring, is very useful for cleaning small quantities of glass for experimental work. It may be applied with an old, flat nailbrush, but rubber gloves should be worn and care taken not to get any splashes on the face or skin, as the chromic acid is very corrosive. The glasses must be very thoroughly washed under the tap afterwards and put into a clean plate-rack to dry; this rack should be kept entirely for this purpose. Another method is to brush them with a hot two per cent solution of caustic soda, afterwards washing thoroughly under the tap. Substratuming is done by dipping them into a dish containing a two per cent solution of chrome alum after the final rinse and racking them *without* further rinsing. They should be dried in a perfectly dust-free cupboard.

As a great deal of the success with test emulsions depends on the efficacy of the drying cupboard, this should next be described. Dust and bacteria are arch enemies of the plate maker. Mold spores are invariably carried on dust particles. A speck of dust dropped on to the gelatin-coated glass may deposit a spore which finds an ideal medium for growth, especially if the plates are dried slowly in a somewhat humid warm atmosphere. The gelatin itself, in the process of manufacture, may

pick up bacteria which remain latent and will ultimately infect the emulsion. Certain types of bacteria develop below the surface (anaerobic types), and cause the formation of tiny liquefied local spots. Micro-organisms in some cases produce alkaline growths, in other cases they are acid. The acid growths will desensitize the emulsion and usually produce white spots in a negative. The alkaline growths tend to produce black
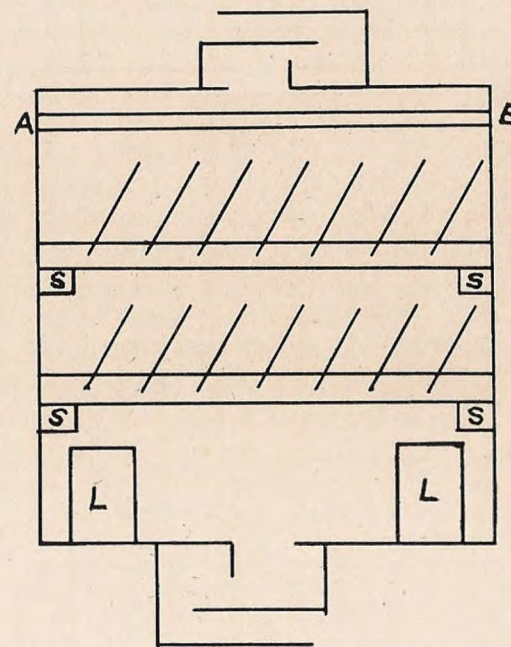
FIG. 36

spots. There is plenty of dust in addition which carries no bacterial infection, but which, if it settles on the film while the plates are drying, may produce spots of one kind or another, or alternatively may cause scratching of the emulsion if the

plates are packed film to film. The usual procedure, of course, is to pack plates with thin card edge-separators between each pair of plates.

A diagram of an easily constructed small cupboard is shown in Fig. 36. If made 36 inches wide inside, 36 inches high, and
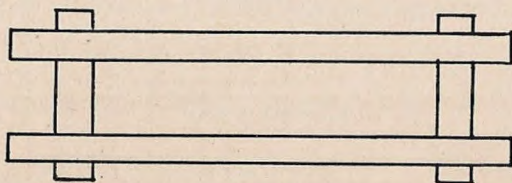

FIG. 37

12 to 14 inches deep it will accommodate a couple of dozen plates or more, 5 by 7 or 8 by 10 inch size, in two racks as indicated. The racks are made movable, resting on the supports *SS* as shown in the figure. If experimenting with papers, several strips of coated paper can be suspended from the crossbar *AB*. Each rack will require two 1 by $1\frac{1}{2}$-inch wood bars, their length being just under the width of the cupboard, attached to two cross pieces as indicated in Fig. 37, so that the complete rack can

FIG. 38

be laid on the supports. The rack bars must be notched at equal intervals as shown in Fig. 38, to support the plates more or less vertically. Ventilation, top and bottom, must be fully light-trapped. An entry at bottom and exit at top can be built up

with baffles in any simple way with a little ingenuity. Two 15-watt Mazda lamps, *LL*, completely concealed by inverted cans with baffled ventilation holes, will provide ample heat for a cupboard of this size, the hot air rising and causing some circulation. The temperature should not rise above 90° F. The cupboard can equally well be mounted on the wall an inch or two above a radiator, the inside lamps being then unnecessary, or a concealed heater such as an electric flatiron, used in series with a resistance to reduce the heat, may be adopted. The heat in any case should not be switched on until the plates have been in the cupboard for at least half an hour. A door is not shown in the figure, but it is best made practically the entire size of the cupboard. It must of course be made thoroughly light-tight, and the whole of the inside should be painted with dead-black varnish.

The coating of the glasses requires to be perfectly even, of a carefully controlled thickness, and free from spots, bubbles, or blemishes. Emulsion is not, as a rule, used the day it is prepared, but is set off after making up and filtering, and re-melted for coating next day, with practically no stirring. Before the coating, it is warmed to 105°–110° F. and stood for
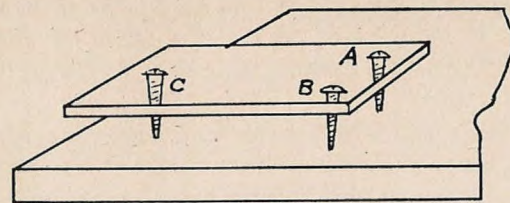
FIG. 39

from fifteen to thirty minutes. A convenient levelling table can be made with a sheet of plate glass three-eighths or one-half inch thick, resting on three two-inch nickel screws (Fig. 39).

The screws are set only about half an inch into the bench or table, leaving an inch and a half above it. Care must be taken that if two such screws are in line, the third must be placed symmetrically at right angles to this line, so that the three screw tops form the corners of an equilateral or isosceles triangle.

The plate glass is laid on top of the three screws and levelled. Setting a spirit level along a line between the two screws *AB*, these are adjusted until that side of the glass is dead level. The spirit level is then laid at right angles, that is, along the line from *C* to *AB*, and screw *C* is adjusted. Butterfly flanges may very usefully be soldered on to the under part of screws so that they can be turned without having to lift the glass plate every time. A piece of 12 by 16-inch glass is a useful size, taking four 5 by 7 or half a dozen 4 by 5 plates comfortably at one time. The plate glass should be kept in a dish of cold water at about 40° F. until just before coating, and the plates laid on it wet, without wiping the surface. For the sake of uniform work it is recommended that the plate glass be cooled to about the same temperature on every occasion. The glasses themselves should be on the warm side, about 70° to 75° F. to assist even flow of the emulsion. Elaborate setting devices made of metal with plate-glass tops, into which ice-cold water or warm water can be run at will, are used by some, but the simple method just described leaves little to be desired from the point of view of results.

Keeping the size 5 by 7 inches as a good working unit for test work, the volume of emulsion needed per plate is about ten cubic centimeters. Transparency or lantern plates are best coated with six to eight cubic centimeters, but if this is found difficult to distribute evenly, the emulsion may be diluted for coating proportionally. A simple trick of getting the exact coating weight is to use two little beakers as shown in Fig. 40. One, *A,* is clearly marked with a black stripe at a measured

content of, say, 20 cc. The other, *B*, is similarly marked at a content of 10 cc. Beaker *A* is filled with emulsion at about 100.° F. to the mark; to avoid bubbles, a piece of washed out cheesecloth or coarse muslin is laid over the top when pouring in. The whole lot, in this case 20 cc, is poured quickly on to
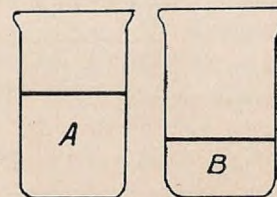
FIG. 40

the middle of the glass plate, which is balanced on the tips of the thumb and fingers of one hand. Quickly, but gently, the glass is tilted so that the emulsion runs to one corner furthest from the coater. It is then tilted in the other direction until it runs to the opposite far corner. By further tilting, it is made to run to the opposite *near* corner, then over to the other near corner. It is given a deft twirling movement to even out the emulsion, and then sufficient emulsion is poured off the glass into beaker *B* to fill it up to the 10 cc mark. The volume of the emulsion left on the plate is obviously the difference between 20 and 10 cc, or the amount required for the area in question. If the glass is not cold, and the emulsion is of the right temperature and viscosity, it will remain perfectly fluid during this operation and will level out nicely. The coated plate is then immediately taken by the other hand at one edge — thumb at the edge and fingers below the glass — and laid on the cold levelling table, and left there until set.

A little practice will make coating come quite easily, and it will be found that plates up to 12 by 15 inches can be coated

quite evenly in this way. But while it is somewhat extravagant, it is strongly recommended that preliminary coating experiments be made with emulsion in white light until the knack has been acquired. The concave side of the glass is coated, and this can be seen by looking along the edge of the glass when held in a vertical position on a level with the eye.
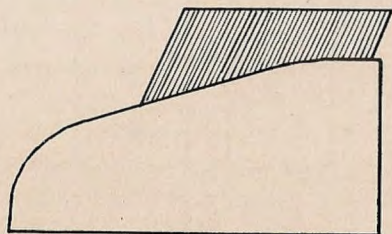

FIG. 41

Setting depends, of course, upon the quality of gelatin used, its concentration, the amount of heat which has been applied, and the finals present in the way of spirit, chrome alum, alcohol and so on. Certain proprietary chemicals are sold to reduce surface tension, and these affect coating to some extent. It should be contrived, from a purely mechanical point of view, that thirty seconds suffices to set the emulsion so that it can be lifted from the levelling table and transferred to the drying cupboard. Evenness of coating can be detected instantly by looking through the coated plate at a low candle-power, clear Mazda bulb. This should not be done with every plate, as it may cause fog. Hand coating of panchromatic plates requires some practice on account of the very low light in which it has to be done, and the curious fact that perspective seems lost in the dim green light of the panchromatic safelight. It is fortunate, however, that panchromatic emulsions are far less sensitive when wet and that, provided *direct* rays are avoided, a

comfortable amount of light is permissible. If the tests on processing show fog, coating light should always be suspected before chemical trouble.

In commercial coating, the glass, having been washed, dried, and stacked in a convenient wooden box (Fig. 41), with the concave sides all one way, is placed on a table near the coating machine, and slightly warmed to a temperature of about 75° F. The sheets are fed on to the machine, the operator wearing white cotton gloves. The principle of the coating machine is indicated in Fig. 42, where the glasses are fed on to a " band " of small diameter rollers, almost touching, which are seen revolving in a clockwise direction. As the plate is laid on the rollers, it is carried forward until it passes under the coating head or spreader, indicated by S. It emerges coated with emulsion and passes on to an endless band of felt or blanket running over
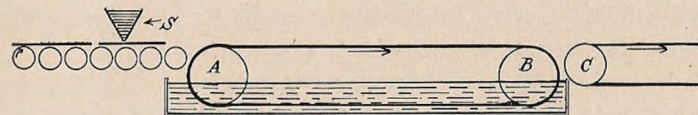
FIG. 42

rollers *AB*, the lower half of the band passing through a tank of cold water to keep it at a sufficiently low temperature to insure setting by the time the coated plate has traveled to the end of the run. The set plates then pass on to a contiguous endless band running over rollers *C*, which are driven at a slightly faster speed. This causes the plates to become separated by intervals of about half an inch, so that they can be easily picked up by the taker-off at the extreme end of the run. The plates are racked, and as each rack is filled it is carried away by another operator and placed in a section of the drying cupboard.

Many variations of this general scheme are naturally possible. In place of the endless band of felt, for example, two parallel metal chains running over a slate or plate-glass bed are frequently used. Chilled water runs along the bed, and the plates actually ride along on the chains with a film of water in contact with the under side. In all cases, it is usual to make a tunnel of the part of the machine where the coated plates are setting, with a light wooden or metal cover, in order to make the travel dust-proof.

A matter that should not be passed over in connection with commercial production, is that certain individuals appear to have a bad effect on the emulsions, and it has not infrequently happened that a man who may be a good coater cannot be employed in this part of the factory. In spite of wearing cotton gloves and although modern hygiene and ventilation, etc., would appear to make such a contingency ridiculous, personal contact and handling of emulsions makes it necessary to suspect and check up personnel when trouble from fog arises after all other likely causes have been properly investigated.

The greatest variation in coating machinery for plates is probably to be found in the character of the spreader. The simplest possible form is that of a V-shaped trough made up of two pieces of flat glass, ground dead true at the bottom; these are inclined to each other at an angle of about 40° by means of two wedge-shaped pieces of wood which also form the ends. As indicated in Fig. 43, the bottom edges of the glasses do not quite meet, but leave a parallel-sided slot of about a sixteenth of an inch, easily adjustable in putting the trough together, through which the emulsion passes to the glass plates as they travel beneath it. The four pieces — the two triangular ends and the glasses — can be taken apart and cleaned after each coating, and then reassembled by means of suitable clips to re-form the spreader. The complete V-trough is supported by uprights at

the sides of the machine, the height above the travel being adjusted to the thickness of emulsion film required. The emulsion is introduced into the trough from a tap leading from a jar standing above the machine, and is maintained at a constant level *in* the trough. In spite of the great simplicity of the V-spreader, in skilled hands it remains one of the most satisfactory coating appliances in practice.
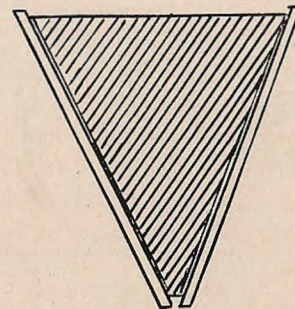
FIG. 43

A more elaborate spreading device was invented by James Cadett, which consisted of a number of tiny silver pumps placed in line, which delivered the emulsion from a number of points to the spreader proper, the length of throw of the pump pistons regulating the volume of emulsion delivered. By controlling this throw, and the rate of the endless band carrying the glass, a very exact quantity of emulsion could be delivered. The emulsion was run out from the pumps on to a silver plate of slightly less width than that of the glass to be coated, and in front of it was a silver roller suspended on cords which almost touched the surface of the plates and distributed the emulsion evenly over the whole width.

The cascade spreader is another type. Here the emulsion is delivered from a tap or set of pumps into a small trough

formed by a strip of silver, AB (Fig. 44), attached to a small tube of silver, T. When the emulsion has filled the trough to the height of the top of the tube, it flows over and falls down
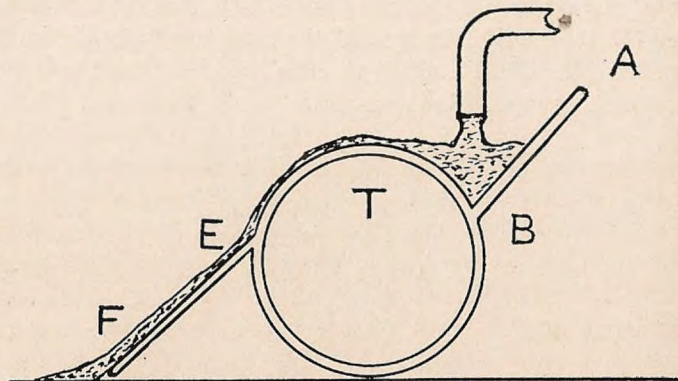

FIG. 44

the cascade, EF, which is another strip of silver sheet, the lower end, F, of which comes below the tube, T, and under which the plates pass in the direction indicated by the arrow. Sometimes a thin strip or " apron " of linen or paper is attached to the bottom of the cascade to provide a more flexible " lead on " to the glass surface. Here again some convenient type of constant level apparatus may be used to control the amount of emulsion falling into the spreader, or it may be controlled by a series of Cadett pumps.

As an example of a commercial plate-coating machine [2] the following details may be quoted:

Feeding-on belt .... 4 ft., 6 in.
Adjustable " fence " for guiding the glass in center of this belt 1 ft., 9 in.
Endless belt under emulsion spreader, kept warm by warm
    water in which the lower part of the belt travels .... 3 ft., 3 in.
Washing rollers to clean under-side of the coated plates ..... 1 ft., 0 in.

First endless belt for levelling out of emulsion, with separate
    under tank of cold water .... 5 ft., 0 in.
First setting belt .... 7 ft., 0 in.
Second setting belt .... 7 ft., 0 in.
    These two are kept cool by water from one long tank below.
Dry blanket belt .... 5 ft., 0 in.

The total overall length of the machine is thus about 34 feet. The setting belts may be of cord, ribbon or flat gauze. Over them is a nineteen-foot cooling tunnel provided with cold coils which cause cool air to fall on the surface of the plates.

A number of points must be taken care of in any form of plate coating. It is hardly necessary to say that uneven distribution is a grave fault, as is any form of streak or friction line running along the length of the plates. Perfect mechanical work and adjustment is needed, and complete freedom from vibration. A direct drive from a worm gear is almost sure to give trouble, and while a high speed motor may be geared down suitably by a worm drive, the drive to the machine should be by belt. The proper control of viscosity, temperature and running rate will have to be found by experiment for any machine, but the emulsion chemist should try to leave the coater as little adjustment to make as possible. Thus all fast negative emulsions should be capable of being coated at about the same speed, while medium slow negative and slow photo-mechanical or diapositive types would form two other groups. The thickness of the glass being usually less in plates which are to be cut to small sizes, some adjustment will be necessary in the height of the spreader or the throw of the pumps, etc., so that here again a whole day's coating of one particular brand or group of sizes is indicated for smooth running.

The modern dry plate must be so perfect to stand up to commercial requirements, that the greatest care is essential in the treatment of the air of the coating and drying rooms. Many

firms — such as Carrier — have specialized in air-conditioning for the sensitized-products industry and will work out details for specific plants, but they must be called in *before* and not after the plans of a new plant are designed. As the humidity as well as the temperature must be carefully controlled, the air is usually taken from outside, after a preliminary filtering by a gauze that will remove gross mechanical dirt, and is pumped through a metal chamber in which large numbers of finely atomized water sprays are so set as to give as perfect contact with the air as possible. In an acid-laden atmosphere, the pH of the spray water may be kept slightly above 7, but ample washing with normal water is soundest practice. The washed air, more or less saturated, is now passed over cooling coils for which some form of refrigeration will be required. The expulsion of the water in the cold chamber, which is provided with baffles to assist the process, naturally lowers the temperature, and the cold, but now dry, air is led through a heating chamber where hot coils raise it to the temperature desired. Coating rooms may be conveniently kept at 70° F. (21° C.). Drying cupboards may be started at a few degrees above this, and gradually warmed up to 90° F. (32° C.), the heat being turned off a short time before the racks are collected. The design of the drying cupboards must be left to individual circumstances. They must be near to the coating machine, so that the racks of coated plates do not have to be carried too far. They should not be too big — a number of small cupboards capable of holding 500 or 600 8 by 10-inch plates each, is better than a few large ones. The racks are run on wooden rails in the cupboards, and both racks and rails must be of the smoothest possible character to avoid friction of any kind.

Assuming that the dust problem is solved by the use of water-washed air, the next most serious problem is that of bubbles. A tiny bubble may get lodged in the spreader and cause lines on

a large number of plates unless it is quickly seen by the coater and removed. Alcohol in the emulsion helps considerably in lowering the surface tension and reducing the tendency to bubbles. A small atomizer filled with alcohol, or a mixture of alcohol and acetone, is usually at hand to remove froth or bubbles. Careful filtering and skill in pouring and keeping the emulsion tranquil, are all helpful. Commercial specifics for lowering surface tension have been introduced in the trade and find useful application. Dull spots, often known as grease spots, sometimes appear on the surface a few seconds or minutes after coating, and a saponifying agent such as an alcoholic solution of saponin may be helpful.

A very even distribution of the air in the drying cupboards is essential, otherwise drying marks may appear which reveal themselves, on development, as local patches of uneven density. Any sudden change in the rate of flow of the air through the cupboards, will also cause drying marks or demarcation lines where the change took place. Some factories remove the racks when the plates are dry and place them in an *after-drying* cupboard for a few hours without ventilation and at an elevated temperature, such as 122° F. (50° C.). This is claimed [3] to improve the keeping qualities and to be of especial value in the case of plates destined for use in tropical climates.

Before cutting and packing, each plate is briefly examined by looking through it at a safelight for bubbles, scratches or other defects. Glass-cutting machines are in general use for dealing with large sizes which have been coated for smaller ones.

Probably only those who have had to tackle the problem of coating plates year in and year out, are aware of the extraordinary diversity of faults which can develop in manufacture. Perfectly good plates may be spoiled by the use of unsuitable packing materials. Not only must the boxes be made of materials which have no deleterious effects — and the glue used is as im-

portant as the card itself — but the wrapping paper must be most carefully tested for its effects, if any, by oven tests. Ten days at 105° F. in an oven maintained at not above 65 per cent relative humidity is a fair test. The plates so " incubated " should show no more than 0.02 extra fog density when compared with controls, and given normal development. The card separators used for keeping each pair of plates from touching, or for grouping each pair together, must also be made from card which has passed the laboratory test. Even outside labels require to be free from contaminating power, as also any slips or literature which may be packed inside the boxes.

It is of course most important to keep a record of batch numbers, and a serial number given to the box, checking with the emulsion laboratory records, will enable complaints or faults to be investigated.

Chapter References

1. L. P. Clerc, Photography, p. 157.
2. T. L. Dixon and Co., Ltd., Letchworth, England.
3. R. Jahr, Fabrikation der Trockenplatten, p. 236. .

Chapter IX
BROMIDE AND CHLORIDE PAPERS

Nature of the Raw Paper — Paper Tests — Baryta Coating — Emulsion Formulas — Laboratory Methods of Coating and Drying — Commercial Coating Machines — Drying Tunnels — Non-stress Coating — Drying, Reeling and Packing

WHILE natural-color photography has re-introduced to a limited extent the transparency picture, which is viewed by transmitted light or by projection, the natural desire in taking a photograph is to have it finally in the form of a print which can be viewed by reflected light. Some form of print is indispensable in any case, if the original takes the form of a negative. A print on any photographic paper is of course also a negative, for printing a negative from a negative reverses the image and produces the positive picture. Certain losses occur in the process, but modern sensitometry has gone a long way towards reducing them to a negligible minimum.

One function of the print is to provide, in fact, some means of control over the negative image and its possible shortcomings. If a negative is too hard, we can use a soft-working paper; if the negative be flat, we can print it on a vigorous paper, and so on. The most practical example of the application of this control is seen in the work of the photo-finisher, who uses perhaps four different grades of paper in making prints from customers' negatives, soft, medium, vigorous and contrasty. By selecting a paper for each negative merely by means of an experienced eye, and taking each print out of the developing solution at the right moment, a remarkable uniformity of quality is obtained in the prints from a range of negatives that, without such facilities, would be almost impossible to deal with.

One of the most important factors in the making of photographic papers is the paper base. The production of a permanent image, provided the paper is handled in a proper manner, is a moral obligation on the part of the manufacturer, and with this in view the testing of the raw paper becomes essential. The manufacture of very pure, strong papers of close texture, durability and uniform weight suitable for emulsion coating, is in the hands of a comparatively few firms, and is a highly specialized department of the art of paper making, of which the literature is somewhat scant. Quality of water has in many cases been a deciding factor in the success of a photographic raw paper undertaking. The paper is ordinarily made in rolls 42 to 44 inches wide, in 500-meter lengths in the card thickness, and 800- to 1000-meter lengths in the lighter weights. A square meter of light-weight paper will weigh 90 to 135 grams, card thickness 210 to 270 grams, while various medium heavy weight varieties come between the two.

The paper must show a uniform texture when examined by transmitted light, and it must not stretch too freely when wet, nor shrink too much when dried after wetting. For this reason papers containing much wood pulp are unsuitable, and a test for wood fibers is usually one of the preliminaries in connection with an unknown sample. The following solution may be used for the test:

Alcohol .... 100 cc
Phloroglucin .... 2 g
Hydrochloric acid .... 50 cc

This solution, freshly prepared, is of a weak yellow color. Its application to the paper sample will cause wood pulp or fibers to turn red. Another useful test is that suggested by Herzberg; [1] a solution of twenty grams of zinc chloride in ten cubic centimeters of water is mixed with five cubic centimeters of

water containing 2.1 grams of potassium iodide and 0.1 grams of iodine. The solution is shaken up, allowed to stand, and the clear portion decanted and used. A sample of paper which has been pulped by boiling with a five per cent solution of caustic soda for a few minutes and well washed is treated with this solution, which shows rag fibers as deep wine red, starchy substances as blue, and wood fibers as yellow.

Impurities in the raw paper come into evidence most frequently in the form of small spots, which may develop in size when the emulsioned material is kept for any length of time before use. Iron particles probably cause the most trouble. These can be checked by soaking a sample of the raw paper in a dilute acidified solution of the ferricyanide and ferrocyanide of potassium for five or ten minutes and then washing with distilled water. The presence of iron will cause a blue coloration; low-power microscope examination may be needed to detect small specks. The paper may otherwise be soaked in a one per cent solution of pure nitric acid, dried, and then transferred to a dilute solution of potassium ferrocyanide; in this solution copper spots will be revealed as brown marks or stains, iron spots as blue. Needless to say, photographic raw papers should be practically free from loading.

Paper is used in the raw state only where a natural surface is required. Otherwise a coating of baryta is applied to the surface to be emulsioned. A mixture of barium sulphate and gelatin, with a suitable hardening agent, is applied to the surface with reciprocating brushes. In a glossy paper about ten parts of medium hard gelatin would be used to one hundred parts of fine baryta; in a mat paper, the proportion of gelatin has sometimes to be raised, on account of the heavier baryta used. Some kaolin may be included. An addition of glycerin, chrome alum (or formalin), and some citric acid usually, together with a small amount of coloring matter, completes the

mixture. Red, yellow, or blue dyes are most popular, but the baryta never looks a good color without *some* dye. A typical baryta coating machine [2] is seen in Fig. 45. The baryta mixture
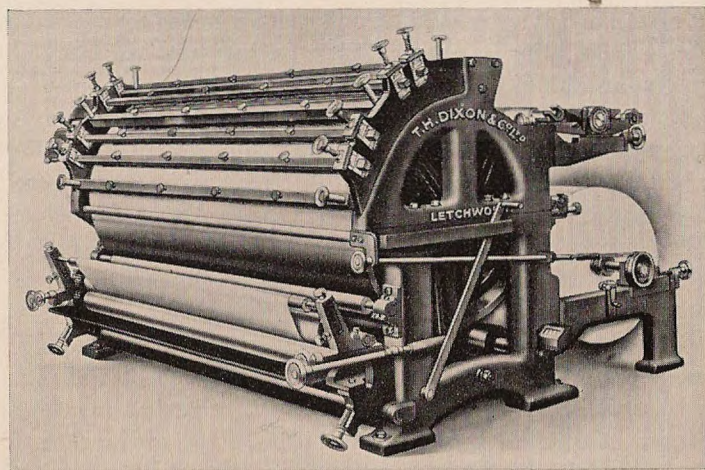

FIG. 45. BARYTA COATING MACHINE

is applied to the paper, which after leaving the machine is run into loops, the festoon traveling along a drying tunnel which is maintained at a controlled temperature and humidity. It is reeled at the end of the run, and is afterwards passed through a calendering process, where it is burnished and given the necessary finish by its passage through highly polished rollers under considerable pressure. According to the baryta formula used and the calendering treatment, the surface produced may be glossy, semi-glossy, half-mat, full mat, or rough mat. The baryta coating keeps the emulsion on the surface of the paper, so that the image lies superficially and is therefore more brilliant. This incidentally makes the emulsion go much further.

Practically all development papers are given a non-stress coating, to prevent abrasion or pressure on the emulsioned surface from causing black marks or streaks. Pressure will cause the film to become developable without exposure. The non-stress coating is a thin application of plain gelatin coated over the actual emulsion, and in modern practice is applied as soon
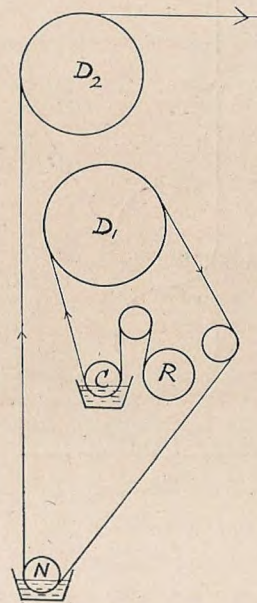
FIG. 46

as the emulsion itself is thoroughly set. The method of applying the two coatings on a double coating machine is seen diagrammatically in Fig. 46. The mechanism for forming the loops is not shown. The raw paper from the roll R is led over a roller C which dips into a silvered trough kept filled with

emulsion at constant level. As the paper is driven forward it touches the emulsion and picks up a quantity which varies with the rate of travel, which may be anything from twelve to fifty feet per minute. The paper, with its emulsion coating, is led over a large-diameter cold metal drum, D_1, where setting takes
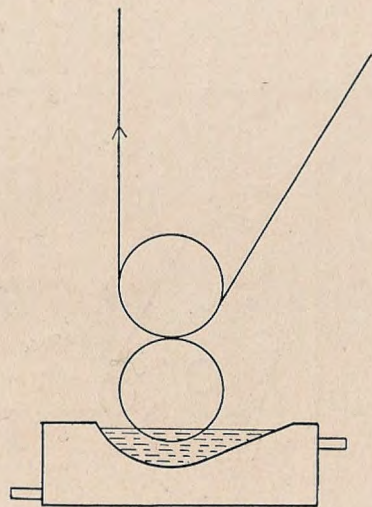
FIG. 47

place, and it is then led over guide rollers to a second coating trough where the non-stress gelatin is applied by the roller N; this is set in turn by the second cold drum D_2. Both coatings can be applied by " kissing " rollers (Fig. 47), instead of by dipping. An advantage of the kissing roller is that it can be made slightly shorter than the width of the paper, so that an uncoated selvedge is left at the two sides on which the leading rollers over the setting drum can ride. In the case of dipping, the emulsion is necessarily applied to the entire width of the
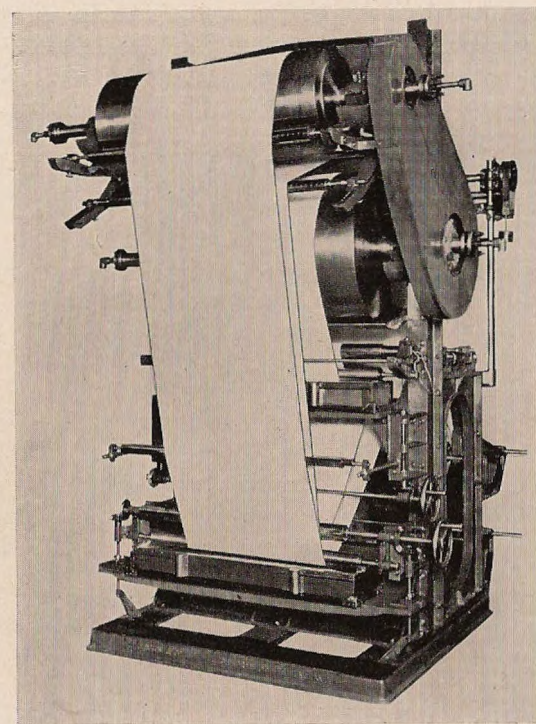
FIG. 48

roll, and if clear edges are needed for leading rollers, a scraping device must be attached to remove the emulsion for about half an inch at the two sides.

By simple mechanical means, the coated band, thoroughly set by the second cold drum D_2, is picked up and formed into loops eight or ten feet long, which depend from sticks that are carried along by endless sprocket chains running along the top of the drying alley. The festoon thus travels slowly down the

alley or tunnel, which may be 200 or 300 feet long. Frequently it is made double, so that loops are carried on the sticks over a turntable at the far end of the tunnel and then travel up again, so that the paper is dry by the time it has reached the *reeling*
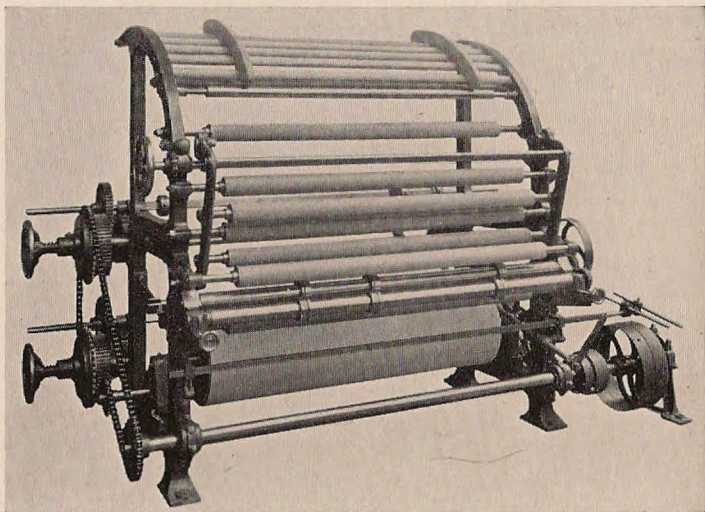
Fig. 49

machine at the coating head end of the building. A double coating machine made by T. L. Dixon and Co., Ltd. is seen in Fig. 48. New rolls of paper can be attached to ends of finished rolls by means of auxiliary gear, so that coating can be continuous. In Fig. 49 is shown a reeling machine made by the same firm; the paper is led in and out of the tension rollers to smooth out irregularities and creases before being wound on the drum.

With a little skill, a very good coating of paper can be obtained in the laboratory with just a dish of emulsion standing in an outer dish of warm water, laying a short, loosely rolled-

up length of paper three or four feet in length on the surface, and pulling it vertically upwards with a quick, steady movement (Fig. 50). The roll of paper will lie on the surface and
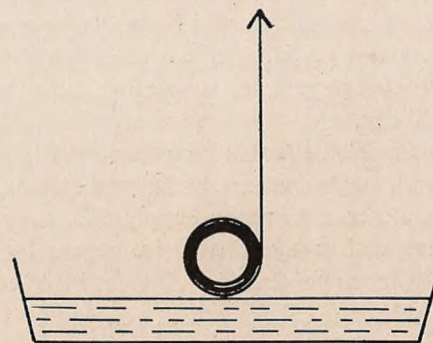
Fig. 50

as it unrolls the action will be substantially the same as that of a dipping machine. If longer lengths are desired, a somewhat elaborated arrangement can be used as shown in Fig. 51. This can be made with a little mechanical help, and indicates a homemade paper-coating machine. A roll of twenty feet or so of raw paper is wound on to a wooden roller the spindle of which is supported by two uprights, one on either side of the coating dish. The dish is filled with emulsion just before coating so that the bottom of the roll dips about one-quarter inch below the surface. The paper to be coated must be attached to a paper " leader " which travels upwards to the roller R_1 which should be fixed as high up as is convenient. It then passes across to a second roller R_2 and down again to a fourth roller or drum on which the coated paper is to be wound. A small motor geared to this drum will drive the paper, and the leader will draw the coated paper over the upper rollers and

down to the drum, when of course coating must be stopped. A length of about twenty-four feet can be coated at one time in this way in an ordinary room, the length depending on the height of the leading rollers above the dish and the distance between them. The motor should be geared to run the paper at ten or twelve feet per minute, and the drum should be belt driven. The coated paper is left suspended, just as coated, over the rollers until dry.

A bromide emulsion suitable for paper coating should give pure black tones, ample contrast, and a good scale of gradation. The manufacturer must of course supply different grades from soft to vigorous, with many different surfaces and weights, and must arrange as far as possible that different brands of the same
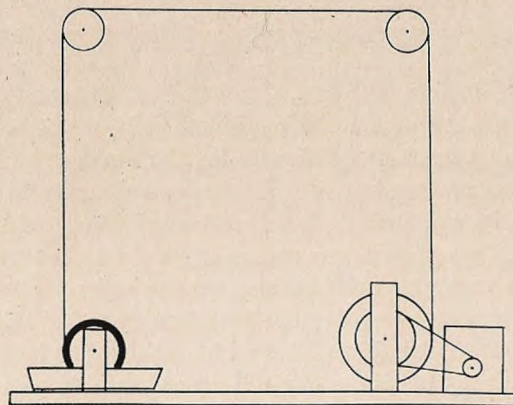
FIG. 51

class have approximately even speeds. Actual speed is of little consequence in a bromide paper, except for enlarging purposes or automatic printing machines, and even then it is of an entirely lower order as compared with negative emulsions. But it is nevertheless important to keep the speed of the different

grades uniform, and this will be found to be by no means as easy as it might seem.

For laboratory or experimental work, the most important thing to be done is to get hold of some raw paper, and here one must depend on the courtesy of one of the manufacturers themselves, who in general do not discourage amateur efforts. Some photographers will wish to coat paper of their own choice in order to secure some particular surface. Use pure rag paper, unsized, such as Rive's or Whatman's. Thick papers are more difficult to handle than thin ones, and may have to be sensitized by floating on the emulsion one sheet at a time in an open dish.

When dealing with paper emulsions, useful information can be obtained by trial coatings on glass. This will show if the emulsion is free from fog, which should not exceed 0.02 density on normal coating, also if it has good latitude and has ample density-giving power. One hundred grams of silver halide will coat eighty to one hundred feet of forty-two inch paper.

The reflection densities of a sensitometric strip depend so much upon the paper surface and its absorption and diffusion qualities that a more *practical* indication of printing characteristics will be obtained from the coated paper. For information, it will be advisable to coat three or four strips say three feet long by eight inches wide, trying to keep the speed of unrolling on the emulsion constant. Each strip may be coated at a different temperature or a different speed to obtain the effect of varying coating weight. The faster the paper is unrolled, or the lower the temperature of the emulsion, the thicker will be the coating. Any form of strip sensitometer or gray step-wedge can be used in an ordinary printing frame for making the tests, but results can be charted as characteristic curves only by use of a reflection densitometer such as is described in Chapter XII.

It is all-important that the coating weight of a paper be correct within reasonable limits. Thus, while negative emulsions

are usually made with forty to fifty grams of silver nitrate to the liter, paper emulsions would be prepared with only fifteen to twenty-five grams per liter. This, of course, assumes that the actual volume of liquid emulsion applied to a given area is of the same order. One liter of emulsion should coat sixty to eighty square feet of paper surface. The viscosity of the emulsion, the surface of the paper, the coating temperature, and the speed of the machine will control coating weight. When dipping, the emulsion picked up is almost directly proportional to the peripheral speed of the coating roller. Good blacks can be obtained only if the coating is sufficiently rich, but too heavy coating is decidedly detrimental. It must be remembered that in the case of a transparency, density and contrast can both be built up over a long range, but in the case of a development *paper* the maximum contrast is attained very early during development, simply because the number of densities that can be distinguished by reflected light from the maximum black is extremely limited. This disadvantage renders it all the more important to limit coating weight to giving in the highest exposures the maximum density that is desired for the particular brand, this maximum to be measured after *normal* development. Brilliance depends on the gloss of the surface, and the contrast and cleanness of the emulsion, and can be largely lost if the latter sinks too much into the paper owing to lack of viscosity or too slow setting.

A bromide paper formula by Trumm is as follows:

A. Water	4000	cc
Gelatin	350	g
Potassium bromide	190	g
Potassium iodide	2.5	g
B. Distilled water	2000	cc
Silver nitrate	250	g
C. Water	2000	cc
Gelatin	600	g

The gelatin in *A* is allowed to swell in the solution of bromide and iodide for half an hour, and is then dissolved by heating the crock to 120° F. (49° C.). The silver solution, *B*, heated to the same temperature, is added, pouring it through a funnel with a fairly fine jet. A plain or separatory funnel can be used for the purpose, attaching to the end, by means of the shortest possible piece of rubber tubing, a 1 or 2 inch length of barometer tubing about 4 mm bore. The funnel is mounted in a stand above the crock so that the jet is near to one edge, leaving ample room for stirring (Fig. 52). The emulsion so made is next
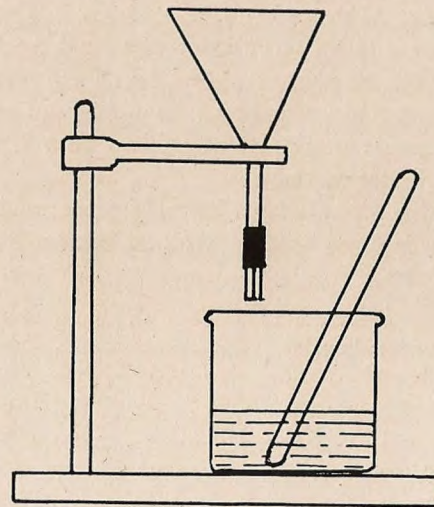

FIG. 52

further heated to 140° F. (60° C.) on a water bath, and maintained at this temperature for one hour. At the end of the hour, solution *C*, heated also to 140° F., is added, and a further one hour's digestion is given. The emulsion is then poured out to set in a cold crock placed in ice water and stirred slowly until

gelling begins. It is then broken up into noodles in the manner already described for fast emulsions, and washed in about twelve changes of five minutes each. The washed noodles are put into a tared crock, remelted and made up, inclusive of finals, to a weight of 16,000 g. Finals are:

Five per cent chrome alum solution .... 150 cc
Spirit .... 1000 cc
Phenol (dissolved in part of the spirit) .... 10 g

If a mat paper is required, 200 g of rice starch ground up in 1000 to 1500 cc of water is added and thoroughly stirred in, prior to filtering. When matting the emulsion, it is best to leave out an equivalent quantity of water when making-up. When made up to bulk, the emulsion is best set off and remelted next day or when required for coating. An addition of an alcoholic solution of saponin or extract of quillaia bark is frequently added to give better coatings.

An alternative formula for a bromide paper emulsion made with ammonia is given by E. J. Wall as follows. Three solutions are made up:

A. Water .... 1800 cc
   Potassium bromide .... 400 g
   Citric acid .... 400 g
   Gelatin .... 150 g

B. Water .... 3750 cc
   Silver nitrate .... 500 g

C. Water (cold) .... 600 cc
   Gelatin .... 150 g

Solution A, the gelatin dissolved, is cooled to 86° F. (30° C.). To solution B is added sufficient stronger ammonia water to redissolve the precipitate. It is then added at the same temperature to A, through a jet, with continual stirring. The emulsion is then poured on to C, which is cold, and the whole stirred

and taken up to 122° F. (50° C.). As soon as the gelatin in C has melted, the emulsion is set. It is then washed as usual, the shreds melted and taken to 104° F. (40° C.) and 450 g of fresh gelatin is added which has been dissolved in 1600 cc of water. Final additions are 600 cc of alcohol and 30 cc of ten per cent chrome alum solution.

Unwashed emulsions have met with a limited amount of success for development papers. Inasmuch as too great an excess of free bromide would not only greatly retard development but cause the " blacks " to have a decidedly greenish tint, it is important that only a slight excess over the combining proportion should be used. Also, on account of the hygroscopic nature of ammonium nitrate, the potassium salt would be used. An unwashed emulsion would be acid in character, and could be made up somewhat as follows:

A. Potassium bromide .... 26 g
   Potassium iodide .... 0.5 g
   Potassium chloride .... 1 g
   10 per cent hydrochloric acid .... 5 cc
   Gelatin .... 30 g
   Water .... 560 cc

B. Silver nitrate .... 37.5 g
   Water .... 300 cc

Heat both solutions to 140° F. (60° C.), and add B to A through a fine jet with mechanical stirring. Digest for an hour and a half and then add 50 g dry gelatin, and stir for ten minutes until dissolved. Then add 50 cc of a two and a half per cent solution of phenol in alcohol, and 5 cc of five per cent chrome alum solution, and set off in ice water. Keep in cold room for three days. Remelt and filter.

Formulas already given for transparency emulsions can with some little adaptation be used for coating bromide paper. Papers requiring a long scale of gradation may be made with di-

vided silvers, using a small amount of ammonia only and allowing a little ripening time. Mixed jet emulsions give excellent results. In all cases, the choice of gelatin must be carefully made; slow emulsions are probably more dependent on gelatin character for their success than rapid ones.

The popularity of chloride papers, or " gaslight " papers as they are known in the English market, is due to the extreme ease with which they can be handled. The early papers of this type were so vigorous that for a time specially soft negatives were necessary to obtain the best results. Studies of the behavior of silver chloride, however, have made it possible to produce chloride papers giving a wide range of contrast. A simple emulsion suited to experimental work is as follows:

A. Sodium chloride	12	g
Gelatin	90	g
Water	1000	cc
B. Silver nitrate	25	g
Water	110	cc

Both solutions are heated to 122° F. (50° C.), and B is added to A either through a fine jet or in small quantities at a time — such as 10 cc. The liquid should be kept mechanically stirred at a high speed. Between forty and fifty minutes' digestion is given at the same temperature, and the finals are then added.

This is an unwashed emulsion, and as such is apt to attack the baryta surface with the formation of minute black or white spots. If the emulsion is washed, it may be used for coating either chloride paper or lantern plates. To the above quantity of emulsion an addition may be made of 5 to 10 cc of a ten per cent solution of citric acid, the lesser amount tending to give bluish blacks and the greater amount greenish blacks. Three or four cubic centimeters of a ten per cent chrome alum solution

and five per cent of the total volume of alcohol should be also added. An emulsion of this type is an interesting one to experiment with, since all the work can be done in the subdued white light of the darkroom. Works-scale chloride emulsions are handled in yellow light.

The brilliance of chloride and chloro-bromide papers can be increased by the discreet use of copper or thallium chlorides, although of most importance is the correct choice of gelatins. Small additions of citric acid, potassium citrate or sodium phosphate may be made to washed emulsions to improve keeping quality, and formalin may be substituted for chrome alum in the case of manufactured material which is destined to get some rough handling in photo-finishing shops. The amount of formalin used would be about fifty to sixty cubic centimeters of forty per cent formaldehyde diluted with ten times its volume of water, for every kilogram of gelatin. Where emulsions are to be washed, hydrochloric or citric acid is advisable in the making; hydrochloric would be added to the salts, but the citric acid may be divided between salts and silver.

Intermediate between chloride and bromide development papers there come, of course, the chloro-bromide variety, designed for giving warm tones. The formula already given for chloro-bromide plates can be used with very little modification. As a starting point for experiment, a mixture of equal parts of bromide and chloride might be taken. The silver halide concentration should be about twenty-five to thirty grams per liter, and the gelatin concentration about double this. The excess of soluble halide should be chloride, not bromide; the precipitation made in the presence of free acid as indicated for chloride emulsions; and after washing, only a trace of bromide should be used, otherwise the tones will tend towards a greenish hue. It has been the experience of some American emulsion chemists that halides of barium, cadmium and other metals give better

warm tones than those of potassium, sodium and ammonium. The inclusion in the emulsion of anything which will tend to restrain development may also help; the citrates and borates are examples. But in both types of paper, chloride and chloro-bromide, the manufacturer has to correlate his emulsion coat-ing with an optimum developer, the latter being essentially worked out for the material in question. Thus A's paper de-veloped with A's formula might work excellently, while used with B's formula the results might be very poor.

Care must be taken to avoid froth and bubbles on the surface of the emulsion in coating. For laboratory experiments, the emulsion should be filtered just before use, through a piece of wetted cheesecloth, and poured down the side of the dish to avoid friction, holding the crock or beaker near to the dish. Large bubbles can be broken by the touch of a moist glass rod; froth can be dispersed by the cautious use of a little alcohol blown from an atomizer. Too much alcohol will cause the emul-sion to coagulate in the form of little strings or flecks which must be removed.

The non-stress coating applied to the emulsioned paper in a double-coating machine, which is composed of gelatin, spirit, and some hardening agent, may suitably contain formalin, chrome alum being preferable in the sensitive emulsion. The double-coated paper takes somewhat longer to dry than paper which is not non-stress coated. It is important, for example, to arrange the inlets of air in the drying tunnel so that warm, dry air is blown gently into the loops from the sides of the tunnel, and that sufficient air is directed on the bottom of the loops, where drying is apt to lag. The amount of air required to be pumped into the tunnel — and it should be pumped in under slight pressure so as to form a plenum, and not merely *extracted* — will naturally depend on the temperature and rel-ative humidity and on the amount of water to be evaporated

during the run from coating head to reeling machine. The in-clusion of a small quantity of Arlex may be made in the case of continuous running, which acts as a plasticizer and is only slightly affected by changes in humidity; some coaters prefer to run the festoon to the end of the tunnel, and to leave the paper for some hours in a 50 per cent relative humidity atmos-phere to get into equilibrium before reeling. This is only pos-sible where comparatively small coatings are made.

A new type of bromide paper has recently been introduced which is capable of giving images of either high or low contrast according to the color of the light used in printing (Defender " Varigam " and Ilford " Multigraph "). These papers are coated with a mixture of two different emulsions, one sensitive to blue-violet only and having, say, a high gamma, the other sensitized to green by means of a suitable dye, and having a low gamma. The contrast obtained with the one paper can thus be varied at will by merely using the appropriate filters over the printing light or the lens of the enlarger, thereby bring-ing into requisition the emulsion required.

Some causes of failure with slow development papers may be given, in conclusion. Weak, grayish images may be due to the emulsion taking up too much water in washing, and hence causing a deficiency of silver. Low viscosity will give the same trouble. Gray images with a tendency to fog are usually due to over-digestion; the remedy is to reduce the time or the tem-perature of the cooking. An unsuitable gelatin may also be the cause. General fog may be due to an unsuitable gelatin, too high temperature for emulsification, insufficient excess of halide, im-pure chemicals, and, of course, too much exposure to light. Black fog indicates an excess of silver nitrate, due to incorrect weighing or miscalculation of a formula. Partial fog is some-times caused in a mixed-jet emulsion through the silver leading the salts and not vice versa. Innumerable tiny black specks on

development, or pepper, are due to coarse precipitates or aggregates of silver halide which, being insufficiently clothed with gelatin, are reduced without exposure. These rarely occur with an ammonia type of emulsion, but are very apt to creep into chloride emulsions, having a serious effect on the brilliancy or maximum density. A cubic centimeter or two of the emulsion just after it has been made, should be spread over the end of a glass strip and examined by transmitted light, for example by looking through it at a low power incandescent lamp. The addition of the second gelatin dry instead of in solution, helps considerably to break up or disperse aggregates; finer nozzles for the silver, better agitation during precipitation, or an increase in citric acid, will help to prevent pepper formation, or again a change of gelatin or its distribution between salts and silver.

Chapter References

1. W. Herzberg, Die Papierprüfung, 1907.
2. T. H. Dixon and Sons, Ltd., Letchworth, England.

Chapter X
FILMS, NEGATIVE AND POSITIVE

Types of Base — Substratums — Substratuming Machines — Negative Film Emulsions — Positive Film Emulsions — Experimental Film Coatings on Roll and Cut Film — Film Coating Plant — the Drying Tunnel — Air-conditioning — Films for Imbibition Emulsions — Static — Commercial Defects — Packing

THE film bases on which sensitive emulsions may be coated are of two kinds. One is celluloid or " nitrate " film, which contains about 85 per cent of nitrocellulose and 15 per cent of camphor, the two being dissolved in about five times their weight of a mixture of about 37.5 per cent of 85 per cent alcohol and 62.5 per cent of ether, to form the dope from which the base is cast. The other base is cellulose acetate film, which is practically non-inflammable, and is compulsory for sub-standard motion-picture film and is becoming used on a very large scale for general photographic materials. Cellulose diacetate is made by heating cellulose with zinc acetate solution and treating the cooled mass with acetyl chloride. It is dissolved chiefly in acetone, to which a plasticizer such as triphenyl phosphate, dibutyl phthalate, etc., is added, together with tetrachlorethane, methyl alcohol or benzene. The recent introduction of triacetate in place of diacetate produces a tougher film, though the use of a special substratum is indicated.[1] The mixed dope is filtered through filter presses, and is generally fed by gravity from an upper mixing room to the casting machines.

The dope is cast into the thin sheet used in film coating by two different methods. One of these is known as the big wheel

system; the dope is distributed by means of a spreading device on to the flat periphery of a large highly polished metal wheel or drum which may be sixteen to twenty-five feet in diameter. The drum rotates at the rate of two or three feet per minute, and as it revolves the dope solvent evaporates and leaves the film sufficiently dry towards the end of the revolution for it to be parted from the metal surface and led into a drying chamber; here the remaining solvents are driven off, after which the band of film can be reeled. Much film base manufactured to-day is cast on an endless band type of machine. By this method, a band of copper about ninety feet long travels slowly over two large drums some three feet in diameter and spaced about forty feet apart; the whole is encased in a metal cover so that the evaporated solvent can be collected and condensed. Over the top of one drum is the spreading device, from which the dope is distributed on to the band. The band itself, however, is usually coated with a skin of gelatin, glycerin and soap. By the time the coated part of the band reaches the end of the run it is dry enough to be parted from the skin, and can then be passed through a final drying chamber and the residual solvent driven off. In the case of triacetate film the base is sometimes given a treatment before being finally dried, which acts as a substratum and anchorage for the emulsion, thereby doing away with the need for the application of a substratum in the emulsioning plant.

In the ordinary way, both celluloid and cellulose acetate require a preliminary treatment to secure satisfactory adhesion of the emulsion to the base, a problem that has involved considerable research to find a satisfactory solution. It will incidentally be found one of the most troublesome parts of the technique in laboratory coatings. The function of the substratum is to etch and attach itself to the film base on the one hand, and to " stick " to the gelatin of the emulsion on the other. The sub-

stratum most commonly used in early practice was thus a solution of gelatin in a solvent such as acetic acid or salicylic acid broken down with methyl alcohol. Ten cubic centimeters of glacial acetic acid may be put in a test tube and powdered gelatin added gradually, warming the tube gently over a Bunsen burner or alcohol lamp until no more gelatin will dissolve. This stock solution can be diluted with 200 cubic centimeters of methyl alcohol, to which two or three cubic centimeters of water has been added. This substratum works well with celluloid, but if it is to be used for acetate film, a part of the alcohol should be replaced by acetone. Five per cent of cellosolve acetate may also be added.

For cut sheet film Wall [2] recommends the following:

Pyroxylin	0.5 g
Gelatin	0.5 g
Glacial acetic acid	33 cc
Methyl alcohol	1000 cc

The gelatin and pyroxylin are dissolved in the acid by heat, and the alcohol then added. The drawback to an acetic acid substratum is that it may lower the pH of the emulsion in contact with it and gradually slow it down, or affect color-sensitizing dyes. An alcoholic solution of caustic potash, to which a small proportion of celluloid solution (celluloid clippings in amyl acetate) is added, is dangerous from the opposite standpoint. Some of the recently introduced compounds of the Carbide and Carbon Chemical Corporation's research department have the advantage of giving a " tooth " to the film by slightly etching the surface through their mild solvent action. Cellosolve acetate is one example. The methyl compound is ethylene glycol monomethyl ether acetate, is miscible with alcohol, soluble in water, and soluble in cellulose acetate dissolved in acetone.

An organic partial solvent, suitably diluted, can be used to give a front etch for adhesion and a back etch for anti-curl

purposes. In some cases the film base is first coated with a thin application of hardened gelatin to offset the curl imparted by the emulsion. This balance is very important, as otherwise, during development in filmholders, cut film would curl and drop out of the grooves, while rollfilm would be unmanageable after
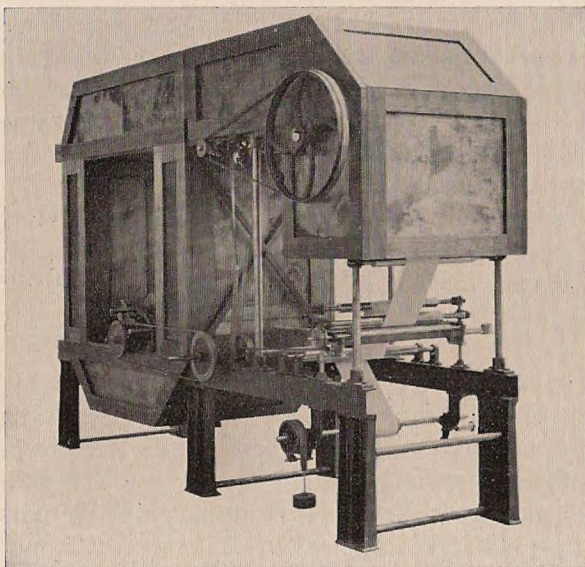

FIG. 53

processing. Too deep an etch will of course give an opalescent appearance to the film, although this disappears if a coating of gelatin or emulsion is applied afterwards.

Any form of substratum must be applied in a dust-proof alley or chamber of carefully controlled temperature and humidity. The average application should dry in three to five minutes at a fairly high temperature such as 95° F., so that the roll of film

base can be run continuously and reeled up at the end of the machine. It should be rolled up on large drums in order to make the base lie flat when running through the emulsioning machine. A large inverted U-shaped substratum machine much in use is constructed by Koebig of Radebeul, Dresden, but a more recent form of apparatus is shown in Fig. 53, a compact subbing machine made by T. H. Dixon of Letchworth, England.

In substratuming base for special purposes, a coloring matter is sometimes introduced, as in the lavender motion-picture film of the Eastman Kodak Company, and the " gray base " film. The latter is claimed to give negatives of better quality, without interfering with gradation. The coloring matter, being incorporated in the water-insoluble base material, will obviously not be removed in processing. While therefore some anti-halation dye may be used, it will be necessary to resort to a dye in the back gelatin coating if such dye would interfere with the printing qualities of the finished negative; dyes which can be eliminated in an acid fixing bath etc., have been referred to on page 80.

Owing to dirt which inevitably creeps in during manufacture, transit, and general handling, the film base may be wiped or cleaned prior to subbing, by passing it through tightly coupled rollers or pads covered with suitable material. The cleaned and substratumed film base is coated at a fairly rapid rate — anything up to forty feet per minute — and after the application of the emulsion, it is passed over a large copper drum filled with chilled water which sets it sufficiently for it to be carried over on rollers to a mechanical festooning device which forms the band into loops depending from sticks as in the case of paper coating. The loops will be shorter and wider, owing to the nature of the base as compared with paper; loops five feet deep are customary in the heavier weights, and longer loops in the case of 5/1000 and 3/1000 base. The festoon travels along the

drying alley or tunnel, which should be constructed with ceiling, walls, and floor, of concrete or similar material sufficiently surfaced that when hosed down no dirt can remain on them; side gutters should be rounded off so that there are no "corners " to trap dust. Needless to say, both temperature and humidity must be controlled, and the circulating of the washed air so arranged that the bottoms of the loops dry in the same time as
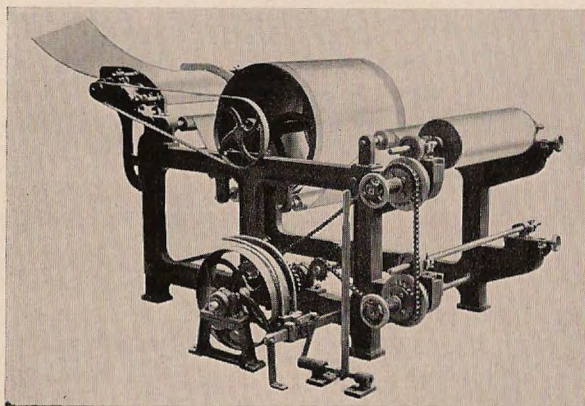
FIG. 54.   REELING MACHINE

the lengths. With a drying alley 300 feet long, that is 600 feet run if the alley is double width with a turntable at the far end, the film should be easily dried by the time it reaches the end of the travel, so that it can be reeled and the coating process thus made continuous. A typical film reeling machine (Dixon) is seen in Fig. 54.

Coating small quantities of film in the laboratory or in the darkroom has naturally to be done on an entirely different basis. For short coatings on an improvised machine, lengths of ten or twelve feet of the 3/1000-inch thickness are recommended. If,

however, cut film is wanted, the 5/1000 or $7\frac{1}{2}$/1000-inch base may be cut into sheets on a clean print trimmer, and individual sheets squeegeed down on to " stickybacks " — glass plates prepared with a non-drying gelatin mixture. A small machine can be made quite easily in the manner indicated in Fig. 55. A cou-
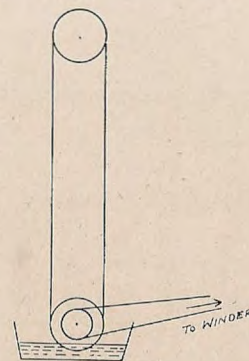
FIG. 55

ple of 10 or 12-inch rollers, turned true and polished in the lathe, of about $2\frac{1}{2}$ inches diameter, are mounted on spindles running in ball bearings fixed in the two uprights shown screwed to the base. The rollers should be given two or three coats of shellac varnish. The distance between the upper and lower roller, of course, controls the length of film that can be coated, as it is fitted over the rollers in the form of an endless band. It is a convenience if one of the rollers can be adjusted in the vertical direction so that the band when fixed can be pulled taut. While film cement may be used for making the join, a piece of one-inch scotch tape will answer the purpose quite well. The lower roller is the " coating roller," the dish of emulsion being brought up to it so that the film dips into it about one-quarter inch; the emulsion dish should be stood in an outer dish of hot water.

While the little machine may be driven by means of a handle connected by a belt to one or other of the rollers, it may equally well be operated by a large driving wheel, belt-driven from a
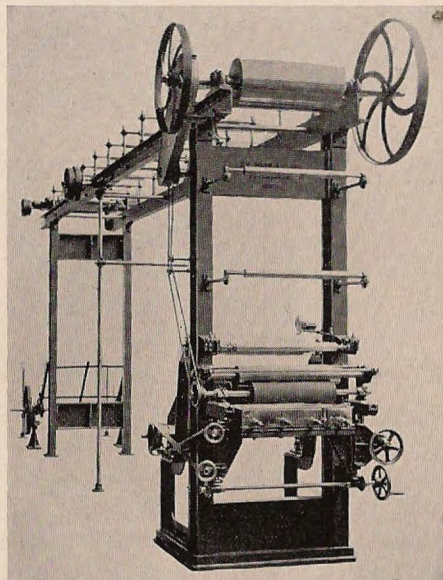
FIG. 56

slow speed motor having a very small diameter driving wheel. The speed of running should be about twelve feet per minute, using a viscous emulsion at a temperature only a few degrees above the setting point. In many commercial machines the band of film, after dipping, is run almost vertically upwards through a rectangular-shaped cold shaft, fitted internally with brine pipes, so that the surface of the emulsion is set by the time it reaches the cooling drum above it. This drum, which is usually of copper with cold water circulating through it, will

cause trouble from condensation and consequent buckling of the film unless continually wiped with a crossbar covered with absorbent material, or unless other equivalent steps are taken. While the pull of the drum may suffice to drive paper forward, film base requires some assistance, and either small weighted
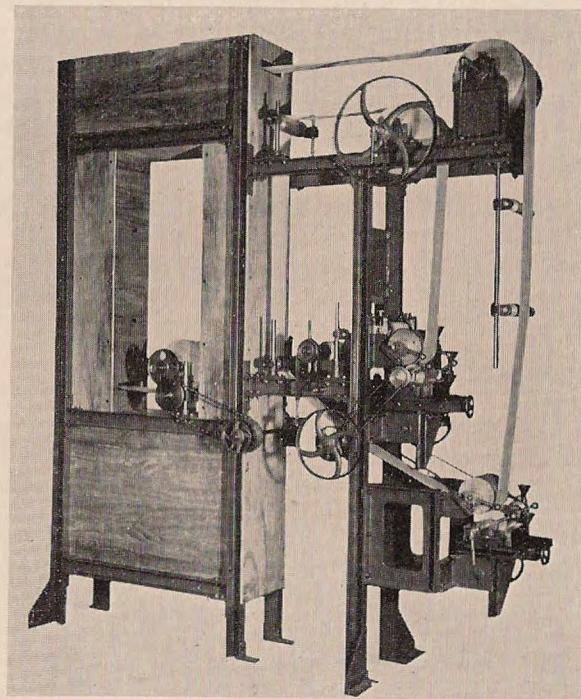
FIG. 57

wheels may be fitted at the edges of the band, to ride on the selvedges, or a suction roller or belt may be applied immediately behind the drum. Suction rollers are used in many industries and can be obtained from a number of American manufacturers.

The roller is perforated, and suction is applied through the hollow shaft by means of a small motor-driven pump; the film clings to the surface under the vacuum and the rotation of the roller pulls it forward and feeds it on to the festoon.

A small laboratory coating machine [3] is shown in Fig. 56, with which the film as it is coated is led by a leader of waste film or paper over the top rollers and down to the reeler. An elaboration of the machine, as manufactured by Dixon, is shown in Fig. 57, where arrangements are provided for double coating. Double coating is used on an increasing scale, and has many advantages. By coating an extreme-speed emulsion on top of a slower type, greater latitude is given and better building up of the image can be obtained, with increased densities in the highlights. Each coating must necessarily be of a lower coating weight than in the case of single coatings; halation is lessened, and by dividing the characteristics between the two layers, a film of improved keeping quality is produced.

Heavier base, the $7\frac{1}{2}$/1000-inch, is the weight most easily coated in the laboratory in small quantities. It may be cut into sheets of a convenient size, say eight by ten inches, and stuck down on sheets of prepared glass, which are then dealt with exactly as dry plates. The celluloid or acetate base should be first substratumed on the side which is to be coated. The " sticky-back " glass is made by coating it with such a solution as the following:

Hard emulsion gelatin	60 g
Sugar syrup	60 g
Glycerin	80 cc
Ten per cent chrome alum solution	5 cc
Water	800 cc

About forty grams of Arlex [4] may be substituted for the glycerin.

The gelatin is swollen in the water in the usual way, then

melted and brought to a temperature of 122° F. (50° C.) and the other ingredients added. Fifty to sixty cubic centimeters of this mixture will coat a sheet of glass eight by ten inches. Another formula for the sticky dope is as follows:

Hard emulsion gelatin	75 g
Arlex	30 g
Sugar syrup	60 g
Dextrin	20 g
Water to make	1000 cc

The gelatin is swollen in 700 cubic centimeters of the water, and is then melted and the sugar and Arlex added. The dextrin is mixed into a smooth paste with water, then thinned down with the balance of the water and heated until it forms a paste. This is mixed in with the gelatin solution, and if needed a little spirit can be added. The filtered material in either case is coated on the glass sheets in the manner of an emulsion. The plates should be given ample time to set, three to five minutes being necessary, and they may require two or three days to " dry." The large amount of glycerin or Arlex keeps the coating always tacky.

A sheet of sticky glass is taken, and a sheet of celluloid, substratumed side up, is slightly curved into a U-shape, convex side downwards, and lowered until it touches the middle of the plate. The two ends are then gently lowered, and with a flat squeegee the sheet of film is brought into firm contact with the tacky surface. The squeegee should be one made of black rubber. A wooden roller coated with billiard cloth or piano felt may be used instead.

In coating such films with emulsion, the inherent disinclination of all film base to take kindly to gelatin makes its distribution and adhesion difficult. Hence, while the plate is balanced on the finger-tips as has already been described in connection with dry-plate coating, it may be necessary to lead it over the

surface with a clean, warm, glass rod about a quarter inch in diameter held parallel to the glass, then carefully laying it on the levelling slab. Owing to the heat-insulating effect of the film base and thick gelatin coating, setting will be slower than in the case of a straight emulsion on glass, and this extra time must be borne in mind.

The coated films are dried on the glass in the drying cupboard in the ordinary way. When dry they are stripped off. Here a word of caution is necessary. One corner should be raised with a clean knife or spatula and taken between the thumb and finger. Holding the plate at the edges with the left hand, on which a cotton glove should be worn, the free edge is taken between the thumb and finger of the right hand and the film gently but firmly pulled away from the glass, taking care always that the plane of the film makes as acute an angle as possible with the glass. The film must never be pulled up vertically or backwards, or it will show stress marks. Too rapid peeling, or the use of any force, or any stop made during the stripping, may produce a static electric charge or a stress, which will appear as a fog mark on development. Buckles in the film show up on development, and are known as swallow marks.

The film should always be coated a little bigger than the size required, so as to provide space for trimming. In trimming, it should be remembered that cut film is about two millimeters less in width and length than the quoted commercial size. Thus in cutting a 4 by 5-inch film, the size would be made about $3\frac{29}{32}$ by $4\frac{29}{32}$ inches, otherwise it will not fit readily into the film sheaths or holders. The cut sheets may be packed emulsion to emulsion, each pair being wrapped in its own black paper folder. The black paper should be of approved quality and thoroughly dry.

Any emulsion may be used for film coating, but as already

indicated it should be of more viscous character than is needed for plate coating. A suitable gelatin for film emulsion is quoted by Heyne as one which requires forty-five seconds when made up as a two per cent solution to flow through the Ostwald viscometer. The same author suggests for a negative film emulsion
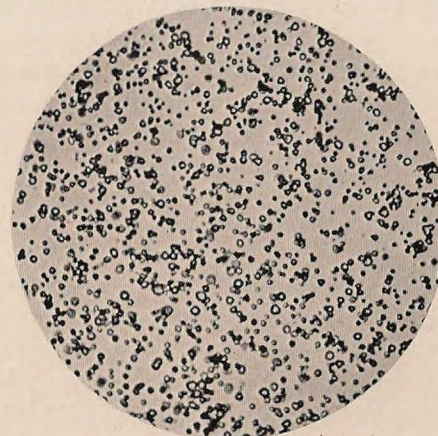
Courtesy DuPont Film Manufacturing Corporation

FIG. 58. MOTION-PICTURE POSITIVE EMULSION GRAINS X 1000

a formula which has been already given on page 68. The problem of keeping quality is somewhat more complicated in film production, on account of the character of the base itself and the substratum employed, and the alteration already mentioned as possible has been prevented to a large extent by the provision of an inert hydrophylic colloid buffered at substantially the same pH as the emulsion, or by treatment of the emulsion itself. Details of the more rapid types of panchromatic emulsion for film coating will be found in Chapter XIV.

A positive emulsion suitable for motion-picture work must

have a small, uniform grain and possess the necessary qualities for both sound and picture reproduction. A fine-grained, long-scale emulsion is needed for both positive and negative sound records. While commercial positive gamma is usually in the neighborhood of two, it must be remembered that the sound is ordinarily restricted to a part of it only; negative gamma ranges from 0.5 to 0.9, and the exposure is so regulated as to keep the maximum value below the shoulder of the characteristic curve. Fig. 58 shows a smear of commercial positive motion-picture emulsion at $\times$ 1000 magnification and indicates the extremely uniform grain, which is nevertheless coupled with a long straight-line portion of the curve.

A formula for a positive emulsion is as follows:

A.	Gelatin	400 g
	Distilled water	2500 cc
B.	Potassium bromide	400 g
	Potassium iodide	15 g
	Water	1500 cc
C.	Silver nitrate	500 g
	Distilled water	1500 cc
D.	Gelatin	350 g
	Water	1000 cc
	Ammonia (s.g. 0.910)	45 cc

This is a mixed-jet type, so that B and C are poured through five- to six-millimeter nozzles, at temperatures of 140° F. (60° C.) and 77° F. (25° C.) respectively, into the crock containing the emulsifying gelatin A, which should be at about 120° F. (50° C.). The emulsion is digested at 120° F. for thirty to forty-five minutes, and is then poured into D, which has been previously heated to the same temperature. The emulsion may be further digested after washing if the tests show it to be necessary.

An all-ammonia positive film emulsion may be made as below:

A.	Water	1200 cc
	Ammonium bromide	150 g
	Ammonium iodide	4 g
	Soft gelatin	120 g
B.	Water	100 cc
	Silver nitrate	200 g
	Ammonia to redissolve.	

Half the silver is poured at 77° F. through a nozzle or jet into the crock containing the A solution (at 105° F.); the other half is then " flopped " in without stirring, and 200 grams of dry, high-viscosity gelatin is then added and stirred in until completely dissolved. The emulsion is maintained at 105° F. or just under, then set in ice water. It is very thoroughly washed in order to get rid of all the ammonia, and made up with spirit and finals to 4000 cubic centimeters. Coating weight should be 90 to 110 milligrams per square decimeter.

In view of the increasing interest in the making of color prints by the wash-off relief process, and by superimposition of three dyed gelatin images on film base, some description of the materials used should be given. The original idea of using gelatin reliefs as matrices for producing the elements of a subtractive transparency must be ascribed to E. Sanger Shepherd, to whom the Progress Medal of the Royal Photographic Society was awarded for this work nearly forty years ago.

A wash-off relief film can be used in two ways. One way is by sensitizing a slow gelatino-bromide emulsion with dichromate, exposing it through the back of the film and developing it in hot water; the washed-out relief image is fixed and washed, when it can be used to imbibe the necessary dye, which can be transferred to paper or left in the film if the latter is to be made one element of a three-color transparency. The other way is to expose the film under a negative and after developing it to

harden the image with a bleaching bath, so that on treatment with hot water the exposed image alone remains, with its tone scale duly represented by graduated thickness of the gelatin relief. This may be used as a matrix for taking up the necessary dyes, which can be transferred to a plain gelatin-coated paper previously treated with a mordanting solution.

A wash-off relief emulsion may be coated either on glass or on celluloid. Glass was used in the Color Snapshots process, nitrate base is used in the Eastman Wash-Off Relief process. An orange dye is used in the latter film to prevent irradiation within the film and to keep the image in the layer nearest the base (exposure is made *through the base*). Any slow bromide emulsion may be used for wash-off relief or imbibition films; but they must contain no hardening agent, and should be dyed with about twenty-five cubic centimeters of 1:200 alcoholic solution of naphthol orange per liter.

Such films may be sensitized with a three per cent solution of potassium dichromate, exposed under a negative through the back, and developed with hot water, then fixed in plain hypo and washed. Or develop in Eastman D-11, rinse well, and bleach for two to four minutes in a mixture of equal parts of:

A. Ammonium bichromate	5	g
Sulphuric acid (conc.)	1	cc
Water	750	cc
B. Sodium chloride	11.5	g
Water	750	cc

Then develop in water at 110° to 125° F., using four or five changes of one minute each, and they are then fixed for one minute in:

Hypo	240	g
Sodium sulphite (dry)	10	g
Sodium bisulphite	25	g
Water to make	1000	cc

Where the dichromatized relief images are stained after being washed out, the three elements in yellow, magenta and blue-green can be assembled to give a three-color transparency. Where the developed, bleached and washed-out images are made, they are used for taking up acid dyes which in turn are transferred to a piece of plain gelatin-coated paper which has been treated with a mordant, as is practised in the well-known Wash-Off Relief process.

Chapter References

1. Charrion and Valette, *Bull. Phot. 6,* 193, 1–10.
2. E. J. Wall, Photographic Emulsions, p. 188.
3. T. H. Dixon and Co., Ltd., Letchworth, England.
4. Product of the Atlas Powder Co., U. S. A.

Chapter XI

PRINTING–OUT EMULSIONS

Salted Paper — Sensitizing Silk — Printing-out Emulsions — Gelatino-chloride Papers — Collodio-chloride Papers — Self-toning Papers — Silver Phosphate Papers

CERTAIN salts of silver will, if applied to paper, give a visible image on exposure to light under a negative, which is of sufficient density to provide a permanent print. Silver chloride discolors or " prints out " a blue-violet color; organic salts of silver, such as the citrate, oxalate or tartrate, print out a redder color. The organic salts appear to be more sensitive to light when in a humid condition, which explains why so-called print-out papers sensitized with a mixture of the two — as is usually done — yield a redder image if the humidity is high. None of these compounds will give a sufficiently intense image by itself to withstand the fixing bath, and an excess of silver nitrate is required for building-up purposes. The visible image consists of metallic silver in a very fine state of division, and in the heaviest densities there is probably not more than half a milligram of silver metal per square decimeter. The reduced silver is colloidal in character, and some of it is held in solid solution in the excess of silver halide; if, on prolonged exposure, the silver chloride becomes saturated, a deposit of bronze-colored silver metal may then appear on the surface in the deepest shadows.

The simplest possible form of printing-out paper is the old-fashioned " salted paper," though this is not actually prepared with an *emulsion*. In this process of sensitizing, the original surface of the paper is retained, and photographs printed on it

may be used as the basis for a drawing or for working up with water colors, the silver image itself being removed afterwards. Any good quality drawing paper, such as Whatman's or Rive's, or good unsized writing paper, can be sensitized. It must first be sized or coated with a solution containing the reacting salts:

Water	450	cc
Sodium chloride	15	g
Citric acid	1.5	g
Arrowroot	15	g

The arrowroot is mixed with about fifty cubic centimeters of the (cold) water, and rubbed into a smooth paste. The remaining water with the sodium chloride and citric acid is next added, and the whole is brought to the boil, stirring continually, and boiled for three minutes. When cooling, a skin may form on the surface, and if so, it is removed and thrown away. The solution is then filtered. If a glossier surface is wanted, five grams of gelatin may be substituted for the arrowroot, when of course boiling is not necessary, the gelatin being dissolved with heat and stirring in the usual way.

The salting solution as described can be applied with a wide, soft, camel's-hair or hog's-hair brush, or the paper may be floated upon it a sheet at a time and hung up to dry. It is a good plan to make a mark in pencil on the back of each sheet indicating that the opposite side has to be sensitized. If bubbles form when brushing on to the surface of a rough paper, a little alcohol (three or four per cent) may be used in the solution. The paper must be dried in a room or cupboard absolutely free from dust.

It is best sensitized the night before use by floating it, sheet by sheet, upon the silver bath, which is prepared as below:

A. Silver nitrate	20	g
Water	100	cc
B. Citric acid	15	g
Water	100	cc

A and *B* are mixed, and twenty cubic centimeters of pure grain alcohol added. The solution is used at room temperature, in a perfectly clean dish. A sheet of paper held by the edges is bent into an inverted U, the convex side brought gently into contact with the surface of the sensitizing bath, and the two sides then lowered until the sheet floats upon the liquid. After a minute it is lifted by one corner to see if there are any air bubbles, and if so, these must be removed and the sheet re-lowered on to the solution for a further two minutes. Thick paper may require four to five minutes in all. Rubber gloves should be worn, or the fingers may get badly stained. The sensitized paper is hung up to dry by the corners, in a warm room or dust-free cupboard. All these proceedings can be carried out in Mazda light.

Printing is done in sunlight, and progress may be examined by opening the frame a few feet away from the window. When all details are clearly visible, and the print is appreciably darker than is desired in the final image, the paper is removed from the frame and washed, toned in a gold bath, and fixed. If it is required only as a guide for drawing, it may be simply fixed in twenty per cent hypo, but it will then take on an unpleasant orange color. The *photographic* image after drawing upon it can be removed with Farmer's reducer.

If separate toning is to be given, it is imperative to wash the print beforehand until all free silver nitrate has been removed; this will be apparent when the wash-water no longer becomes milky through the formation of silver chloride. A good toning bath is as follows:

Gold chloride	0.1	g
Sodium acetate	2.8	g
Water	400	cc

When the print has acquired a purple tone, it is rinsed and

fixed for five minutes in a ten per cent hypo solution, and is finally well washed. By the use of a combined toning and fixing bath the print can be put without washing into the solution, toned and fixed simultaneously, and then finally rinsed. Such a bath may be made up thus:

Water	300	cc
Hypo	100	g
Lead acetate	0.3	g
Gold chloride	0.15	g
Powdered chalk	7.5	g

Shake up well, stand overnight, and decant the clear solution for use.

SENSITIZING SILKS AND FABRICS. — For printing photographs upon silk or other fabric, sensitizing is best done with the substitution of Iceland moss for arrowroot, starch, or gelatin. This is a dried seaweed collected on Atlantic coasts, and is made into an " infusion " by mixing 2.5 g of the moss with 500 cc of boiling water. It is decanted and filtered, and when cold is of a syrupy consistency. To it is added:

Sodium chloride	20	g
Glacial acetic acid	50	cc

The mixed solution is used in a dish, and the pieces of material are gently lowered on to the surface, the object being to coat the surface of the material only, and to prevent as far as possible the solution from penetrating through to the back. After two minutes' flotation, the pieces of silk, etc., are lifted by two corners and hung up to dry on a stretched cord, and left until they no longer smell of acetic acid. They are then sensitized by floating on:

Silver nitrate	25	g
Citric acid	20	g
Grain alcohol	20	cc
Water to make	250	cc

A high-contrast negative should be used for printing (γ 2 to 2.5), and the image printed deeply and then treated with a combined toning and fixing bath. Wash and dry and smooth out cautiously with a moderately hot iron.

Plain salted paper as above described was followed by a much more stable product, prepared with a coating of salted albumen and sensitized afterwards with silver nitrate, which held the field for many years. After this era of albumenized paper came the far more practical gelatino-chloride paper popularly known as printing-out paper in America, and as P.O.P. in England. This was baryta paper coated with a single emulsion of silver chloride in gelatin, containing a large excess of silver nitrate, and it had both before and after use comparatively high keeping qualities. It printed rapidly, gave a superb range of tone, and could be toned with gold, platinum or palladium, giving an image which would last for ten years or more.

The need for an excess of silver nitrate makes it necessary to select paper of great purity for coating gelatino-chloride emulsions, and fairly heavily baryta-coated rag paper has been used. After printing-out in daylight, the excess of free nitrate is removed by washing, and the prints are then toned and fixed. To avoid the trouble of toning, a soluble gold salt such as the thiocyanate was incorporated in the emulsion itself, making self-toning papers which acquired a gold purple tone during fixation.

One form of print-out emulsion giving brilliant prints but of only moderate keeping quality is made as follows:

A. Water	750	cc
Ammonium chloride	2.5	g
Sodium potassium tartrate	5	g
Gelatin	80	g
B. Silver nitrate	25	g
Citric acid	10	g
Water	250	cc

Solution B is added to A in a slow stream while the crock is kept stirred, both solutions being at 105° F. (40° C.). The mixed emulsion is almost transparent at first, but soon becomes turbid. After about ten minutes, forty to fifty cubic centimeters of denatured spirit is added, and slowly, with stirring, twenty cubic centimeters of a 2.5 per cent solution of chrome alum. The emulsion is filtered through felt, or two thicknesses of linen, and coated at once. It cannot be set off and remelted. Increase in the amount of citric acid tends to give higher contrast; substitution of an equivalent amount of ammonium citrate for the Rochelle salts (sodium potassium tartrate) tends to give fuller half-tones. The addition of ten cubic centimeters of a twenty-five per cent solution of stronger ammonia water will give increased sensitivity and somewhat bluer tones. When ammonia is used, however, the emulsion should be stood after its addition for half an hour at 105° to 110° F. before coating. To mat the emulsion, fifty grams of rice starch, ground to a paste with a little water, is added before filtering. The mat emulsion is best coated on *glossy* baryta paper.

Another reliable formula for a printing-out emulsion is the following:

A. Gelatin	24	g
Ammonium chloride	0.8	g
Water	200	cc
B. Tartaric acid	0.8	g
Sodium bicarbonate	0.4	g
Potash alum	0.5	g
Water	30	cc
C. Silver nitrate	10	g
Citric acid	2	g
Water	45	cc

A and B are heated to 110° F. and mixed; solution C is then added slowly with stirring, at the same temperature. Final ad-

ditions are twenty cubic centimeters of grain alcohol and five cubic centimeters of 2.5 per cent chrome alum solution.

It has been suggested that the decomposition of the gelatin by free silver nitrate can be obviated by the use of a sufficient amount of organic salt, such as ammonium or potassium citrate, to take up the excess of silver nitrate over the combining weight of chloride. Thus for 100 grams of $AgNo_3$, 18.3 grams of sodium chloride and 29 grams of potassium citrate would be used, keeping the citric acid at about sixty per cent of the silver.

The use of collodion in place of gelatin offers some attraction, and collodio-chloride printing-out papers have enjoyed considerable popularity. The drawback to the use of collodion in laboratory experimentation is its very high inflammability. The solvents used are not only inflammable to a marked degree, but when diluted with air may form highly explosive mixtures. In factory practice not only can fire risks be eliminated by suitable precautions, but methods are adopted of recovering the solvents for use again.

A formula which may be made up successfully in small quantity is given below:

A. Pyroxylin or " celloidin "	10	g
Ether (methylated)	200	cc
Alcohol	200	cc
Castor oil	2	cc
B. Lithium chloride	1.2	g
Strontium chloride	1.2	g
Alcohol	35	cc
C. Silver nitrate	10	g
Distilled water	10	cc
Alcohol	25	cc
D. Citric acid	2.5	g
Alcohol	35	cc

Mix C and D, and add gradually to the collodion A in a large

flask, with constant agitation. Then add B very gradually, with constant shaking. Lastly add 2.5 cc glycerin. Stand for twenty-four hours before coating on baryta paper.

An alternative formula [1] runs as follows:

A. 4 per cent collodion	500	cc
B. Alcohol	50	cc
10 per cent aqueous solution of strontium chloride	3	cc
10 per cent aqueous solution of lithium chloride	1	cc
C. 50 per cent solution of silver nitrate	24	cc
Alcohol	50	cc
D. 25 per cent aqueous solution of citric acid ..	60	cc
Alcohol	25	cc

A and B are thoroughly mixed at room temperature, a two-liter Pyrex flask being very convenient. C and D are then mixed together and added to the mixture in the flask, ten to fifteen cubic centimeters at a time, with vigorous shaking. When emulsification is completed, the following finals are added:

50 per cent castor oil in alcohol	3 cc
Alcohol	25 cc
50 per cent glycerin in alcohol	8 cc

This emulsion can be made self-toning by adding 0.15 grams of gold chloride dissolved in ten cubic centimeters of alcohol; the addition of ammonium thiocyanate or lead acetate or nitrate has also been suggested. Self-toning emulsions are usually unstable and should be coated at once.

The coating of collodion emulsions for experimental purposes is by no means easy. Baryta paper *can* be unrolled on the emulsion placed in a dish, as has been described elsewhere (p. 163), but the film may form in tiny wrinkles and give a broken surface. Small pieces can be coated individually by

turning up the edges about a quarter-inch all around, laying the sheet on glass, and coating as a glass plate. If an excess is poured on, and after setting for a few moments is poured *off*, the paper may be held at one corner and given a zigzag movement to prevent wrinkling. The warning against the high inflammability of collodion and its solvents, especially when used in open dishes or during evaporating when drying the paper, must again be emphasized. Positively no naked lights may be used, no smoking, and no use of electric heaters having bare resistance elements. The room should be kept cool, and should be well ventilated.

Stripping-collodion may be made by first coating baryta paper with an eight per cent gelatin solution, then with the collodion emulsion. The gelatin coat is, of course, first dried. After the print has been toned and fixed, immersion in warm water will soften the gelatin, and the collodion image can be floated off.

While printing-out papers have gone out of fashion on account of the convenience of development papers and their greater working rapidity, they are capable of giving exceedingly beautiful results, and there is some indication of their reintroduction. The experimenter in emulsion work will certainly find a great deal of fascination in the printing-out field, and ample scope for investigation.

SILVER PHOSPHATE SENSITIZERS. — Phosphate of silver is formed by the reaction of sodium phosphate, Na_2HPO_4, or tribasic sodium phosphate, Na_3PO_4, with silver nitrate. It is more sensitive than the chloride, and must therefore be dealt with in yellow light. It gives a somewhat exaggerated latitude, so that it is best suited to hard, vigorous negatives. A precipitate of silver phosphate dissolved in an organic acid, such as citric acid, can be applied with a brush to raw paper, or the salt itself may be precipitated in collodion as suggested by Valenta.[2] Here 2.9

cubic centimeters of phosphoric acid of specific gravity 1.265 was added to 200 cubic centimeters of collodion, together with 7 grams of citric acid previously dissolved in 14 cubic centimeters of alcohol. This was then mixed with:

Silver nitrate	10	g
Water	125	cc
Alcohol	20	cc
When dissolved, add Lithium carbonate	7.5	g

When the evolution of carbonic acid has ceased, 1.5 cubic centimeters each of glycerin and grain alcohol are added.

Silver phosphate images may be developed with a weak solution of metol acidified with acetic or tartaric acid.

Chapter References

1. A. Truum, Die Herstellung photographischer Papiere, p. 300.
2. E. Valenta, *Phot. Korr., 37,* pp. 313, 419, 1900.

Chapter XII

TESTING EMULSIONED PRODUCTS

Testing Equipment — Estimation of Speed and Quality — Interpretation of the Characteristic Curve — Measurement of Color-sensitivity — Photometers and Density Meters — Keeping Tests

AN important part of the routine of sensitive material manufacture lies in the adequate testing of the finished products. In any form of investigation, exhaustive tests of the coated plates, films or papers will be more productive of results than the making of numbers of more or less random experiments. Some form of sensitometric test is required, and the character of different emulsions must be deduced and compared. Sensitometric work demands suitable apparatus, which may be somewhat costly, but it must be regarded as absolutely indispensable and a very sound investment where commercial work is envisaged. Where the products are being made for experimental purposes, and do not have to compete with other manufactured articles, a great deal can be accomplished with the aid of more modest equipment.

The main characteristics of plates, films, and papers are most simply represented by the type of curve originated by Hurter and Driffield, which shows the relationship between the photographic response of any individual material after development and the exposure to light required to produce it. As we have seen, emulsions are, in general, sensitive not only to visible light of 400 to 700 mμ, but to radiations of shorter wavelength, especially the ultra-violet, X-rays and the radiations emitted by radioactive bodies. A developable effect is also produced by a static discharge in contact with the film, and to some extent

by pressure. Bloch states [1] that pressure or abrasion marks render the emulsion *insensitive* to subsequent light action.

The developed image consists of reduced metallic silver grains, and the mass of reduced silver per unit area is proportional to the logarithm of the opacity. Opacity is the ratio of the incident to the transmitted light, or the reciprocal of transmission, $\dfrac{I}{T}$. The need for expressing it logarithmically can be seen from the simple table showing that the quantity of light transmitted by an increasing number of layers of an absorbing material each one of which absorbs *half* the incident light, proceeds geometrically and not arithmetically, as under:

	Proportion of light transmitted	Opacity
1 layer	$\frac{1}{2}$	2
2 layers	$\frac{1}{2}$ of $\frac{1}{2} = \frac{1}{4}$	4
3 layers	$\frac{1}{2}$ of $\frac{1}{4} = \frac{1}{8}$	8
4 layers	$\frac{1}{2}$ of $\frac{1}{8} = \frac{1}{16}$	16
5 layers	$\frac{1}{2}$ of $\frac{1}{16} = \frac{1}{32}$	32

and so on. Expressed as logarithms to base 10, we have (approximately):

$$\log \text{ (opacity) } 2 = 0.3 \qquad (2 = 10^{0.3})$$
$$\log 4 \qquad = 0.6 \qquad (4 = 10^{0.6})$$
$$\log 8 \qquad = 0.9 \qquad (8 = 10^{0.9})$$
$$\log 16 \qquad = 1.2 \qquad (16 = 10^{1.2})$$
$$\log 32 \qquad = 1.5 \qquad (32 = 10^{1.5})$$

and so on.

The logarithm to base 10 of the opacity is termed the density. The density of the coated film bears a constant relation to the logarithm of the exposure over a range of illumination $I \times T$ which is dependent on the particular emulsion. The curve connecting density with *log* opacity, usually referred to as the H

and D curve after Hurter and Driffield, or the characteristic curve, takes the general form shown in Fig. 59. It will be seen
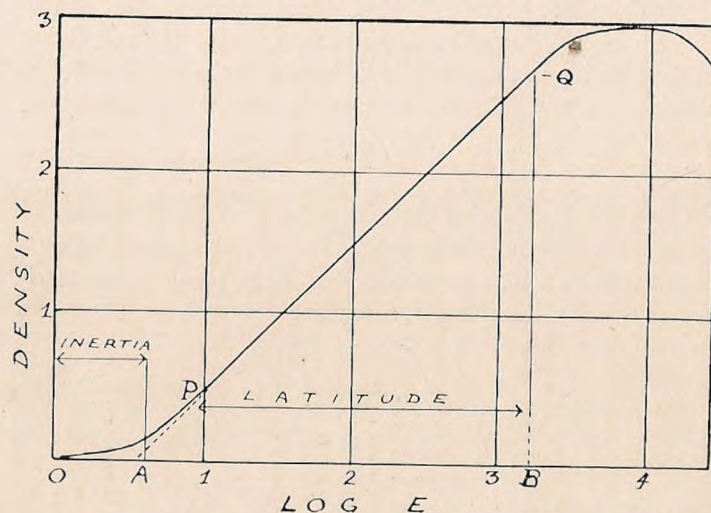
FIG. 59

that the increase in density for increase in *log* exposure is not equal for the lower exposures, but is progressively greater as exposure rises, and that the shape of the curve *is* curved in these lower densities, known as the foot or toe. After exposure has exceeded a certain amount, however, density increases by regular amounts over a *period of correct exposure* represented by the straight-line portion *PQ*, this part of the curve giving us a measure of the *latitude* of the emulsion. On very considerable exposure, the curve is seen to turn over, when still further increases in exposure (*over*exposure) actually produce less density instead of greater. This is the region of solarization or *reversal,* and is usually encountered at an earlier stage in the

case of fast large-grained emulsions than it is in slower, more fine-grained emulsions.

The characteristic curve gives us an immense amount of useful information, enabling us to make a very complete post-mortem of an experimental emulsion, or the effects on its quality of any variations which may have been made in the course of experiment. It will be seen in Fig. 59 that on extending the straight-line portion to cut the *log* exposure axis, it cuts it at a point, *A*. The length *OA* represents the *inertia* of the material, and this is inversely proportional to the so-called *speed*. It must be emphasized, however, that the characteristics exhibited by any such H and D curve, and the inertia and speed deduced therefrom depend upon the particular developer used, on the time of development and its temperature, and — to some extent — on the spectral quality of the light used in exposure.

If *log* exposure is spaced along the horizontal axis equally with density along the vertical, so that for example *log* exposure of 3 measures the same as density 3 on the graph, then we obtain a universally recognized means of measuring contrast or gamma, γ. If the straight-line portion of the curve be at an angle of 45° with the *log* E axis, then gamma = tan 45°, or 1. Generally, $\gamma = \tan \theta$, where θ is the angle made by the straight-line part of the curve with the *log* E axis.

As contrast depends on the amount of development, and inasmuch as the rate of development depends on the temperature of the solution, it is usual practice to publish Time/Temperature/Gamma curves. An exhaustive series of these will be found in Morgan and Lester's " Photo Lab. Index," measured for practically all marketed materials. Such curves are also being extensively published by manufacturers, and their preparation and issue with new sensitized materials should be regarded by new entrants into the manufacturing field as in-

dispensable. An example of the form in which sensitometric
data is supplied is seen in Fig. 60, reproduced from " Kodak
Films."
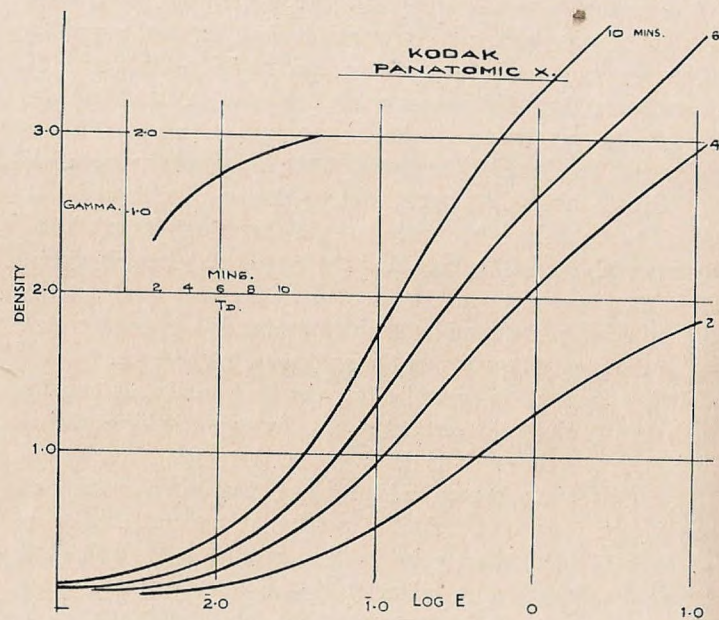
FIG. 60

In Fig. 61 we see a number of curves plotted for one material,
developed for increasing times. The contrast is low at short
development, rising with increasing time of development until
the top curve is reached after a gradual falling off of the rise with
time. In this case after eleven minutes at 70° F., longer de-
velopment fails to increase contrast. In other words, *gamma
infinity* has been reached, denoted by γ_∞. While, therefore,
gamma is a measure depending on a particular developing solu-

tion, its temperature, and the time of development, gamma is
a concrete factor which gives a definite idea of the ultimate
performance of an emulsion. Gamma infinity is largely in-
dependent of the wavelength of the light used in exposure if the
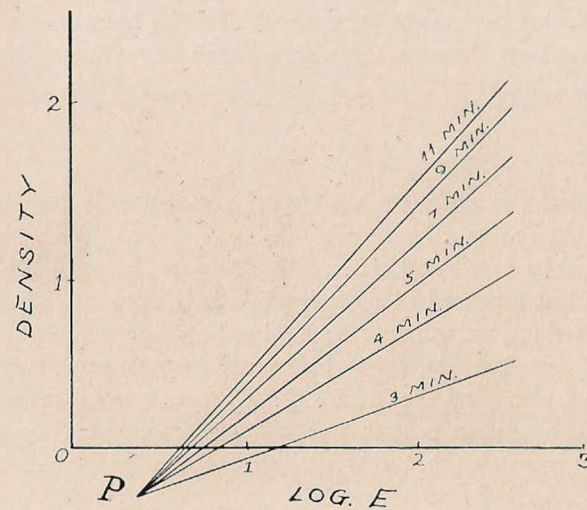
FIG. 61

plate be developed to gamma infinity [2], whereas a color-sensitive
emulsion *not* developed to γ_∞ is definitely dependent on wave-
length.* It is for this reason that the yellow printer negative
in one-shot camera work (exposed through the blue-violet fil-
ter) is generally given a time of development increased from
twenty-five to one hundred per cent over the times allotted to

* Certain recently introduced emulsions of the panchromatic type are
claimed to give a consistent gamma throughout the spectrum, and the yel-
low, red, and cyan printers can thus be all given the same time of develop-
ment.

the red and cyan printers. In cases where narrow-cut filters are used in separation work from color transparencies, the time of development should actually be varied for each of the three. Gamma infinity being an important factor from an emulsion-making point of view, the following simple formula for deducing it from the gammas obtained for two times of development, γ_1 for a time T, and γ_2 for a time $2T$, one double the other, is given:

$$\gamma_\infty = \frac{\gamma_1{}^2}{(2\gamma_1 - \gamma_2)}$$

In using this formula, the higher of the two gammas should not be too close to γ_∞.

It will be noted that the family of curves shown in Fig. 60 all meet at a point below the *log* E axis if extended. This is accounted for, according to Nietz,[3] by the presence in the emulsion of free bromide, without which the meeting point would be substantially on the *log* E axis. Practically all commercial bromide emulsions contain free bromide, which not only minimizes general fog, but assists in preventing edge formation of fog on coated plates.

It has been stated [4] that " the method devised by Hurter and Driffield in 1890 for studying the properties of a photographic emulsion has been extremely fruitful and still furnishes the most complete information on the different properties of sensitive emulsions, and represents them graphically under the most favorable conditions. At the same time the mode of numerical expression of sensitivity proposed by them, (H and D speed) has now scarcely any significance. At the time of Hurter and Driffield, already long past, the different types of emulsions all had characteristic curves of the same general form, and in order to express the relative sensitivity of two plates it was sufficient to measure (parallel to the exposure axis) the distance between

the corresponding curves after the two plates had been developed to the same gamma. Since 1910, however, new types of emulsions have appeared with characteristics very different from these old emulsions, and it is impossible to imagine a single numerical value which defines at the same time the form of a curve and its position relative to another one."

A simple example of the position can be seen in Fig. 62. This
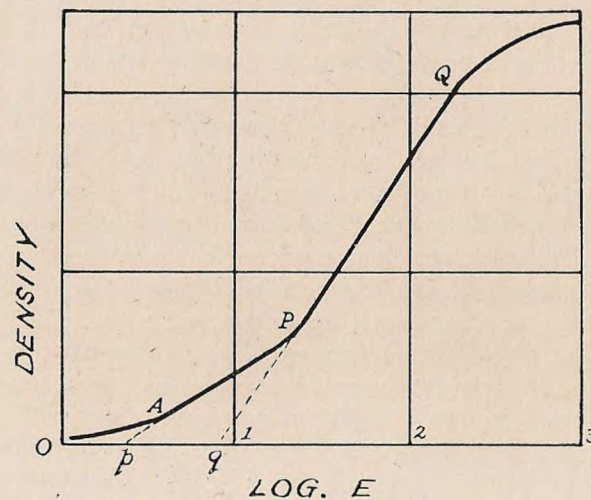
FIG. 62

is a curve representative of many super-speed emulsions. It may be considered as having two straight-line portions, the earlier of them really a prolonged foot. If we extend the foot portion, *AP,* to meet the *log* E axis, it gives an inertia of *Op;* whereas if we extend the straight-line portion, *PQ,* it meets the *log* E axis at *q,* giving an inertia of *Oq.* The speed of the emulsion, obtained by dividing *Op* into a constant as would be done in H and D practice, is obviously far greater than the

speed measured by dividing Oq into the same constant. Yet the studio portraitist may do all his work with low densities on the foot portion and find the material extremely fast, while the man who wants heavier densities must use the PQ part of the curve, and will find the emulsion quite moderate in speed. This case is typical of mixed emulsions, and can occur to a very appreciable extent in the case of split silvers, where one silver is re-dissolved and the other added plain, etc. The emulsion-maker's art is to provide a smooth curve with long straight-line portion, no matter how he divides his silvers and manipulates his ripening.

The broad H and D method is nevertheless generally used in the United States for sensitometric work. A typical example of its application is seen in the motion-picture industry where a staff is continuously engaged in making sensitometric tests of all film stock used for camera work, sound recording and printing, and for controlling and checking developing and other solutions for performance, exhaustion and so on. In many branches of technical photography, small differences in the shape of the toe of the characteristic curve may have the highest significance, as for example in sound recording, radio facsimile and photo-engraving. Needless to say, refined sensitometric work of this type is not possible without adequate laboratory plant and physical apparatus, and more particularly in the absence of machine-coated materials.

In experimental work with emulsions, a great deal of useful information can be obtained as to the effects of variations in treatment, modifications in formula, and so on, with a good step-wedge, a stable light source, temperature-controlled development, and some dependable form of densitometer. The step-wedge provides us with an intensity scale of exposure, as against the time scale of the Hurter and Driffield or Scheiner sector wheels. The usual sector wheel of Hurter and Driffield

has nine slots (Fig. 63), each one subtending double the angle of the previous one, thus giving an exposure range of 1:256, the ratio being $\times$ 2 for each step. The disc W (Fig. 64) is mounted

FIG. 63

vertically on a shaft driven by motor. A plateholder P, behind the upper half of the disc, receives light through the slots as the disc is rotated by a driving wheel, D. A controlled light source, L, filtered to daylight and thoroughly screened, is placed at a fixed distance — usually one meter — from the sector wheel, which may be turned rapidly (when the intermittency effect creeps in), or through one complete turn for the entire exposure. The lamp, L, which must be housed in a dead-blacked box with suitable aperture facing the sector wheel of say one inch square, is run from a storage battery B, through a resistance R, with regulating contact K. An accurate voltmeter such as a Weston meter sensitive to within $\pm$ 0.2 per

cent, is shunted across the lamp terminals, and the resistance is set to give, say, 5.8 volts with a 6-volt lamp. This slight under-running tends to give uniformity and to increase the useful life of the lamp. Hurter and Driffield used a " standard candle " as their light source; Eder subsequently adopted a small benzene lamp; Sheppard and Mees employed an acetylene flame burning under constant pressure. Today secondary standards are most conveniently obtained with incandescent lamps, but it must be understood that photographic sensitiveness varies quite considerably with the spectral quality of the
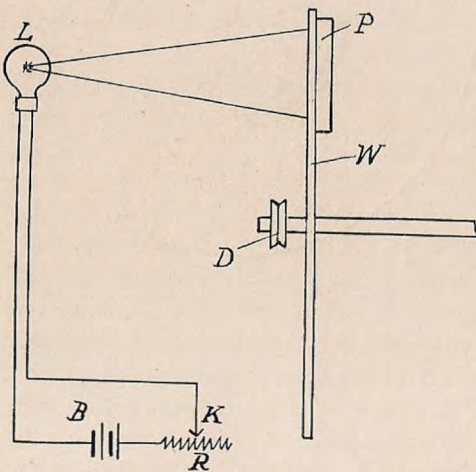
FIG. 64

light used, so that this must be correctly defined and properly controlled. The spectral energy distribution of incandescent lamps varies greatly with filament temperature, which in turn varies with applied voltage.

Probably the most useful type of step-wedge is one having

twelve steps — no density at the first ($d = 0$), complete opacity at the twelfth ($d = \infty$), and ten intermediate steps of:

Density	0.3 having approximately transmission	1/2
	0.6	1/4
	0.9	1/8
	1.2	1/16
	1.5	1/32
	1.8	1/64
	2.1	1/128
	2.4	1/256
	2.7	1/512
	3.0	1/1024

The Eastman Kodak Company supplies wedges having twenty-one steps with densities ranging from 0.15 to 3.0, the step increments being 0.15 instead of 0.3, the opacity ratio of successive steps being thus $\times \sqrt{2}$ instead of $\times 2$. The Ilford Company, Ilford, London, England, specializes in step-wedges, making them to any reasonable specification. A four by five inch step-wedge with ten steps costs fifteen to twenty dollars. Alternatively, by obtaining some neutral gray gelatin of three or four densities, a step-wedge can be built up on a piece of glass, using different combinations for the successive steps. Eight strips one-half inch deep and four inches wide can be mounted on a 4 by 5-inch glass, leaving the top half inch clear to give total transmission and blocking out the last half inch with a strip of dead black paper to give total opacity.

The wedge must be used in a solid plateholder or frame of ample dimensions, as shown in Fig. 65, which can be placed on the bench at a measured distance from a suitable and controllable light source, such as a 6 or 8-volt motor headlamp run from a storage battery with a potentiometer at a voltage preferably of rather less than six volts. A tungsten-to-daylight filter such as the Wratten 78 will filter the light and give results more closely approximating practical daylight use.

Sensitometry connected with emulsion-making experiments is not quite on a par with the general testing of photographic materials, as in most cases comparisons of speed and characteristics of members of a series of similar emulsions are the chief
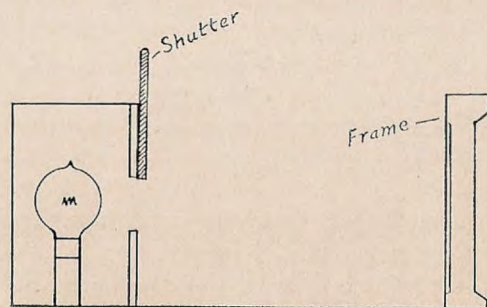
FIG. 65

concern.   Relative speeds can be obtained by means of the points on the *log* E axis at which the straight-line portions of the curves, when prolonged, intersect it.   The antilog of the difference between the *log* E readings will give the speed ratio. Contrast can be estimated by measuring the slope of the straight-line portion of tests developed to gamma infinity, and the materials can then be classified for general reference into groups such as:

Flat	when γ_∞ is less than 1.2
Normal	when γ_∞ lies between 1.2 and 1.6
Medium	when γ_∞ is greater than 2.0
Contrasty	when γ_∞ is above 2.7
Hard	when γ_∞ lies between 3.5 and 4.0
Extremely hard	when γ_∞ lies between 4.0 and 5.0

Such comparisons may be made with any stable light source, and the necessary exposure to give a reasonably straight-line portion of the curve.   If, on the other hand, densities be plotted

against exposures measured in lumens per square meter $\times$ seconds, or measured from a light source of known candle power of geometrically decreasing strength as obtained with a wedge, comparative speed determinations can be made with considerable accuracy.   The step-wedge which can be used in a plateholder at a fixed distance from a standard light source, which distance can be varied with slow or extreme speed emulsions, is probably the best for experimental work, while an accurately cut sector-wheel with a satisfactory secondary standard light source is more generally useful in works laboratories.

In view of the very high humidity experienced in many parts of the country, and the utterly inadequate means of dealing with it which are found in most amateur laboratories, attention should be drawn to the effect which humidity may have on sensitometric tests.   The importance of this effect was emphasized by Renwick,[5] in connection with the testing of negative and positive motion-picture film stock.   A simple method of partial control in use by the author may be recommended.   This is to place the samples of sensitive material to be tested in a large desiccator for forty-eight hours before they are required, using a saturated solution of sodium chloride (kitchen salt) in the bottom.   This maintains an " atmosphere " of about seventy-five per cent relative humidity, which is more or less representative of average conditions in summer time in the United States. It was found by Dimitroff [6] that the background density in many cases increases with decrease of humidity, and that in some cases the graininess of an emulsion appears lessened if the plate is treated with dry air.

The control of development is of prime importance.   It has been pointed out that the characteristic curve depends upon the particular developing formula used, so that the need for a standard solution, used at a definite temperature, is self-evident.

The old pyrogallol-soda formula recommended for a long time for H and D determinations, should be replaced by such a formula as D-11, D-72 or one of the fine-grained type, although a developer *without bromide* is desirable for investigation work. If a number of comparative sensitometric tests be made, it is important that they all be made together for the same time and with as nearly as possible the same amount of agitation. For such a purpose the use of a Dewar vertical vacuum flask may be recommended, where three or four strips can be attached by rubber bands to the sides of a triangular or rectangular stick of wood and immersed in the temperature-controlled solution.

To recapitulate, the emulsion chemist should use, for each family of tests,

  (*a*) a constant developing solution, freshly made.
  (*b*) a constant time of development.
  (*c*) a constant temperature.

Where a gamma/time curve is required, conditions (*a*) and (*c*) must be enforced, the time alone varying, with a short-stop bath used between development and fixing or the immediate transference of the test from developer to a strong acid fixing bath. A vertical developing tank standing in an outer bath of water is recommended for gamma/time work, the tests being suspended vertically in dilute developing solution, giving of course proportionally longer time. The liberation of halogen in the process of reduction of the silver bromide during development and its conversion by the accelerator into alkali bromide, will restrain development in adjacent strips and give erroneous or streaky densities unless proper agitation is applied. Developing sensitometric tests in a flat dish and removing the by-products of development by gentle brushing with a soft camel's-hair brush, has been recommended. Agitation of the plate or film, however, increases the rate of development, so that means must be adopted of giving an average amount of agitation to

each batch of tests. Much valuable information on the effects of agitation has been published in Eastman Kodak research communications.

Densities can be measured directly by means of their absorption of a beam of light as recorded by a photo-electric cell. Articles describing the construction of *densitometers* of this
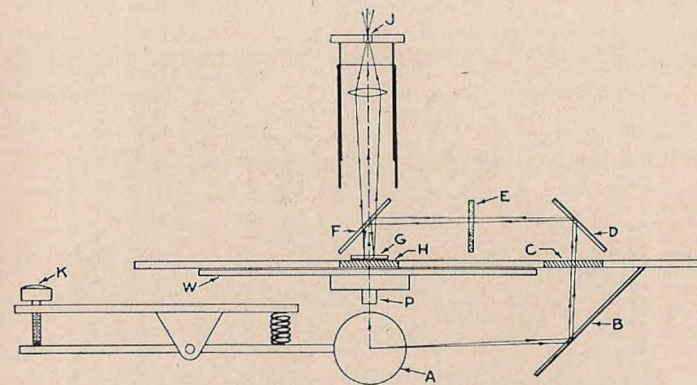
FIG. 66. DIAGRAM OF CAPSTAFF DENSITOMETER OPTICAL SYSTEM

type have appeared many times in recent photographic literature. Two beams of light may be compared in another type of instrument, one passing straight through the density to be measured, the other being extinguished by suitable means until it matches it. Such instruments depend on the use of crossed Nicol prisms, or on the use of a graduated gray wedge. The Hüfner spectro-photometer and the Hilger-Nutting spectro-photometer are examples of the first-named, while the density meter worked out by the British Photographic Research Association depends upon matching the direct and the wedge-extinguished beams by means of a photo-cell.

Another type of densitometer throws the two beams from the
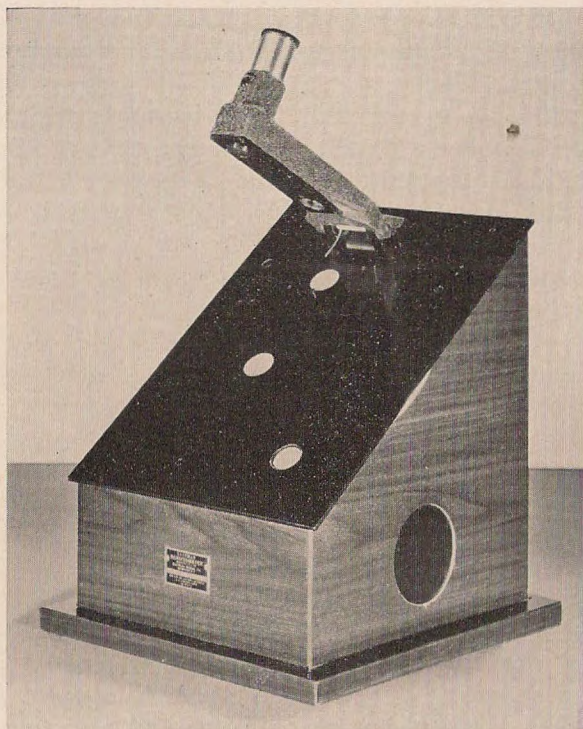
FIG. 67.   CAPSTAFF DENSITOMETER

density patch and the gray wedge into an eyepiece, the wedge being brought to a position where it equalizes them visually. The position of the sliding or revolving wedge is read off on a calibrated scale in densities direct. An instrument of this type, due to Capstaff and Purdy,[7] is manufactured by the East-man Kodak Company; a more elaborate model is made with which reflection densities as well as transmission densities can

be measured. The Capstaff instrument measures silver deposits from a density of 0 to 3.0, and will deal with areas of only one-half square millimeter, being particularly designed for use in the motion picture industry. The optical system is seen in Fig. 66.

Light from source A illuminates at H the density to be measured, and furnishes the comparison beam. A photometric field at G is obtained by the aid of mirrors $B, D, F,$ and $G. W$ is a circular wedge, shown in Fig. 68, for decreasing by a known amount the intensity of the light illuminating the density. J is an eyepiece for viewing the field, in which the density is seen as a central spot in a circle of variable density; when the two beams are matched, the central spot vanishes. The combined
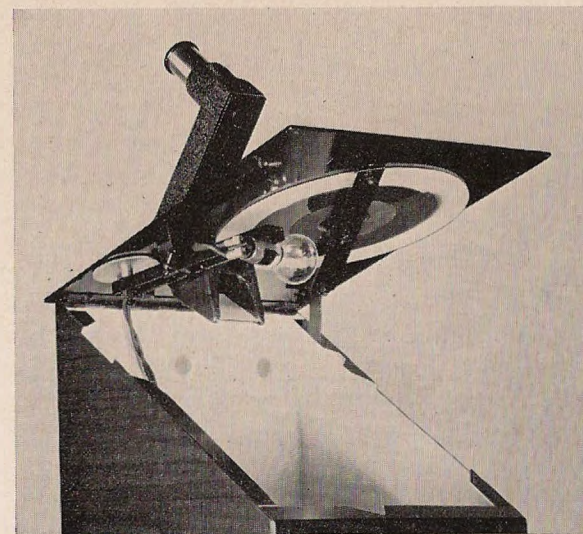
FIG. 68.   DENSITOMETER HEAD RAISED SHOWING CIRCULAR WEDGE

densitometer for measuring negative or print reflection densities is seen in Fig. 67.

In connection with density measurements, it must be borne in mind that the reduced silver grains scatter the light to an extent depending on the emulsion characteristics, and that a density reading obtained by a beam of parallel rays will differ from that obtained by diffuse light. Diffuse density meters have a small opal or finely ground glass directly under the plate or film so that the light is completely scattered. The ratio of density (parallel) to density (diffuse) can yield valuable information as to the physical quality of the developed emulsion.

A simple and inexpensive wedge densitometer designed by Sanger Shepherd and improved by W. B. Ferguson [8] is shown in Fig. 69. Light falls directly on the front of the inclined in-
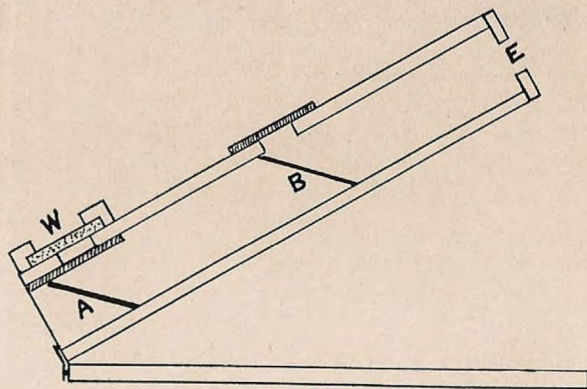
FIG. 69

strument, as from a north window. One beam of light passes through the calibrated gray wedge, W, and is reflected into the eyepiece, E, by the mirror A. The other beam passes through the density patch to be read (laid over the middle aperture), and is reflected by the mirror, B, so as to appear in the eyepiece

contiguous to the first beam. Both beams are scattered by opal glass. The wedge, W, is slid along until the two beams appear of equal brightness. Readings can be obtained with an accuracy of about $\pm$ two per cent.

A simple photo-electric densitometer devised by Schoen is seen in Fig. 70. E is a lamp run at controlled voltage by means
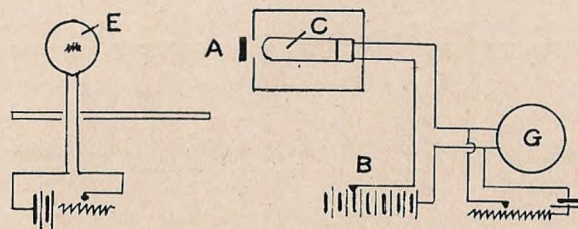
FIG. 70

of a potentiometer. A is a slot over which the density patch is placed. C is a thalofide cell (Case) coupled up with a galvanometer and battery, B. The galvanometer, G, is brought to the null point with the shunt circuit shown, and the density then introduced at A and measured by means of a previously calibrated dial or by a table prepared from known density measurements, or by interpolation on a prepared curve.

If an emulsion be exposed through a small circular hole placed in contact with the film, for increasing times of exposure, the diameter will spread as exposure is increased, and the slope of a curve connecting diameter with exposure was termed by Goldberg the turbidity factor; this was found to be zero in the case of Lippmann plates (p. 135), although no absolute relation between the factor and the grain of a plate was established. The *sharpness factor* of an emulsion has been given by Goldberg as

$$\frac{\text{gamma}}{\text{turbidity factor}}.$$
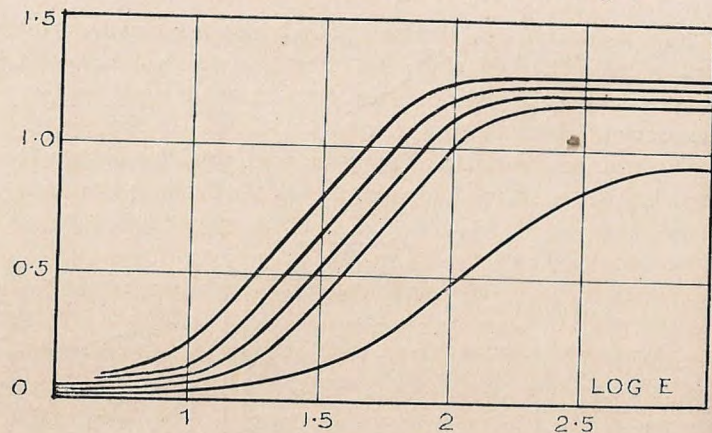
FIG. 71

Translated into practical language, an emulsion to give sharp images should have a high development factor (gamma) and low turbidity, a long straight-line portion to its characteristic curve, and should rise to the maximum slope at as low a density as possible, i.e., not have a long, rounded toe.

So far, we have been dealing with measurements of transparent images only, such as negatives or transparencies, on glass or celluloid. When, however, we come to deal with development papers, we must make measurements of the light reflected from the *surface* of the image. The contrast as seen by reflection increases rapidly at first, and then becomes stationary, all the deeper tones being lost or merged in papers having too high a contrast when fully developed out. This is seen from the characteristic curves given by Mees (Fig. 71), for a bromide paper. It will be noticed that the latitude and gamma remain fairly constant over most of the range, due largely to a considerable regression of inertia with increasing time of development, indicating that good prints can be obtained of varying contrast

by a well-coordinated variation of development time and exposure.

For sensitometric tests of development papers, a reflection densitometer is needed, and probably no more convenient one exists than the Eastman Kodak meter already referred to, of Capstaff and Purdy. An excellent densitometer is made, however, by W. Watson and Sons, Ltd., of High Barnet, Herts, England. This is the outcome of many years' work with the original selenium instrument designed for the British Photographic Research Association by Toy and Rawling.[9] The design of the negative density meter is seen in Fig. 72. C is a photo-electric cell, and W is the neutral gray wedge. A carrier, E, holds the cell and is provided with suitable adjustments for bringing two windows into correct alignment in relation to two diffusing opals O_1 and O_2. The wedge is held in a U-shaped bracket which is
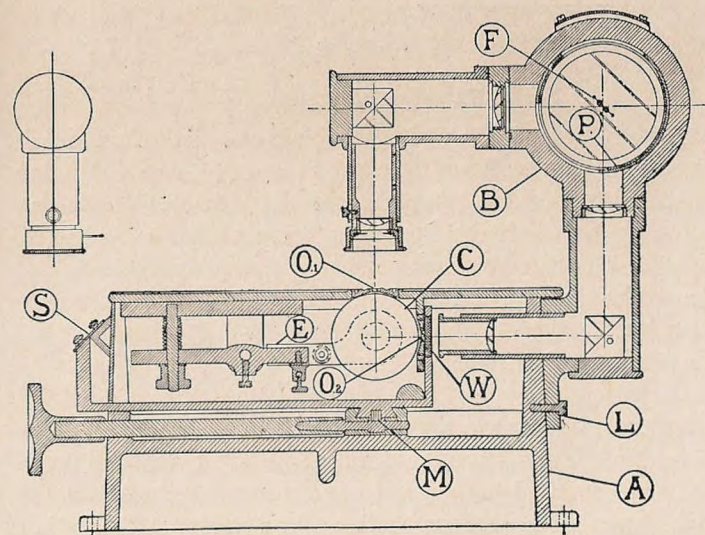
FIG. 72

fixed to a slide provided with a rack, M, by means of which the wedge can be moved across the light beam. The other end of the bracket carries a vernier which moves on the scale S. A single light source, F, is used. The light beam is alternately directed by means of a lever on to the cell through the density
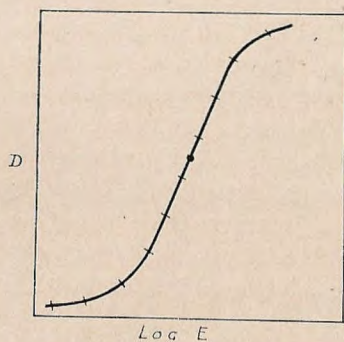
FIG. 73
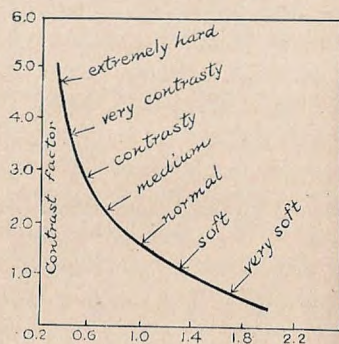
FIG. 74. NEGATIVE RANGES OF CONTACT PRINTS

patch and through the wedge, until a spot of light from a galvanometer in circuit with the cell remains at zero, indicating that the negative density equals the wedge density. The instrument has been elaborated to read reflection densities and to record directly on graph paper, and can be strongly recommended for works practice. The cost of the density meter, galvanometer, lamp and scale, single-tube amplifier and automatic plotting device is, in England, $625.

Some care must be taken in considering reflection density measurements because the character of the image can be considerably affected by the surface of the paper, the coating of the emulsion, and the type of pre-coating (baryta coating or sizing) used before the application of the emulsion. The effect of the non-stress coating should be negligible. The coating

weight can also affect the differentiation of the heavy densities, which are easily lost by too much silver. In dealing with any serious sensitometric work on development papers, the reader is particularly referred to the papers of L. A. Jones on paper contrast,[10] and to the Hurter and Driffield Memorial lecture (1926) of F. F. Renwick.[11] The latter suggests a determination of the apparent integral contrast of a paper calculated from tangents read at not fewer than ten equal intervals along the characteristic curve, covering the whole useful range of the paper. Figure 73 shows ten such points, the black spot in the middle indicating the average at which the contrast factor would be taken. A chart connecting negative ranges and contrasts of seven different grades of paper measured in this way is seen expressed in Fig. 74.

Development papers do not cover the entire range of tones in the subject. While Jones finds that chloride papers for amateur photo-finishing have a short scale of between 1:5 and 1:20, Renwick finds a 1:20 range for mat surface papers and as much as 1:50 for glossy. Reproduction of the tone values of a negative must necessarily be limited by the straight-line portion of the characteristic curve of the printing paper, and as the range of reflectance in this region is considerably less than the overall range, some sacrifice must be accepted at both ends of the scale.

The great attention now being devoted to the making of color prints on paper naturally introduces the problem of measuring colored images by reflected light. A step-wedge is used in the manner already described, but colored steps on Carbro, Chromatone or Wash-Off Relief paper are measured as *grays* by interposing in the light beam a filter of color complementary to that of the strip concerned. Thus in measuring a magenta strip, a green filter (minus magenta) would be interposed in the light beam or in the eyepiece. Such readings enable us to determine

the effect on gamma of variations in the pH of dye baths used in Wash-Off Relief; the effect of modifications in color toning, imbition, etc., on density range, latitude and contrast; and the effects of concentration of dichromate in sensitizing carbon tissue; and so on. In the case of silver halide emulsions, tests coated on glass are of great additional value, as they are not obscured by the physical characteristics of the paper support.

COLOR-SENSITIVENESS. — An important field of investigation in the testing of photographic materials is the analysis or recording of their response to color. This must be done by exposing the emulsion to the various colors of the spectrum and measuring its response by the density recorded in different regions. It is somewhat unfortunate that anything in the way of a spectrograph or means of photographically recording color response should be so prohibitive in cost, when an excellent and moderately accurate instrument can be made with a little skill for a few dollars. The simplest form of spectrograph is probably that designed by A. K. Tallent, a diagram of which is seen in Fig. 75. Light from a lamp, L, is focused by a condensing
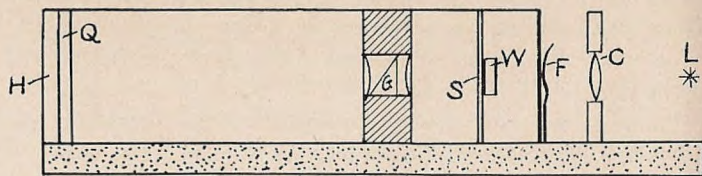
FIG. 75

lens C, on to a slit S, passing through a filter at F when desired, and through a small optical wedge, W, if wedge spectra are to be recorded. G is a prism-grating giving " direct-vision " dispersion so that an image of the spectrum falls upon a plate

or film in the holder, H. In front of the plate when exposed a wavelength scale, Q, can be thrown in.

The author designed many years ago a simple spectrograph capable of doing thoroughly good work, many of which have since been made and used in different factories for routine testing. For the information of those who wish to build such an instrument for themselves, the following particulars are given. The general design is shown in Fig. 76. A box of the
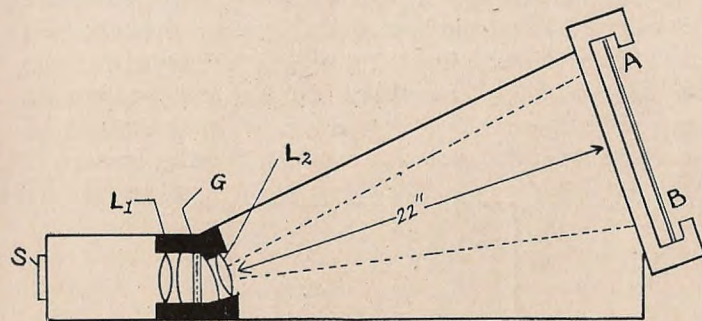
FIG. 76

approximate shape indicated is built up of seasoned mahogany about three-eighths of an inch thick. On a front about two by two inches, or a little larger, is mounted centrally the *slit*. A wooden block is made to take a short focus lens, L_1. This may be a cheap achromat of about five and one-half or six inches focal length. Immediately behind it is fixed a diffraction grating replica. Celluloid casts of diffractions gratings, mounted on plane glass, are obtainable from Central Scientific Co. for as little as $2.50. The size is 25 by 21 millimeters, and there are 5,900 lines per centimeter. The collimated light, parallelized by the slit being placed at exactly its own focal length from the lens, falls on the grating, the plane of which is parallel

to that of the collimating lens. The light, after passing through the grating, is diffracted, and will cast a first-order spectrum at an angle of about 18° or 20° on a screen, AB (in this case the emulsion); this must however be focused, and for the purpose an objective lens, achromatic of course, is fitted behind the grating in the manner shown, also at its own focal length from the plate plane AB. The longer the focus of this lens, the longer will be the spectrum, and a lens of sixteen to twenty-two inches focal length is suggested for a four by five inch plateholder. The image of the slit will be magnified by the ratio of the focal length of the objective lens to the collimating lens, in this case say 22/6, or 3.66, times. The dispersion, and therefore the length of the spectrum, will depend also on the number of lines per centimeter of the grating, increasing with ruling fineness.
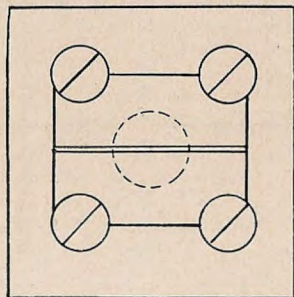
FIG. 77

A four by five inch plateholder is a very convenient size, and a back must be fitted to the camera body such that it can be slid along for successive exposures. A manufactured slit is an expensive item, though always worth-while; a homemade slit which will work remarkably well can be made in the manner indicated in Fig. 77. Two safety-razor blades, carefully paralleled, are screwed down over a central hole about three-quarters

of a centimeter in diameter, with flat-headed screws. For test work, the blades should be about a quarter of a millimeter apart. The camera back must be solid except for a slot slightly smaller than the spectrum, such as five-eighths or three-quarters of an inch wide and four inches long. Everything must be thoroughly dead-blacked, and to prevent scattered light from being reflected on the plate during exposure, it is a good plan to fit a piece of dead-blacked corrugated card along the bottom of the box.

Some sort of wavelength scale will be needed. This can be made as follows. A light source such as a carbon arc is focused by a condensing lens upon the slit, the poles being brushed with a solution of common salt, lithium chloride, a little calcium chloride, if possible a trace of thallous chloride, and a few drops of hydrochloric acid. A spectrum taken on a panchromatic plate will give the following lines:

Violet	Calcium	wavelength	394	mμ
	Calcium	"	396	"
Blue	Lithium	"	460	"
Green	Thallium	"	535	"
Yellow	Sodium	"	589	"
Orange	Lithium	"	610	"
Red	Lithium	"	671	"

Measuring the distances between the lines for the various wavelengths, a magnified scale can be drawn in India ink on Bristol board, and filled in for wavelengths from say 380 to 750 mμ. A great advantage of the grating over the prism for the dispersing medium is that the distance between lines is directly proportional to the difference between wavelength, as against the abnormal dispersion of the prism. As the plateholder is *flat* and not therefore equidistant along its entire length from the center of the objective, a slight loss of definition is inevitable. The scale is next photographed down, on a process plate, so that the spectrum lines fall in their right places. This is ascertained by

moving the negative over the focusing screen until the lines coincide. The scale when developed is cut out the exact size to fit easily into the slot in the back of the spectrograph, and mounted on a slider so that, when the plateholder slide is drawn, it can be pushed in as near to the sensitive film as possible.

It will be noted that many of the spectrograms published in this book and in current literature are of the *wedge form*. This is very useful, as, if a logarithmic wedge be employed, it gives a measure of the relative sensitivity at the different wavelengths. A small gray glass optical wedge can be mounted on the slit, or a neutral gray wedge can be obtained to fit over the wavelength scale or slot. If the slot is three-quarters of an inch by four inches, the wedge should be ordered the same size or a trifle longer, and graduating *across the width* from 0 to 2.5 or 0 to 3 density. In the latter case the transmission is 1 to 1/1000.

A simple, but useful bit of color-testing apparatus can be made with a printing frame and a rectangular step-wedge, across the steps of which are gummed a number of strips of gelatin filters, mounted side by side along the length of the wedge. Half a dozen such strips one-half inch wide and four and one-quarter inches long would be used in the case of a wedge three and one-quarter by four and one-quarter inches. A suggestion for the filters is:

	Wratten No.
Violet *	36
Blue	50
Blue-green	75
Green	74
Orange	58 + No. 15
Red	29

* All violet filters pass a considerable amount of deep red. This can be filtered out by the use of a liquid cell of weak copper sulphate solution, the concentration being adjusted by trial with the spectroscope so as to extinguish the red up to about 650 mμ.

This will give a useful comparison of the relative color sensitivity of various materials, and of the relative sensitivity to individual colors of any particular material. Any such comparisons are of course affected by the efficiency or transmission factor of the various filters.

COATING WEIGHT. — It is important to be able to make a chemical analysis of the amount of silver or silver halide in a given area of plate or film. The following particulars are due to Eggert and Noddack. One square decimeter (ten centimeters square) of the coated film or plate is taken. It is put into a porcelain dish and fifty cubic centimeters of a hot ten per cent nitric acid solution is poured on it. To make this solution, ten cubic centimeters of concentrated nitric acid and ninety cubic centimeters of distilled water are mixed. When the emulsion is dissolved in the hot dilute nitric acid, twenty cubic centimeters of a forty per cent solution of caustic potash is run in. This neutralizes the nitric acid. It is of extreme importance that the nitric acid be *completely neutralized,* as the next step is to run in thirty cubic centimeters of twice-decinormal $\left(\dfrac{N}{5}\right)$ potassium cyanide solution from a burette, stirring well. Any excess of nitric acid would liberate hydrocyanic acid at this stage, the breathing of which is usually fatal. It is for this reason that the excess of caustic alkali is first of all run in. When making up the standard solution of KCN, the cyanide should be weighed out in a room where the ventilation is good, and not in a stuffy darkroom, on account of the noxious fumes that it gives off.

When the silver halide has gone into complete solution, the contents of the dish are transferred to a flask and the film or plate is rinsed several times with hot distilled water and the rinsings added to the contents of the flask. A further small

quantity of the potassium cyanide solution (2 cc) is then run in, and 3 cc of the following indicator added:

15 per cent solution of potassium iodide .... 50 cc
Ammonia (s.g. 0.910) .... 50 cc

The whole is then titrated back with standard decinormal silver nitrate solution until the end point — a faint persistent opalescence — is reached. A similar determination must be made with a blank; the difference between the blank and the actual titration gives the amount of silver ($AgNO_3$) equivalent in the sample.

When positive or reversal type emulsions coated at below eighty milligrams of silver halide per square decimeter are being estimated, it is advisable to use *two* square decimeters rather than one of the material. It should be remembered that potassium cyanide is not anhydrous, and should always be standardized against the silver nitrate solution. The reaction is:

$$AgBr + 2KCN = KAg(CN)_2 + KBr$$
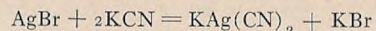
The potassium cyanide should therefore be of 2 molar concentration, or thirteen grams per liter. But in view of the salt not being completely anhydrous, fifteen grams per liter may be used. If 15.74 grams of silver nitrate per liter be used in making the decinormal standard silver solution instead of 17.0 grams, the titration will read directly in milligrams of metal.

In making pH determinations of coated film, a definite area of film is cut into pieces and soaked in freshly distilled water and the water tested against a similar quantity of freshly distilled water as a control. Colorimetric tests can be made with an indicator having a range somewhere between 5 and 8 pH; or if necessary, two tests may be made with indicators each of half the range. For tests of dyed or colored materials, an electrometric apparatus such as the Beckman is necessary; in England portable apparatus is made for pH determinations by

the Cambridge Instrument Co. Owing to the rapidity with which even freshly distilled water decreases in pH in the atmosphere of big manufacturing towns and cities, the water used should preferably be freshly distilled a few minutes before the test is made.

KEEPING TESTS. — An estimate of the probable keeping quality of sensitized materials is of importance in laboratory work and is essentially part of the ordinary routine in commercial production. It might be imagined that the faster the emulsion is, the poorer would be its keeping qualities. This, however, is not always the case, some slow emulsions being troublesome in this respect. Thinly coated plates are liable to go off at the edges (to fog round the edge on development without exposure), and any products which have given evidence of slight fog on testing after being emulsioned must always be regarded with suspicion. There is a tendency for any emulsion that has been pushed too far for speed, or over-heated, to give veil, but reference to this will be made again in Chapter XIV. The veil, or fog, must be deducted from all readings in sensitometric work, and for a practical test the developer that is recommended for use with the material should be used in making that test.

While a slow positive or process emulsion should not, on normal development without exposure, give a higher fog reading than 0.02, that on an ultra-rapid emulsion may legitimately be of the order of 0.1. On keeping for any length of time, the fog reading usually increases, especially if the material is stored under warm or humid conditions, and in order to get an estimate of the *life* of the product, it is common practice to subject it to an oven test. The material, wrapped in the packing which it is intended to use, is kept in a thermostatically controlled hot air or water oven at a temperature of 105° or 110° F. for about ten days. It will then have developed approximately the same amount of fog as would be anticipated from, say, six months'

storage in the average dealer's stockroom. The humidity of the oven is an arbitrary matter, but 55 to 65 relative humidity is suggested as being fair.

When making fog tests, it is customary to pack the material in two halves, one being kept in the oven, the other being kept at room temperature, under the best possible conditions. The initial laboratory tests will, of course, also have been made for reference. After the period of ovening or " incubation," the control and the oven samples are developed together in total darkness and fixed, and the fog readings compared. A sensitometric test will also reveal any loss or gain in speed or alteration in the development factor.

While at first sight keeping tests seem simple and straightforward enough, they are complicated by the fact that when material is stored in an oven, the sides, top and bottom of the inside of the package do not necessarily experience the same conditions. An elaboration of the tests is to place the packages in a cage which rotates in the center of the oven; many other suggestions have been made. Highly red-sensitive and infrared emulsions, owing to their natural reaction to the longer wavelengths, are apt to develop fog in warm climates quicker than color-blind varieties.

The oven test is invaluable in checking up on wrapping materials. No wrapping papers, nor cardboard boxes, should be accepted for the packing department's use unless and until they have been demonstrated by an oven test to be harmless in the way of fog production. In the case of rollfilms which are merchandised in aluminum containers, sealed or unsealed, the oven test should be made with the spooled films in these, so that absolutely practical conditions are obtained. Materials destined for tropical work or expeditions which are to be supplied in soldered tin boxes should again be submitted to an oven test so packed, the reason being that at 110° F., or thereabout, a

certain amount of moisture may be evolved in which the sensitized materials may show some alteration.

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Chapter XIII

VARIOUS METALLIC PROCESSES

Carbon and Carbro Tissue — Gum-bichromate — Iron Printing Processes — Ferroprussiate — Cyanotype — Kallitype — Platinotype and Palladiotype — Diazotype Papers — Bleach-out Color Processes

THIS method of printing depends upon the action of light upon a dichromate in the presence of organic matter. The response to light was shown by Cartwright[1] to be most active in the region between 350 mμ and 420 mμ. Attempts have been made by Ronald Trist and others to sensitize dichromated gelatin or fish glue to green and red rays by color-sensitizing, without particular success. On exposure to light in the colloidal medium, the dichromate is converted into a brown chromo-chromate consisting of uncertain proportions of chromic acid and the green oxide of chromium:

$$x.K_2Cr_2O_7 \quad . \quad . \quad . \quad . \quad y.Cr_2O_3, z\ CrO_3.$$

According to Eder, the insoluble image consists of gelatin in combination with chromium oxide, while Lumière and Seyewetz found that under normal conditions the proportion of chromium oxide combined with the gelatin is considerably higher than that which combines with gelatin treated with chrome alum in the ordinary way. The exposed dichromated gelatin swells much less in cold water, and is insoluble in hot water. So the printed image, on washing with hot water, consists of insolubil-ized gelatin with the unexposed *soluble* gelatin removed.

It was found by Abney that the insolubilizing action of light continued after a short preliminary exposure, indicating the formation by the action of light of a photo-catalyst,[2] which continues the tanning action by reaction with the excess of di-chromate and colloid. Unfortunately, sensitized " tissue," as

paper coated with the gelatin and dichromate is termed, rapidly becomes insoluble on keeping in the dark, and hence it is customary, in fact necessary, in manufacturing practice to supply the gelatin-coated paper which merely has the necessary dye or pigment incorporated with it. Some firms supply sensitized tissue, but it will keep in good condition for only a very limited time.

Owing to the important property, possessed by dichromated gelatin, of giving an almost perfect scale of reproduction, the carbon process and its ally, Carbro, give unsurpassed three-color prints from a correctly balanced set of separation negatives. The carbon process is largely responsible for the excellent tone reproduction in photogravure, and its use for this process makes it an important item in manufactured products.

Carbon tissue is paper coated with a mixture of gelatin and pigment, which the user sensitizes shortly before use by immersion in a solution of potassium or ammonium dichromate which may be varied from one per cent for weak negatives to six per cent for vigorous negatives. In making the tissue, a moderately hard gelatin which does not swell excessively should be selected, as soft gelatins have a tendency to wash out too easily in development. Heinrich's hard emulsion gelatin or a comparable American variety can be recommended. The raw paper selected should not be too highly sized, but well calendered. For experimental work, a plain smooth paper such as is used as wallpaper for covering ceilings will be found very suitable.

An advantage of the carbon process is, of course, that any suitable pigment can be used which is fast to light, so that prints can be made in any color. This is of especial importance in natural color photography, since coloring matter can be used which complies with theoretical requirements as regards spectral composition. Thus yellow, magenta and blue-green papers are probably the types most demanded at the present time. For small-scale work the moist water colors supplied by art dealers

in collapsible tubes make good media, although certain pigments may be found to react with the dichromate, causing insolubilization without exposure.

For commercial mixings, these formulas are suggested:

Sepia	Burnt sienna	90 parts
	Lampblack	10 parts
Warm black	Chinese white	25 parts
	Vandyke brown	40 parts
	Carmine	40 parts
Brown-red	Indigo red	40 parts
	Chinese white	35 parts
	Alizarin red	25 parts

Prussian blue and indigo are largely used also. The pigments are weighed out and mixed with an equal weight of water, and five per cent of the total weight of glycerin is added. The mixture is well ground in a color mill, and then added to twenty times its weight of the following:

Gelatin	125 g
Water	1000 cc
5 per cent alcoholic solution of phenol	50 cc
Soft soap	20 g
Sugar	25 g

After thorough mixing, the bulk is filtered at a temperature of 105° F. (40° C.), and coated on a paper-coating machine, preferably by kissing roller.

A formula for black tissue given by Clerc [3] is:

Gelatin	500 to 800	g
Cut sugar	100 to 200	g
Salicylic acid	2.5	g
Vegetable black	100	g
Carmine	10	g
Indigo	5	g
Glucose syrup	100	cc
Water	2500	cc

For preparing a ready-sensitized tissue, fifty grams of potassium dichromate and ten grams of potassium citrate would be added, first dissolved in 250 cc of water, to which sufficient stronger ammonia water has been added to change the color from orange to pale lemon-yellow. Such tissue must be used within three or four days.

The sensitized tissue is printed under the negative and soaked in cold water, then brought into contact (under the water) with a sheet of either temporary or permanent transfer paper. If single transfer paper is used, the image naturally becomes reversed in the process. Such paper may be coated with:

Medium viscosity gelatin	50 g
Water	1000 cc
5 per cent chrome alum solution	10 cc

The addition of 250 cc of a twenty per cent alcoholic solution of shellac will provide a mat transfer paper. The support paper and printed tissue, when withdrawn from the cold water, are squeegeed firmly together and allowed fifteen to twenty minutes between blotting boards before they are immersed in warm water, pulled carefully apart, and the unexposed coating washed away from the transferred image.

The image may be developed out on a temporary support, which may be paper coated with shellac and rolled, or some material such as celluloid, aluminum sheet, sheet indiarubber, etc., first prepared with a waxing medium. The temporarily transferred image is re-transferred to a final support, which may be a paper coated with the formula above given, but the weight of paper base should be heavier.

Plain slightly subbed nitrate or acetate base coated with a seven or eight per cent solution of gelatin containing no chrome alum may be sensitized with dichromate and used for making three-color prints from separation negatives. A slow bromide

emulsion with no hardening agent may be coated on film base for the same purpose. The silver salt plays no part in the process, but makes the image much more plainly visible in printing, and more controllable. Two minutes' immersion in a three per cent solution of potassium or ammonium dichromate will suffice for sensitizing, and this can be done in yellow light. The material is printed *through* the base (the gelatin or emulsion side away from the film of the negative), and after exposure the image is developed in hot water of about 160° F. (72° C.). Washing-out must not be too vigorous, as a very thin film of gelatin should remain over the faintest highlights. If a bromide emulsion has been used, the film must of course be fixed after washing out, and finally well rinsed. Such gelatin relief images can be stained up with appropriate dyes and mounted in register as three-color transparencies.

GUM-BICHROMATE. — While the image from a negative printed upon carbon tissue must be transferred to another base to be developed, a mixture of coloring matter with gum arabic, sensitized with dichromate, can be applied to paper, and the dry paper exposed under a negative in daylight and developed with cold water without any transfer. The unexposed gum-pigment remains completely soluble and washes away, while the exposed parts remain and provide the image. The gum-bichromate process, as it is familiarly known, is very suitable for prints of bold subjects, especially in the larger sizes, but does not lend itself to the reproduction of fine detail. The carbon process, on the other hand, is capable of yielding the finest detail, as is evidenced by its application to photogravure, where halftone screens of 150 to 175 lines to the inch are used.

Gum arabic is best crushed into small pieces and suspended in a muslin bag in distilled water; it takes some time to dissolve, but the dirt ordinarily present in the gum will remain behind in the bag. The gum should be dissolved in about one

and one-half times its weight of water. To one hundred cubic centimeters of such mucilage is added:

Potassium dichromate .... 10 g
Water to make .... 100 cc

To such a mixture sufficient pigment is added to give a coating — when applied with a brush to paper — of a density which will allow the finger to be seen through the paper when examined by transmitted light. In other words, the tint applied to the paper should be considerably less than that required to form the shadows of a print. Rouge (iron oxide), lampblack, burnt sienna, Prussian blue, indigo, and alizarin red, being inert to the chemicals employed, are the best pigments to use. Another formula for gum-bichromate is the following:

Gum arabic solution 1:1 .... 50 cc
Ammonium dichromate, 10 per cent solution ... 100 cc
Pigment .... 25 g

The prints are best developed by floating face down on cold water, and gently washing out until the whites are clear. Five minutes in a five per cent solution of potassium alum before the final wash will render the film hard.

IRON PRINTING PROCESSES. — Iron forms two principal types of salts, ferric and ferrous. The ferric salts are combined with half as much again of the acid radical as the corresponding ferrous salts. The action of light upon the ferric salt of an organic acid was early noted, and is to reduce it to the ferrous state; an iron process was based on this phenomenon in 1842 by Herschel, who used the ferrous compound to react with ferricyanide and form a permanent image. Ferric citrate and ferric oxalate are reduced respectively to ferrous citrate and ferrous oxalate; similarly potassium ferricyanide, $K_3Fe(CN)_6$, is reduced to ferrocyanide, $K_4Fe(CN)_6$. These ferrous salts form many highly colored pigments by reaction with salts of other

metals with which they form insoluble ferrocyanides, best known of which is Turnbull's blue. If paper sensitized with a ferric salt is exposed under a negative and developed with a suitable reagent, a permanent colored image will result; the most familiar example is the engineer's blueprint; this is made on paper sensitized with a mixture of a ferric salt and potassium ferricyanide. Printed under a design or translucent drawing until the lines appear of a light brown color, a mere wash in cold water will effect the reaction and leave a deep blue image of ferrous ferrocyanide.

This process, known as ferroprussiate or cyanotype, is used on a very large scale, although it has experienced some competition in recent years from the vapor-developed diazotype papers to which reference will be made later. The sensitizing solution can be applied in strong yellow light, and any good quality, pure paper can be treated. It offers the simplest possible method of printing photographs, and can be applied to printing on cotton or linen fabrics; these, if printed and developed in water in the usual way, can be toned to a beautiful violet or purple by treatment with a boiling solution of alizarin.

The paper is usually prepared with ferric ammonium citrate, which may be obtained in the form of brown or green scales. The green scales have the average composition of $(C_6H_5O_7)$, $Fe_2(NH_4)_3$, while the brown scales are $(C_6H_5O_7)_2H_2Fe_2$-$(OH)_3(NH_4)$, $3HO$. Valenta found that the green compound gave very much quicker printing with brighter blue images. A reliable formula for a sensitizing solution is:

A. Potassium ferricyanide .... 40 g
    Water .... 250 cc
B. Green ammonium ferric citrate .... 95 g
    Water .... 250 cc

If the brown citrate is used (which is claimed to give rather better keeping quality for manufactured ferroprussiate paper),

the quantity may be increased to 110 g, and the water in B increased from 250 to 500 cc. The latter sensitizer also gives greater contrast and is useful for copying plans, tracings, etc., while the first formula would be preferred for photographic prints. The two solutions are mixed, filtered, and used cold. It is very important that the mixture is orange-brown colored and not *green*. It is advisable to use large crystals of potassium ferricyanide and before weighing them to rinse them with a little distilled water; this will remove any yellow ferric salt with which they may be surface-contaminated. The salt should be dried on filter paper after rinsing, before weighing. If stock solutions are made up, a trace of sodium formate may be added to prevent the formation of mold.

Another formula, suitable for coating larger quantities, provides for a mixture of stock solutions:

25 per cent solution of ferric ammonium citrate .... 400 cc
15 per cent solution of potassium ferricyanide .... 150 cc
10 per cent solution of citric acid .... 300 cc

The ferric ammonium citrate should be freshly made, and paper sensitized with the formula will keep in good condition for two to three months if stored in a dry place. The addition of phosphoric acid to the sensitizing solution has been suggested to stabilize the lines and the blue background.

For commercial manufacture, sensitizing by dipping will be found suitable practice. In the laboratory, the solution can be applied with a wad of cotton about the size of a golf ball tied with thread to the end of a glass rod. A wide soft brush may also be used. The paper is laid out on a flat board or piece of thick cardboard and held down at the four corners by pieces of scotch tape. It is then brushed over as evenly as possible. The board is best inclined to the table at an angle of about thirty-five degrees. In machine coating, an excess of

solution is applied, and the paper wiped by a doctor just beyond the coating roller, leaving the desired thickness evenly applied. Commercial coating weight is about 60 to 65 g of iron salts per 100 square meters — roughly one grain to the square foot. The coated paper should be dried in total darkness.

Printing is best done in sunlight, though arc or mercury vapor is satisfactory. Ferroprussiate paper gives a deep blue image on a white ground, and of course gives a " negative " of a line drawing, white lines on a blue background. If, on the other hand, blue lines are wanted on a white background, this effect can be obtained by coating with a solution of gum arabic sensitized with ferric salts, and after printing, developing it with a ten or twenty per cent solution of potassium ferrocyanide, on which it is usually floated. An alternative method, given by Pizzighelli,[4] admits of simple development by washing in water; the sensitizing solution is as follows:

```
20 per cent solution of gum arabic ....................  200 cc
50 per cent solution of ferric ammonium citrate .........  80 cc
50 per cent solution of ferric chloride .................  50 cc
```

On mixing the above, a very viscous solution is produced, but after standing for a few hours it disperses and becomes thin enough to be applied with a brush or wad of cotton. As this paper is considerably more sensitive to light, it should be made in yellow safelight and dried in complete darkness.

KALLITYPE PAPER. — This is printing paper sensitized with ferric oxalate, which is reduced by the action of light to the ferrous state; the strong reducing action of the ferrous salt is then used to develop a silver image, but, owing to its insolubility, the presence of an organic salt such as potassium oxalate is required to act as a solvent. The printed paper may be put into a bath containing silver nitrate, or the silver — or part of it — may be incorporated in the sensitive coating. The simplest

means of sensitizing is to use a composite solution such as the following:

```
Ferric oxalate ............................  22.5 g
Potassium oxalate (neutral) ................  5.5 g
Silver nitrate ............................  5.5 g
Distilled water ..........................  100  cc
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A smooth, thin drawing or water color paper or plain raw photographic paper is first sized with a paste made by mixing three grams of starch with a little water until smooth, and then stirring while sufficient boiling water is added to bring the bulk up to two hundred cubic centimeters. This solution is boiled for five minutes, cooled and poured into a beaker or crock. When cold, a skin will be found to have formed on it. This is removed, and the liquor is strained through a piece of washed muslin into a clean dish. The paper is best coated by floating, unless a small coating machine such as has been described elsewhere is available.

When dry, the paper is printed in daylight until the shadows are just visible, and is then developed with an alkaline solution of Rochelle salt. A basic formula is:

```
Warm water ...............................  500 cc
Rochelle salt ............................  30 g
Borax ...................................  15 to 25 g
10 per cent solution of potassium dichromate ..  5 cc
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The full quantity of borax gives black tones, a smaller amount giving warmer tones.

When printing from weak negatives, a slight increase in the proportion of dichromate may be used. If the contrast is too high, the print can be removed from the developer and transferred to a separate bath containing no dichromate. When developed to completion, the print is fixed in a two and one-half per cent solution of plain hypo rendered just alkaline by the addition of a few drops of ammonia. An attractive feature of

kallitype is that the image can be toned afterwards with a gold bath, such as is used for printing-out paper, or with platinum or palladium.

PLATINOTYPE. — The successful results obtained with kallitype led W. Willis in 1878 to substitute platinum for silver, and so to produce what still remains the finest printing medium available to photographers — platinotype. Prints made by this process have an exquisite range of gradation. The image is absolutely permanent. If we take the tone range of a contrasty chloride paper as 1:10 and of a good bromide paper as 1:50, then we may justly say that the gradation of platinotype is 1:100.

The paper itself, needless to say, must be of pure quality, and especially free from iron spots or specks. It must not be sized with an animal (glue) size, though a first coating with a one per cent solution of the purest emulsion gelatin may be applied. A three per cent solution of arrowroot, boiled and filtered, is better. The paper may be immersed in the solution for five to twenty minutes, according to the surface, and then dried slowly in a cool atmosphere.

For sensitizing, three stock solutions are prepared:

A. Potassium platinum chloride .... 1 g
   Water .... 6 cc
B. Ferrous oxalate .... 1 g
   Water .... 4.5 cc
C. Ferrous oxalate .... 10 g
   Potassium chlorate .... 0.2 g
   Water .... 45 cc

For sensitizing, mix 5 cc of A and 3 cc of B; add 2 cc of C and 4 cc of water. For contrasty negatives, the C solution may be omitted and equal parts of A and B only used. The sheets of sized paper, cut to size, should be laid on a sheet of clean glass or in the bottom of a porcelain dish, and the sensitizing mixture

applied as evenly as possible with a soft camel's hair brush. This may be done in Mazda light.

Paper prepared as above described is printed in sunlight until the dense shadows are of a light orange-brown color; no details should be seen in the extreme highlights. The print is developed with a hot solution, 100° to 180° F., of:

Potassium oxalate (neutral) .... 300 cc
Oxalic acid .... 5 g
Water to make .... 1000 cc

Alternatively, cold development may be used if the sensitizing bath be somewhat modified as follows:

A. Solution as in above formula.
B. Ferric oxalate .... 10 g
   Lead oxalate .... 0.5 g
   Water .... 45 cc
C. Potassium dichromate .... 1 g
   Water .... 10 cc

4 cc of A is mixed with 6 cc of B. To this mixture is added 10 drops of C mixed with 3 cc of distilled water.

A printing-out platinum paper for giving a visible image can be made as below:

A solution as above .... 4 cc
50 per cent solution of sodium ferric oxalate .. 6 cc
50 per cent gum arabic solution .... 4 cc
C solution as above .... 5 drops

Paper sensitized by brushing it over with this solution (after the usual sizing) is printed fully out, and then finished off by washing or placing between wet filter papers. All platinum papers should be given several final rinses in water acidulated with one or two per cent of hydrochloric acid.

Owing to the difficulty of making entirely satisfactory platinotype papers in the laboratory, Clerc recommends [5] the easier

procedure of sensitizing the paper with ferric salts and using the platinum compounds in the developing solution. The sizing solution recommended is:

Gelatin .... 8 g
Water .... 1000 cc
When melted and dissolved, add
    Potassium alum .... 2 g

The paper is floated on this solution, used hot, and the upper surface (hereafter the back side) should be marked with a pencil. The sized paper is brushed evenly with the sensitizing bath below:

Ferric oxalate .... 25 g
Oxalic acid .... 2 g
Lead oxalate .... 1 g
Hot distilled water to make .... 100 cc

The lead oxalate may be made by mixing equal volumes of a ten per cent solution of lead acetate and a four per cent solution of oxalic acid, filtering and washing the white pasty precipitate left in the filter paper several times with distilled water. The image on printing is much less visible than in the case of the papers previously described, and can be judged only by experience or by comparison with some form of print-out actinometer. The developing solution, containing the platinum salts, is made thus:

Stock Solution

Potassium oxalate (neutral) .... 200 g
Di-sodium phosphate .... 50 g
Water to make .... 1000 cc

To 20 cc of this stock solution is added 2 cc of a ten per cent solution of potassium chloroplatinite. Development is done with a flat camel's hair brush, moved over the image " with a quick light movement, dipping it in the developer for each

stroke so as to insure equal and uniform action of the solution." When evenly coated with developer, it is left until completely developed, fixed in weak hydrochloric acid, and washed.

Owing to the high cost of platinum, palladium has been used on an increasing scale. Palladium salts may be substituted for platinum in many of the above formulas, particularly in developing formulas where the paper itself is sensitized only with the iron salts.

PRINTING WITH COPPER SALTS. — A formula for sensitizing with copper salts has been suggested by Thiebaut [6] for use on paper previously substratumed with gelatin:

Potassium dichromate .... 90 g
Copper sulphate .... 50 g
Water to make .... 1000 cc

The paper is exposed in daylight until the highlight detail is clearly visible, and is then developed in a five per cent solution of anilin hydrochloride acidulated with sulphuric acid. Green images are given by this process.

URANIUM PAPER. — This is prepared by the application to *unsized* paper of:

Uranyl nitrate .... 16 g
Water to make .... 100 cc

The suggestion has been made of adding four grams of copper sulphate to this solution. It is printed in daylight, preferably under a vigorous negative, and developed with a five to eight per cent solution of potassium ferricyanide. Warm sepia or brown images are given by the process, and various metallic toners can be applied.

DIAZOTYPE PROCESSES. — Methods of photographic printing have been successfully based on properties of certain aromatic diazo compounds which become bleached on exposure to light. The unexposed parts remain unaltered, and on development

with an alkali, or with ammonia vapor, an image remains consisting of a permanent azo dye, thus giving a positive image from a positive original.

In the Feertype process,[7] on the other hand, a dye is formed in the exposed portions of a diazo compound which can be developed in acidulated water. A sensitizing formula of this nature is as follows:

Iso-sodium toluol diazo sulphonate .... 25 g
Beta naphthol .... 25 g
Sodium hydroxide .... 8 g
Water .... 1000 cc

In Ozalid paper,[8] Koegel produced positive from positive prints in purple lines on a slightly colored background. The paper was impregnated with a solution of a diazo-anhydride and resorcin equilibrized with tartaric acid. The diazo-anhydride is decomposed by light, but the unexposed material is converted to an intense purple-brown on exposure to ammonia vapor. The fact that the paper is developed dry eliminates distortion. Under the name of Ozafilm, diazo compounds have been introduced into viscose for sub-standard motion picture films, having a thickness of only a thousandth of an inch, so that the bulk of the reel can be greatly reduced.

More recently, chinonazide has been used as a sensitizer; this compound is diazotized para-aminophenol, which under the action of light becomes converted into hydroquinone. If the paper, after printing, is treated with a weak solution of silver nitrate, a latent image is formed which can be physically developed with a metol-sulphite-silver bath.

On exposure to light a diazo compound loses its faculty of coupling with a coupling component, being probably decomposed into a phenol. In those parts where the light has not acted, and the diazo retains its original composition, it is able to form an azo dyestuff by the combined action of the coupling

component and an alkali.[9] In the simplest case, the coupling component can be mixed with the diazo compound, when, after printing, development can be carried out with ammonia vapor. An alkali can, on the other hand, be mixed with the azo coupling component. An example of such a sensitizing solution is:

p-amino-dimethyl anilin hydrochloride,
    diazotized with nitrous acid .... 20 parts
Tartaric acid .... 2 parts
Barium chloride .... 100 parts
Water to make .... 1000 parts

Paper sensitized with the above is printed and developed with a weak alkaline solution of β-oxynaphthoic acid anilide. This gives a black image on a white background.

Another formula is as follows:

para-amido-ethyl anilin hydrochloride,
    diazotized with nitrous acid .... 20 parts
Potassium citrate .... 0.5 part
Barium chloride .... 100 parts
Water to make .... 1000 parts

This gives a dark brown image on development with an alkaline solution of β-naphthol. The barium chloride prevents bleeding of the developed azo dyestuff; the use of a catalytically acting substance called an anti-oxygene such as pyrogallol or meta-phenylendiamin has been suggested by F. van der Grinten.

PRINTING-OUT NATURAL COLOR PAPERS. — Very little information is available as to the preparation of sensitive coatings of fugitive dyes with which direct printing-out effects can be obtained from natural color transparencies, yet this is a field for experiment which may well see immense developments. It was noted by Grothuss that certain dyes were destroyed by the light radiations which they absorbed; in other words, a fugitive magenta dye would be bleached by green light, a blue dye by yellow light, and so on. A black mixture of blue-green, magenta,

and yellow dyes applied to paper and printed out under a color transparency would yield a color print.

Bleach-out color papers were made by Neuhauss, Worel, and others, but they were too insensitive to be of practical value; J. H. Smith, however, succeeded in producing a black bleach-out paper which gave a fairly creditable print from an Autochrome in one to three hours' exposure to strong sunshine. The author at one time experimented with Dr. Smith to employ arc light printing, but the speed did not justify the continuation of the work. Also the bleach-out images, though fixed in various ways, were not by any means permanent.

An example of possible advance in this direction may be seen in the very marked increase in light-sensitivity of methylene blue if used in the presence of certain thiourea derivatives. Three dyes of the subtractive colors sensitized in a similar way and balanced so as to bleach out at equal rates after allowance had been made for the relative transmissions of the primary colors of the transparency, would yield a natural color printing medium, provided the sensitizers could be destroyed after printing, and the remaining dyestuffs rendered reasonably permanent.

Indirect processes employing more light-sensitive coatings which would, under the influence of light, react in turn with the dyes and destroy them, figure among present attacks on the problem.

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Chapter XIV
EXTREME–SPEED EMULSIONS

Super- and Hyper-sensitizers — Sulphur Compounds in Gelatin — Anti-fogging Agents — Speed Characteristics

IN considering the faster emulsions which have been recently introduced, one is tempted to raise the old question: "What is speed?" It has already been seen in Chapter XII that if the toe of the characteristic curve of a fast emulsion is sufficiently straight to permit of the whole tone range being recorded on it, that is, provided that such density range as it offers will suffice for the work in question, a very much higher effective speed is obtained than with the same emulsion developed to a higher gamma and the upper straight portion of the curve used. Similarly if the free bromide be removed from the emulsion, the whole curve may rise from AB to $A'B'$ (Fig. 78), the speed being thereby raised from $\dfrac{K}{OC}$ to $\dfrac{K}{OA'}$. If therefore the need for free bromide could be dispensed with by the use of an anti-fogging agent, an immediate rise in speed could be obtained. The removal of the bromide is substantially what happens when a plate or film is "hyper-sensitized" by bathing.

The line of thought which actuated many emulsion-makers in the stage intermediate between the first really fast ortho-chromatic and panchromatic emulsions and the more recently introduced extreme-speed variety may be gathered from a comparison of the two following formulas, one of which was published as an indication of how the other basic one might be "pushed" for greater sensitivity:

		Fast	Extreme speed
A.	Potassium bromide	120 g	132 g
	Potassium iodide	3 g	4.5 g
	Gelatin	50 g	30 g
	Water	1200 cc	1000 cc
	Erythrosin 1:1000	— cc	50 cc
B.	Silver nitrate	150 g	150 g
	Water	600 cc	500 cc
	Redissolve.		
	Temperature of reacting solutions ..	30° C.	40° C.
	Emulsifying time	rapid	slow, taking 6 minutes
	Ripening time	25 to 40 minutes	30 to 50 minutes
	Ripening temperature ...,........	40° C.	50° C.
	Bulk gelatin	120 g	140 g

The gelatin is soaked for half an hour, drained and remelted, and added at 45° C. in each case; after ten minutes' stirring, the emulsions are set in ice water. The fast emulsion is washed next day, the extreme speed one, after keeping at 3° to 8° C. for two to three days. In the case of the extreme speed emulsion, further gelatin may be added again after washing; the emulsion is then warmed to between 40° and 42° C. and stood in a room at about 22° C. for two to three hours.

It will be recognized that this difference really amounts to a gentle push all the way around. With a well-selected gelatin, the speed may be raised from say 650 to 1500 H and D in this manner, but the author's experience of forcing an emulsion on these lines is that it is liable to yield variable results, and that some of the best emulsions so prepared, which are perfectly clean at the time of making, turn out disappointing from the keeping standpoint, developing fog and steadily losing speed.

A good deal of progress in the direction of speed has been

made as the result of more critical testing of gelatins. One example of this, of outstanding importance, is the fact that by giving a sufficiently long digestion, what had hitherto been regarded as a " slow " gelatin may be made to give the speed of a " fast " sample. This digestion may have to be very protracted, lasting for many hours instead of from twenty minutes to an hour or so. But the time-factor appears to be of vastly more importance than had been previously recognized.
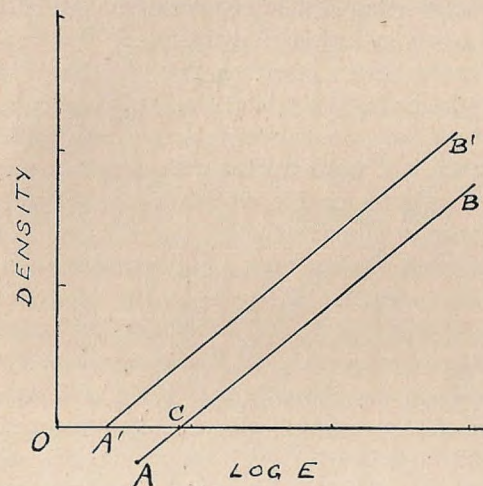
FIG. 78

As stated elsewhere, the great advance in panchromatizing-dye chemistry has given a fictitious but perfectly practical increase in speed to some color-sensitive negative emulsions, the response to light of the longer wavelengths making an important addition to their sum total of response. The discovery that certain dyes act as super- or hyper-sensitizers, greatly increasing the sensitivity induced by another dye the color-sensitizing region of which they do not affect, has given another jump in

speed, of important practical value, although the phenomenon looks at first sight a little like perpetual motion.

The great rapidity of recently introduced emulsions can be ascribed largely to the use of stabilizers, the addition of which to an emulsion in the making renders it possible to force the speed or to add " sensitizers " without pushing a proportion of the grains too far and rendering them developable without exposure as " fog." An instance is the use, suggested by Kendall,[1] of a 2-mercaptan-4-hydroxy-pyrimidene, or one of its alkyl, aralkyl or aryl substitution derivatives.

We must to some extent associate color-sensitizing with hypersensitizing; the carbocyanins and similar products in general use, as we have seen, are extremely sensitive to light, but become stable to light when treated with certain derivatives of thiourea; yet thiourea or thiocarbamide, $CS(NH_2)_2$, by itself, is one of the most effective emulsion sensitizers. The choice of sensitizer must obviously be coordinated with that of the color-sensitizer; indeed, one may be largely dependent on the other.

The sensitizing property of allyl isothiocyanate, $H_5C_3 \cdot NCS$, which as we know was isolated from gelatin by Sheppard, and shown to be chiefly responsible for emulsion " speed," cannot be used *ad libitum;* in other words we cannot, by doubling the quantity used, obtain double the speed. Indeed, for many years after the publication of the function of allyl isothiocyanate, the general speed of plates and films went up very little, and such advances as were made were *not* directly due to its exploitation. Allyl isothiocyanate is the essential oil of mustard, and can be obtained by macerating black mustard seeds with water, after first removing the fixed oil, then distilling. When mixed with ammonia and subjected to ammonia gas, it yields allyl thiourea or thiosinamin, $NH_2NH(C_3H_5)CS$; this is a weak base, soluble in water, alcohol and ether.

A test for these sulphur compounds in gelatin has been given by Luther,[2] who suggests the use of a solution of twenty to twenty-five per cent of caustic soda (sticks) in 100 cc of distilled water, in which 3 to 4 g of pure lead nitrate has been dissolved. One volume of this alkaline lead nitrate solution is mixed with one volume of a fifteen to twenty per cent solution of the gelatin to be tested, and placed in a test-tube in a boiling water bath. A good quality gelatin (containing the most useful proportion of sulphur compounds) will show a brown coloration after about half an hour, which will remain visible after one hour.

Selenium compounds have been largely investigated, for their uses both as sensitizers and as anti-fogging agents. Thus addition of an α-thione or α-selenone of a heterocyclic nitrogen compound such as thiazole, quinoline, pyridine, etc., has been suggested for speed-sensitizing, while the incorporation of a sulphinic or seleninic acid or soluble salt of either has been used as a stabilizer against fogging.[3] Amino-purines have been suggested for the same purpose, that is, stabilization. A compound of the purine series has also been employed, containing a hydrogen atom which is replaceable by silver attached to a nitrogen atom, when promoting *ripening* by means of a sulphur compound.

While a very large number of patents have been granted since about 1933 for the protection of color-sensitizers, color hyper- or super-sensitizers, and emulsion sensitizers and stabilizers or anti-fogging agents, there must always remain a clear field for experimentation and further research. The addition of any extreme-speed sensitizer must first be tried out with a few pre-selected gelatins, among which an iso-electric sample may well be present; sensitizers which promise success must then be tested in conjunction with anti-fogging or fog-retarding compounds, until a suitable balance is obtained. The sensitizers

may or may not be intimately associated with a color-sensitizer in the case of panchromatic emulsions. The final emulsion may be further assisted by appropriate buffering, which may well be made to function in the undercoat of a slower, stable emulsion in the case of double-coated film stock.

The H and D speed of modern emulsions, while it increases with prolonged development, appears according to Trivelli and Smith[4] to reach a breaking point long before the gamma has reached its maximum value; beyond this point the speed diminishes. This is an important point, as although the observation applies to some extent to older-type emulsions it emphasizes the necessity for careful sensitometric testing of a super-speed emulsion in order to determine the conditions under which its optimum speed can be realized.

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