

# THE SILVER SUNBEAM

A Practical and Theoretical Text-Book

ON

SUN DRAWING AND PHOTOGRAPHIC PRINTING:

COMPREHENDING ALL THE

WET AND DRY PROCESSES  
AT PRESENT KNOWN, WITH

Collodion, Albumen, Gelatine, Wax, Resin, and Silver;

AS ALSO

Heliographic Engraving, photolithography, Photozincography, Celestial Photography, Photography in Natural Colors, Tinting and Coloring of Photographs Printing in Various Colors; the Carbon Process; the Card-Picture, the Vignette, and Stereography.

*BY*

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"And God said, Let there be light: and there was light."

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## Chapter I.

# HISTORY OF PHOTOGRAPHY.

EVERY step, whether thoughtlessly or discreetly taken, is the commencement of a new era in a man's life. As in a game of chance—where either red or black must occur at the cessation of motion in the finger of the dial-plate—the probability that red will prevail over the black the next time, because black has occurred for twenty times in succession, is not valid; it is equally probable that black will be the successful color; so, in the game of life, each successive move is a new beginning; and, as a single twirl of the roulette may be the bane or the boon of the career of an individual, so the slightest event, the most insignificant indeed, may turn out to be the center of incalculable results. New developments in the science of nature are not limited to their own immediate sphere; they act and react upon the past and the future, by illustrating phenomena that before were dark and not understood, or by eliciting truths which hitherto were utterly unknown. Thus it is that the invention of a machine, the improvement of a part of a machine, or the discovery of some new chemical ingredient, may be the date of the commencement of a new history. The verification of this idea is pertinently made manifest in the change from the simple double convex lens to the achromatic combination by Dolland;<sup>1</sup> in the change from the signal telegraph on the mountains to the electric telegraph in the closet; in the improved application of steam by Watt; in the development of a picture on the iodized plates of silver by the vapor of mercury; and in the discovery of the hyposulphite of soda, cyanide of potassium, pyrogallic acid, and the protosalts of iron. For from the moment that chromatic and spherical aberration could be reduced, the telescope and the microscope became altogether new instruments in the hands of the natural philosopher, by which many crude notions were quickly laid aside as false, and many new truths as quickly denuded of their cloudy habiliments. Astronomy, one of the oldest of sciences—one whose history can be traced back to the time of the Chaldeans entered, at the time of the introduction of the achromatic refracting telescope, upon an epoch as distinct in its history as the transition from the system of Hipparchus to that of Copernicus. At the same time, too, Physiology received a new impetus, by the deductions drawn with the aid of the compound achromatic microscope, so that Biology, since then, is gradually becoming more and more of a science. By means of the former improved instrument, our eyes are permitted to revel amid the enchanting scenes of the starry firmament, by the latter to scrutinize the realms of minute organisms of the earth, and by both to become acquainted with the secrets of creation. For the investigator of nature in the great and the minute, this is a new era in the history of the world as it exists and acts. In like manner the age of steam and the telegraph commenced a new history in the social existence and actions of men. The mild tenets of the Gospel, which would seem to have no connection whatever with the subject, have been more powerfully, more efficaciously implanted in foreign soils, by the accessory instrumentality of these agents, than by any preceding direct operations of the missionary organization; the superiority of the race of men that have invented and that yield such mighty instruments for weal and for woe, is so distinctly marked, that admiration and awe have engendered, in the minds of the ignorant and less enlightened, respect for the creeds of religion and morality of their superiors. Coexistent with the steam-engine and the electric telegraph, and equally important as these in its

influence on the ways and means of life, is the art of sun-drawing. It is one of the great wonders of the phenomena of created matter, so far eclipsing the seven vaunted wonders of the world, that these recede into dark nooks, like the wired dolls of an automata puppet-show. This art, and the science that explains the different effects produced in its manipulations, form the subject of the present volume. The art and the science are of modern origin and of recent date.

Sun-drawing, Heliography, and Photography are synonymous expressions for the same phenomenon, although etymologically the two latter are somewhat different-heliography signifying *sun-writing*, whilst the word photography signifies *light-writing*. Not one of these expressions is strictly correct, because actinic impressions can be obtained from rays emanating from the moon, from artificial light, or the electric spark. Actinic drawing would probably be the best name, although as regards the representation of facts by words, it is immaterial for the masses of mankind whether these words have an intrinsic or root-meaning or not. The phenomena comprehended under any one of the above synonymous expressions, depend immediately upon what is termed *light* as the force or cause, and upon the property, which only certain substances apparently possess, of being affected according to the intensity of the light employed. The principal of these substances are the *salts of silver*, the *salts of iron*, *bichromate of potassa*, and certain resins, as the oil of *lavender* and *asphaltum*. That light acts upon organized substances is a phenomenon which must have been observed by the first occupants of earth; they could not fail to remark the brilliant hues on the side of an apple that received the direct rays of the sun, and to contrast these resplendent mixtures of red, crimson, green, purple, yellow, orange, and other colors, on the one side, with the white, or greenish white, on the side exposed simply to the diffused light of day. The variegated foliage of a tropical clime, as contrasted with the continual merging into green, according to the increase in latitude, gives evidence of the influence of actinic action; and this change of green into white in the leaves and stalks of similar plants, when supplied with heat and air, and not with light, is a still stronger proof of heliographic influence. But this species of influence is not limited to the vegetable part of the earth; it is perceived, in all its beauties, in the blooming cheeks of a maiden from Kaiserstuhl in the Black Forest, or from the pasturing declivities of the Tyrolese Alps; and its deficiency is quite as apparent in the pale, white, and lifeless facial integuments of the unfortunate denizens of crowded cities, as in the blanched stalks of celery in a dunghill, or the sickly white filiform shoots of potatoes in a dark cellar. These phenomena are full of wonder, no less so than any of the operations of sun-drawing on paper or collodion, and quite as inexplicable; but they have long failed to excite astonishment, from the frequency and commonness of their occurrence.

The first remark in reference to the cause of the change of color in silver salts is due to the distinguished Swedish chemist, Scheele.<sup>2</sup> He regarded the blackening effect of chloride of silver, when exposed to the rays of the sun, as caused by a species of reduction of the salt to the metallic state and the accompanying formation of hydrochloric acid. He undertook a course of experiments, to ascertain whether all the colors of the spectrum had an equal influence in coloring or blackening this salt, and arrived at the conclusion that the maximum chemical or decomposing action of the spectrum was in the neighborhood of the violet part, and that it gradually diminished toward the red, where it

was scarcely perceptible. The researches of Scheele in this track terminated here; and no application of the property of blackening of the chloride of silver to photogenic purposes was made until after the lapse of several years.

In 1801 Ritter<sup>3</sup> not only corroborated the experiments of Scheele, but demonstrated that chloride of silver was blackened to some distance external to the spectrum, on the violet side. The scientific investigators of the time repeated the experiments without any further developments.

Dr. Wollaston<sup>4</sup> published a report of experiments which he made with gum-guaicum, when acted upon by the different colored rays of the spectrum. The violet rays t[illegible]d I paper, stained yellow by a solution of this gum in a[illegible]ol, to green, which was soon changed back to yellow by the red rays; he discovered afterward, however, that the heat of the red rays was sufficient of itself to reproduce the yellow color of the tincture of the gum.

The same results were obtained by Bérard. He experimented with half the spectrum at a time, which was condensed by a lens to a focus, and made to impinge at this point upon chloride of silver. The half next the violet, or more refrangible rays, were very efficacious in discoloring this salt of silver; whilst the other half, or red side, and least refrangible rays, although far more luminous, produced no blackening effect. The experiments of Seebeck seem to show that light transmitted through colored glass produced the same general effect as the different colored rays of the spectrum. He furthermore ascertained that a piece of paper dipped in a rather concentrated and neutral solution of chloride of gold, in the dark, was not reduced, as long as it was kept in the dark; whereas if it had previously been exposed to the direct rays of the sun, it gradually turned purple in the dark chamber. Sir Humphry Davy observed that the oxide of lead, in a moist condition, is acted upon very differently by the red and the violet rays of the spectrum; by the latter, the puce-colored oxide is turned black-by the former, red. He ascertained, too, that hydrogen and chlorine, when exposed to the rays of the sun, frequently enter into combination so vividly as to produce an explosion in the formation of hydrochloric acid; but the two gases may be kept in contact, in the dark, without undergoing much change. A solution of chlorine in water remains unchanged, as long as it is kept out of the light; but is soon converted into hydrochloric acid, by decomposing the water, when exposed to the sun. A similar case of decomposition is effected by light, when carbonic oxide and chlorine are exposed to light; they then enter into combination chemically, condensing into a substance denominated *phosgene gas*.

The preceding remarks comprehend the sum and substance of the knowledge of the chemical effects of light previous to its application to the taking of impressions of pictures by the salts of silver or otherwise. It is true that a certain Hoffmeister published some vague remarks about the sun being an engraver, several years previous to Daguerre's publication; but they were the mere remarks of one who probably thought the thing possible without possessing the most distant idea of the mode of its effectuation. And in the report which Arago made to the Chamber of Deputies in reference to Daguerre's discovery, this distinguished philosopher mentions the name of Charles as

having been in possession of a process for communicating pictures, by the aid of the sun, to prepared surfaces. No publication has been discovered to corroborate this assertion, and the details of the operation have never been disclosed.

The first recorded attempts by Wedgwood<sup>5</sup> and Davy,<sup>6</sup> to take pictures by the rays of the sun on a prepared silver surface, were published in the year 1802. The receptacle of the picture was either paper or leather, or some other convenient material, stretched upon a frame, and sponged over with a solution of nitrate of silver; over this prepared surface a painting on glass was placed in direct contact and exposed to the rays of the sun. It is evident that the picture thus obtained would be inverted as to light and shade. The difficulty, which at this time could not be overcome, was the fixing of the picture; and the process was abandoned on this account. No chemical substance was known whose peculiar properties were of such a nature as to dissolve the unaltered salt of silver and leave the portions on which the image was projected untouched or uninjured. These experiments of Wedgwood were actually made several years previous to the publication in 1802; because at that date he had been dead for seven years. The surface prepared with nitrate of silver was not sensitive enough to receive an impression in the camera obscura, although Sir Humphry Davy succeeded in getting a very faint image in the solar microscope, where the picture was very much condensed in size or situated very near the focus of parallel rays. From that date to the year 1814 not only no other publication appeared, but there are no accounts of any one having prosecuted the study of sun-drawing. At this time a new laborer entered the field of investigation and directed all his mental energies to the discovery of means of making sun-pictures. From the work of Daguerre, which was published several years later, it appears that Niepce<sup>7</sup> was the first who obtained a permanent sun-picture; to him we are indebted for the, first *idea* of a fixing material; it was he who first *employed* silver and the vapor of iodine. The process of Niepce had been so far perfected as to admit the use of the camera, which, by reason of the want of sensitiveness in the materials used; had remained a useless optical arrangement. Niepce, in his experiments, discarded the use of the silver salts, and substituted in their place a resinous substance denominated the 11 Bitumen of Judea." He named his process "Heliography," or "Sun-drawing." His pictures were produced by coating a metal plate with the resinous substance above alluded to, and then exposing this plate, under a picture on glass, or in the camera, for several hours in front of the object to be copied. By this exposure to light the parts of the bitumen which had been acted upon by the rays underwent a change according to the actinic intensity, whereby they became *insoluble* in certain essential oils. By treatment afterward with these essences, as, for instance, the oil of lavender, the picture was developed, the *shadows* being formed by the brilliant surface of the metal exposed, by the solvent action of the essential oil in those parts of the resin on which the rays of light had not impinged; whilst the lights were represented by the thin film of bitumen which had become altered and insoluble in the oleaginous substance employed in fixing. Some of the specimens produced by this method at this period exist still in the British Museum; some of them are in the form of etchings, having been acted upon probably by the galvanic current. It is evident that Niepce was acquainted with a method of fixing his sun-drawings; but his successes were limited to productions which now would be regarded very trivial and unsatisfactory. After ten years' labor in the prosecution of his favorite investigation, by some accidental

disclosure, Niepce became acquainted with Daguerre,<sup>8</sup> who had been experimenting independently in the same path. Daguerre's experiments with chemical processes and the camera date from the year 1824; and in 1829 these two great originators of sun-drawings entered into partnership for mutually investigating this enchanting art. In 1827 Niepce had presented an article to the Loyal Society of London on this subject; but as yet Daguerre had not arrived at any successful results, nor had he published any thing in reference to them. The process of Daguerre aimed to perform the same operation by the same method, that is, by light; the materials for the sensitive surface, for developing and fixing alone, being different. In this process are found the use of the camera, iodide of silver on a metal plate, mercury as a developer, and hyposulphite of soda as a fixing agent; in that of Niepce, bitumen on a metal plate, iodine as a developer, and oil of lavender in place of the hyposulphite of soda. The use of the latter substance was probably suggested to Daguerre by the publication of a paper, by Sir John Herschel, on the solubility in this menstruum of the insoluble salts of silver. The image formed on the iodized surface was quite *latent* until brought out by the vapor of mercury. It seems wonderful how Daguerre should hit upon the idea of using this vapor, or that a latent image was on the surface. Knowing the latter and the possibility of such a development, the chemist has only to persevere in a systematic exploration among the infinite number of chemical substances, in order finally to meet with success; but Daguerre could not *à priori* be furnished with such positive knowledge; hence our admiration at his success, at the hardihood and perseverance of his character in search of this success, can not be otherwise than boundless. Niepce, too, is entitled to an equal share of honor; for without Niepce, in all probability, sun-drawing would still be a latent property of nature; as also, without Daguerre, the discoveries of Niepce would not stand out in that bold relief in which they are now exhibited.

The plates which Daguerre used for the reception of the heliographic image were of silver, or of copper plated with silver. The silver surface, highly polished, was subjected to the vapor of iodine in the dark-chamber; the iodide of silver thus formed being very sensitive to the actinic influence, the plate was ready for the reception of the latent image. This mode of sensitizing the surface had reduced the time of exposure from hours to minutes; and an increase of sensitiveness was attained at the suggestion of Fizeau, who recommended the use of bromine-water; and about the same time the chloride of iodine was recommended as an accelerator by Claudet; and the bromide of iodine by Gaudin. By means of these accelerators the time was again reduced from minutes to seconds. In this state of perfection we will now leave the art of heliography, or of the Daguerreotype as it is more frequently denominated, and observe only, in conclusion, that this discovery of Daguerre was reported to the world in January, 1839; but the process was not communicated until after a bill had been passed by the French government, which secured to Daguerre a pension of six thousand francs a year, and to Isidore Niepce, the son of Daguerre's partner, an annual pension for life of four thousand francs, one half of which was to revert to their widows.

That Mr. Fox Talbot was acquainted with the experiments of Niepce and Daguerre is very doubtful, because the result of these experiments was kept secret until the pensions had been granted; but Mr. Talbot states, in the communication which he made to the

Royal Society on the thirty-first of January, 1839, six months before the publication of Daguerre's process, that he had been applying the property of discoloration of the silver salts by light to useful purposes. This application consisted in preparing a sensitive paper for the copying of drawings or paintings, by direct contact. The paper was dipped, in the first place, in a solution of chloride of sodium, and afterward in one of nitrate of silver, whereby a film of *chloride of silver* was formed--a substance much more sensitive to light than the nitrate of silver, which had heretofore been employed for photographic purposes. The object to be copied, which had to be transparent, or partly so, was applied in direct contact with the sensitive paper, and exposed to the rays of the sun. By this means, a copy of the object was obtained, in which the lights and shades were inverted. This was the *negative*, which, when fixed, was superimposed on another piece of the sensitive paper, and exposed in its turn to the rays of light, whereby a *positive* print was obtained of the object, in which the lights and shades were exhibited in their natural position.

The communication of Talbot is the first, which laid the foundation of multiplying copies of a picture by the combined action of light and chemical material; it gave the *first idea* of photographic printing.

In the year 1841 another method was devised and patented, called *Talbotype* or *Calotype*. The process consisted in preparing paper with the *iodide of silver*, which, when exposed to light, became the recipient of a latent image, which afterward was made to appear by the application of a developer, and was fixed with hyposulphite of soda. This method is the essential point in the present collodion process; it is, in fact, the very foundation of photography. Talbot, therefore, merits an equal position in history with Niepce and Daguerre. These three--this much to be honored trio--are the undisputed originators of that branch of natural science which hereafter will occupy a prominent part of human intelligence.

The paper, in the Calotype process, was immersed in a solution of iodide of potassium, or floated on its surface; as soon as dry, it was floated on a solution of nitrate of silver for a certain time. By this operation, a film of iodide of silver was formed by the double decomposition of the two salts in contact. The excess of iodide of potassium, or of nitrate of silver and the nitrate of potassa were afterward removed by washing in several waters. These operations had to be performed in the dark chamber, by the aid of a small candle or lamp. When the paper was required to be used, it was brushed over with a solution of one part of nitrate of silver, containing fifty grains to the ounce, two parts of glacial acetic acid, and three of a saturated solution of gallic acid; or the paper was floated on the surface of this *gallo-nitrate* of silver, as it is called, for a few seconds, and the excess of fluid removed by blotting-paper. By this mode of treatment, the paper was rendered very sensitive, sufficiently so to receive an impression of a living person, by means of the camera obscura. An exposure of one second, or of a fraction of a second, was found effective in producing: an impression on the Calotype paper. This impression might be totally invisible, partly visible, or distinctly visible, according to the circumstances of time, intensity of the light, and sensitiveness of the prepared paper. The latent image, or partially visible image, was then developed to any degree of depth of shades, by washing

the surface of the paper with one part of a solution of nitrate of silver, of the same strength as before, and four parts of the saturated solution of gallic acid. The image gradually becomes developed by this treatment, and in a few minutes reaches its maximum degree of intensity. The fixing solutions were bromide of potassium and hyposulphite of soda. The first impression, thus obtained, was in this process, as well as in that with chloride of silver, a *negative*, which, by continuing the process and using this negative as an original object, either in the camera or by direct application, produced a *positive*, with the lights and shades in their appropriate positions.

The difficulty in this process is the want of homogeneity, and of a sufficient transparency, in the structure of paper. The want of transparency probably was regarded the greatest drawback in the production of negatives; whilst the irregularities in the fiber of the paper could never yield a surface to compete with the brilliant and even surface of a polished piece of silver for the reception of positive pictures. To obviate these disadvantages, Sir John Herschel proposed the use of glass plates, and was the first to employ them.

In the year 1847 Niepce de St. Victor, the nephew of Daguerre's partner, to whom we are indebted for many interesting publications on the Chromotype, managed to fix a film of albumen on the glass plates. This film is intimately mixed with the iodides or bromides, and flowed upon the surface of the glass. Such albumen plates are employed by many very distinguished artists at the present day, who exhibit specimens of fine and sharp definition and softness of tone in their stereographs, that have not been surpassed by any other process; as, for instance, regard those beautiful productions of Ferrier.

The next important improvement in photography was effected in 1851; it is the foundation-stone of a new era. Legray originally suggested that collodion might be used as the receptacle of the sensitive material, in place of albumen; but we are indebted to Archer for the practical application of the solution of gun-cotton, and of the mode of employment, pretty much as it now stands. Archer substituted *pyrogallic acid* for the gallic acid that had been previously used in the development of the latent image. Pyrogallic acid, although still used as a developer, has been since pushed aside, in a great measure, by another substitute, the *sulphate of the protoxide of iron*, at the Suggestion of Talbot. It is now limited principally to the operation of intensifying.

Collodion is a solution of a substance very much resembling gun-cotton in ether and alcohol. A decided improvement, in many respects, has been made in this solution, at the suggestion of Sutton, the editor of the *Photographic Notes*, who recommends an excess of alcohol. When this solution is poured upon a piece of clean glass, it forms a very thin, even, and transparent film, which quickly dries, and can scarcely be distinguished from the surface of the glass beneath it. It contains the materials for sensitization. The discovery and application of this substance have given rise to what is denominated the *collodion process*. It is impossible to calculate the impetus given to photography by this discovery, or its value to society, in the promotion of comfort and happiness; much less can an idea be conceived of the resources to which it may give rise by its future developments.



In the year 1838 or 1839, Mr. Mungo Ponton pointed out a very important discovery in reference to bichromate of potassa, when acted upon by light, whereby this salt, the chromic acid, or (as Mr. Talbot advances) the organic matter with which the salt is in combination, becomes insoluble. The paper for experimenting on this point is uniformly coated with a mixture of bichromate of potassa, gelatine, and lampblack in cold distilled water, and allowed to dry in the dark room. When dry, it is ready to be placed beneath a negative. The time varies from four or five minutes to a quarter of an hour or upward. The impression obtained in this way is quite latent, and is made to appear by dissolving off, with hot water, those parts that have been entirely or partially excluded from the actinic influence of the light. The picture resulting from this treatment is a positive print, in black and white, of which the shades are produced by the carbon of the lampblack. This discovery gave rise to carbon-printing.

In the year 1852 a patent was taken out in England by Talbot, reserving to himself the sole use of bichromate of potassa and gelatine in the production of photo-engravings on steel. Three years after this date, that is, in 1855, Poit evin patented a process for making carbon prints by means of the same materials combined with coloring matter, as well as for obtaining a photographic image on a lithographic stone, capable of being printed from by the ordinary lithographic press. In Talbot's process the steel plates were covered with a coating of bichromate of potash and gelatine, the operation taking place in the dark chamber. A transparent positive is then placed on its surface, and the plate is then exposed to the light. The latent image is developed as before alluded to. Afterward the edges of the plate are raised with wax, or some resinous preparation, so as to form a sort of dish, into which is poured the acid or etching-fluid, which etches away the parts exposed by the removal of the soluble gelatine. The etching-fluid used by Talbot was the bichloride of platinum. Poit evin's process is in principle the same. The disadvantage in the latter process arises from the want of durability in the image, which, being formed out of organic matter lying, as it must do, between the ink and the stone, is liable to be soon abraded after a few pictures have been printed from it. These attempts have created a number of improvements, by which matrixes can now be furnished, by the aid of photography, for the engraver's press, the lithographic press, and the typographic press.

Messrs. Cutting and Bradford took a patent out, in this country, for a process in which the image is formed directly of greasy ink used in lithography.

The next important step in photo-lithography is that in which the picture is first formed by bichromate of potash and gelatine on lithographic *transfer-paper*, that is, paper coated with a layer of albumen. A negative is placed in direct contact with paper so prepared, from which an image is obtained, that is, after certain other operations, transferred directly, in lithographic ink, to the stone. This process was patented in 1859, at Melbourne, in Australia, by Mr. Osborne, for which he was awarded by the government of the colony of Victoria the sum of one thousand pounds. This process promises to be the basis of the most successful operations in photo-lithography.

Asser, of Amsterdam, invented or used the transfer process at the same time that Osborne was using it in Australia.

Colonel Sir Henry James makes use of zinc, upon which he transfers the image formed in ink; the image having been produced on engraver's tracing-paper by the means adopted by Talbot, Poit vin, and Osborne.

In the year 1859 another process for photo-lithographic purposes was patented in Vienna, in Austria, in which asphaltum is again brought into the field. The developer is oil of turpentine and water. The latent image is produced in a film consisting of a solution of asphaltum in chloroform, by means of a collodion negative exposed for a number of hours. As soon as the soluble asphaltum has been removed, the remaining insoluble parts which form the shades of the image are coated with a layer of ink by the printer; the image is then gummed in, and slightly etched; after which it is ready for the press.

Poit vin has just published a new method of direct carbon-printing on paper. It depends upon the insolubility communicated to certain organic matters, such as gum, albumen, gelatine, etc., by the per-salts of iron, and on a new fact observed by him, namely, that this matter, coagulated and rendered insoluble in cold and even in hot water, becomes soluble under the influence of light, and in contact with tartaric acid, which, by the reduction of the iron salt, restores to the organic matter its natural solubility. The paper for carbon-printing is floated in a bath of gelatine dissolved in water and colored with a sufficient quantity of lampblack, or other coloring matter, and maintained at a lukewarm temperature. The paper becomes thus uniformly covered with the colored gelatine.

The sensitizing part is performed in the dark room by plunging each sheet into a solution of sesquichloride of iron and tartaric acid in water. By this immersion the gelatine becomes quite insoluble even in boiling water. The sheets are taken out and dried. The prints are obtained by placing transparent positives in direct contact with the paper in the printing-frame Two or three minutes' exposure to the rays of the sun will be found sufficient to render those parts through which the light has passed soluble in boiling water, which is the developer and fixing agent at the same time. A little acid water is used toward the end of the washing, in order to remove all traces of the ferruginous compound.

Poit vin has other methods of producing direct carbon-prints, which, together with this and others preceding, will be fully discussed in their proper place.

Niepce de St. Victor has long been experimenting in his favorite study of the chromotype. He has succeeded in producing photogenic impressions endowed with certain colors of the original. Yellow is found very difficult to transfer to the heliochromic plate at the same time with other colors. Red, green, and blue, it appears, could be formerly reproduced satisfactorily. In the fifth memoir of Niepce on this subject, the author states that he can now reproduce yellow along with other colors in a definite manner. The trouble with these heliochromic specimens is still their want of permanence. At the very most, the colors can not be preserved longer than two or three days. The problem to be settled is the means and mode of fixation.

## Notes

- <sup>1</sup> Dolland, J., was born in London, in the year 1706, and died in 1762.
- <sup>2</sup> Scheele, Charles William, was born on the nineteenth of December, 1742, at Stralsund, Sweden. He died on the twenty-first of May, 1786, at Koeping, on Lake Moeler.
- <sup>3</sup> Bitter, John William, was born at Samitz, in Silesia, in 1776, and died in 1810.
- <sup>4</sup> Wollaston William Hyde M.D., was born on the sixth of August, 1766, at East-Dereham, and died December twenty-second, 1848, in London.
- <sup>5</sup> Wedgwood, Josiah, was born at Newcastle-under-Lyne, in 1730, and died in the year 1795.
- <sup>6</sup> Sir Humphry Davy was born at Penzance, in 1778, and died at Geneva, in 1828.
- <sup>7</sup> Niepce, Joseph-Nicéphore, was born at Chalon-sur-Saône, and died in 1833.
- <sup>8</sup> Daguerre, L.J.M., was born at Cormeilles, in 1787, and died in 1851.

## Chapter II. PRELIMINARY OBSERVATIONS.

THE art of Photography comprehends all the operations of taking a picture on a sensitive surface by means of light and chemical reagents. These operations are as varied as the different substances on which they are taken, or by which they are taken. In all cases, whatever may be the process, the conditions required in the operation of producing a photographic image are, firstly, a suitable groundwork or receptacle, such as paper, metal, glass, or stone; secondly, a coating of substances called sensitizers, which are very sensitively affected by light and altered according to its intensity; thirdly, chemical ingredients, denominated developers, that act differently upon the parts that have been changed by light from what it does upon the parts upon which light has not acted at all or feebly; fourthly, fixing agents or chemical solvents of the sensitizing agents that have not been changed by light. Other important conditions are comprehended in the light, requiring it to be of a certain intensity, in a certain direction, and in a certain quantity.

The various sorts of matter for the reception of the photographic image have given rise to a variety of processes, whose appellations refer rather to the material employed than to any difference in the actinic principle; thus, on paper, exist a number of so-called processes, as, for instance, printing by direct contact, and printing by development; the plain-paper process, the wax-paper process, the resin process, and the albumen process. On glass are found the negative process, the positive or ambrotype process, and the transfer process. On metal the melainotype and daguerreotype processes and photo-engraving; and on stone, photolithography. In addition to these may be mentioned the

card-picture process and that of the stereograph. In reference to the materials used in the sensitized photographic film, or rather to contain the sensitizing ingredients, stand out most prominently; the Collodion processes, wet and dry, the Tannin process, and the Albumen process.

The sensitizing substances most generally used are the salts of silver in combination with organic matter. In the carbon process, as also in photo-lithography, photoengraving, photo-zincography, and photo-glyphography, the sensitive materials are gelatinous or resinous substances in combination with certain chemical reagents that render them insoluble, and in which the solubility, in certain menstrua, is again restored by the agency of light. The salts that have hitherto been used are the bichromate of potassa and the sesqui-salts of iron; the receptacles, asphaltum and gelatine; and the solvents, hot water, oil of turpentine, and oil of lavender. The fixing agents or solvents of the undecomposed iodides, bromides, and chlorides of silver in the collodion, albumen, or surface-sensitized film, on which the rays of light have not acted, or but partially acted, are hyposulphite of soda, cyanide of potassium and sulphocyanide of ammonium. The chemical reagents that either develop the latent image or perfect that which light has already commenced, are the proto-salts of iron, ammonia, gallic and pyrogallic acid, formic acid, and, in the daguerreotype-plate, mercury. Other materials are used in addition to intensify the image already formed by the ordinary developers. The principle involved in the strengthening of negatives is, first, probably by certain electrical decompositions, to produce a deposit of the shadows formed by means of silver, mercury, lead, or iodine; and secondly, to blacken this deposit by sulphurizing or reducing agents, or by the alkalies.

The great divisions into which photographic operations may be divided are those which treat of *negatives* and positives. A negative is an actinic impression on glass or waxed paper, in which the lights and shadows are inverted, as also the figures and the different items that form the picture; that is, right becomes left, and left right. The negative is the matrix from which photographic prints are obtained either on paper or other material; these prints are produced either by direct contact of the paper or glass with the negative, or the negative is placed in one focus of a camera, and the paper or glass in its conjugate focus. Such prints or impressions, whether by reflected or transmitted rays, are *positives*, in which the lights and shades, as well as all the delineations, are in their true and natural position. There is another class of positives in which the shading is natural, but the delineations are inverted; these are exemplified in the Daguerreotype, ambrotype, and melainotype, which are exhibited only by reflected light.

As the present work is intended for practical men, it will be necessary at the very outset to give a list of all the articles and arrangements required in the successful pursuit of the photographic art.

### **LIST OF A PHOTOGRAPHIC OUTFIT.**

1. Glass-house, or room in the garret furnished with a sky-light.
2. Dark room, for sensitizing plates or papers.
3. Operating room, for collodionizing plates, mounting prints, etc.

4. Screens (white, gray, blue, and artistic) for the glasshouse.
5. Lenses, ( $\frac{1}{4}$ ,  $\frac{1}{3}$ ,  $\frac{4}{4}$ , etc., stereoscopic and orthoscopic.)
6. Cameras, (for portraits, views, stereographs and for copying.)
7. Ornamental carpets, chairs, stands, curtains, pillars, balustrades, etc.
8. Head-rests, etc., camera-stands, mirrors, brushes, combs, pins, needle, and thread.
9. Washhand-stand. pitcher and basin, soap and towels, clothes-brush and nail-brush.
10. Stove, tongs, shovel, poker, coal or wood-box.
11. Antechamber, suitably furnished with lounges, etc.
12. Show-cases for artistic productions, and cases for chemicals, etc.
13. Collodion, (negative and positive,) acetic acid, nitric acid, citric acid, tartaric acid, protosulphate of iron, gallic acid, pyrogallic acid, formic acid, carbonate of soda, carbonate of lime, (chalk,) chlorineted lime, nitrate of silver, citrate of soda, phosphate of soda, blue litmus-paper, red litmus-paper, sulphide of potassium, sulphocyanide of ammonium, ammonia, oxide of silver, iodide of potassium, iodide of ammonium, iodide of cadmium, iodine, tincture of iodine, bromide of potassium, bromide of ammonium, bromide of cadmium, bromine, nitrate of uranium, bichloride of mercury, gum-arabic, starch, gelatine, glue, shellac, chloride of gold, acetate of soda, alcohol, ether, distilled water, loaf-sugar, cyanide of potassium, hyposulphite of soda, pyroxyline, sulphuric acid, rotten-stone, tannin, sesquichloride of iron, oxalic acid, varnish, hydrochloric acid, acetate of lead, caustic potassa, salts of tartar, chloride of Sodium, chloride of ammonium, bichromate of potassa, asphaltum, copal, chloroform, cotton, nitroglucose, mastic, resin, thus, benzoin, benzine, wax.
14. Funnels, filtering-stands, collodion-glasses, developing and fixing-glasses, porcelain or photographic-ware baths and dishes, filtering-paper, plain paper, plain-salted paper, albumen paper, arrowroot paper, tinted paper, resinized paper, wax paper, blotting paper, plate-cleaners, plate-holders, Canton flannel, cotton cloths, silk cloths, brushes, colors, pencils, scale and compasses, magnifying-glass, cases, mats, preservers, glass plates of various sizes, (transparent and ground,) melainotype-plates, black leather, black velvet, black varnish, black paper, scissors, pliers, pens, ink, paper, post-stamps, envelopes, pocket-knife, black lead-pencils, gutta-percha dishes, pails, towels, pitcher, ice-cooler, soft water, focussing-cloths, brooms, hand-brush, diamond, cutting board for glass, shelves for negatives, drawers for mounts, papers, etc., beaker-glasses, wash-tubs, scales, weights and graduated measures, dropping-tubes, test-tubes and rack, evaporating-dishes, crucibles and furnace, tongs, coal or wood, door-mats, hat-stand, artificial paraphernalia, as stuffed birds, beasts, etc., skeletons, vases, printing-boxes, fuming boxes, forms for cutting out stereographs, card-pictures, etc., card-board, mounts of various sizes, spatula, pestle and mortar, India-rubber, lamps, candles, frames for photographs, solar camera and its appendages, solar microscope and accessories, glue-pot, tea-kettle, changing-box for dry plates.
15. For out-door work will be required extra: a small hand-cart and tent, or dry collodion or tannin-plates, wax-paper, graduated tape, saw, hatchet, hammer and nails, negative-holder.

### Chapter III.

## SPECIALTIES IN REFERENCE TO THE ARTICLES IN THE PRECEDING CHAPTER-THE GLASS- HOUSE, ETC.

THE first thing which claims the attention of the photographer, is to secure to himself suitable rooms. In many instances the artist has the privilege of superintending the construction of his glass-house or operating-rooms; in this case he must not only know what is required in such a construction, but he must know what arrangements are the most appropriate. The success of many an artist depends upon the fortuitous advantages of his glass-house; but these fortuitous advantages depend upon fixed laws and principles which the photographer must learn, if he is still ignorant of them. To be brief, contrast between light and shade is agreeable to the eye, whether tutored or untutored; whereas uniformity of light or of shade is very displeasing. It is not known why this is so any more than why harmonious combinations of notes are delightful to the ear, or why noncoincident vibrations produce discord. By means of a *happily arranged* contrast of light and shade, a stereographic roundness is communicated to pictures which, where this contrast is deficient or quite wanting, are flat and in no way satisfactory; and where the contrast is exaggerated-where the lights are very bright and the shades very deep-where the transition from one to the other is direct, and the line of demarcation between them is almost visible-the roundness becomes a complete distortion of solidity. This distortion, arising from a vulgar contrast, is sometimes so great as to cause the sitter to disclaim his own picture. The qualifications of an artist are very distinct from those of a mere operator; the former, by reason of his qualifications, can associate with gentlemen and the intelligent; the latter can aspire to no higher companionship than with the ignorant and vulgar. But the qualifications in question are attributable, in a great measure, to a thorough knowledge of light in reference to his art, whereby *nature becomes natural*.

If an object be placed so that the light in one direction, whether brilliant or dull, falls perpendicularly upon its surface, the picture will be flat and disagreeable, because there is no contrast; if the light falls obliquely, the contrast will be displeasing according to its intensity, because the shadows will be elongated and distinctly marked from the lights. A single light, therefore, can scarcely be said to produce an artistic satisfaction.

*Two equally bright* lights, in opposite directions, or rather in directions at right angles to each other, are very objectionable, because either produces a bright circle of light in the eyes, which is repugnant to an artist's feelings, from the fact that the picture is severely flat for want of contrast.

If lights proceed from two directions, at right angles to each other, or somewhere in the neighborhood of this angle, *of which one is more brilliant than the other*, then it is possible so to arrange the sitter or model as to satisfy a cultivated taste.

The greater the brilliancy of the light, the more unmanageable it becomes in the production of that soft merging of light into shade which in photography is so much required. It is, therefore, quite objectionable to use the direct rays of the sun in taking portraits. But during the day these rays proceed from three directions of the compass—in the morning from the east, at noon from the south, and in the evening from the west; from the north alone, in the northern hemisphere, the rays never emerge. But the northern sky or space is illumined by the direct light from the sun, which, by reflection and diffusion, has parted with much of its offensive brilliancy, and is rendered soft and manageable. The direct light into the glass-house, therefore, must *enter from the north*; this is the light which performs, or is to perform, the principal part in the production of a negative. Now this single light, which enters from the northern part of the hemisphere, or a portion of it at least, may be softened down by reflection from side-screens, and so directed by them upon the sitter as to make any degree of agreeable contrast. With these principles in view, the glass-house must be constructed. If the operating-room is situated in the highest story of a house, this house ought to be at least as high as the adjoining or contiguous buildings; and the glass window on the roof must be quite unobstructed by chimneys or trees in a direction perpendicular to its surface.

Supposing the ends of the building in which it is required to construct a photographic establishment face east and west, the following arrangement is one which I would recommend

Let the southern side-wall be raised until it is as high as the ridge of the roof; in like manner fill up to the same height the triangular space in the end-wall between the chimney and the southern wall now raised, either on the eastern or western end, as it may happen to be; at a distance of fifteen feet from the end-wall raise another, equally high, and parallel with it, from the southern side to the ridge of the roof. Next construct a water-tight flat roof; beginning at the side and running toward the north about ten feet. Where this terminates, introduce the wooden frame, the southern portion inclining to the horizon toward the north at an angle of forty-five degrees, to contain the sky-light, which may be fifteen feet wide by twelve feet deep, and inclined at an angle of forty-five degrees with the horizon and facing the north; the southern part of the frame and the window, therefore, comprehend a right angle. Where it is practicable, it is well to have a window in either of the end-walls, furnished with sets of tight shutters about four feet wide, and proceeding (in direct contact, at the commencement, with the part of the sky-light nearest the north) downward to within two feet from the floor. Such side-lights can frequently be used instead of screens; and by the adjustment of the shutters, light can be admitted as required, either as regards quantity or direction, that is, from the west in the morning, and from the east in the evening. From the lowest part of the skylight downward, and right across the room, the space is boarded up about four feet deep, and then the remaining part overhead is a flat ceiling as far as the northern side of the building. The length of this room must be about thirty feet. The dark-chamber and the ordinary work-room may be constructed on the northern side, the window of one being glazed with an orange-yellow colored glass, in order to absorb the actinic rays, and the other with common crown-glass. On the outside of the side-windows, small platforms are formed for the reception of the printing-frames, where no other room can be had

separately and especially for the direct-printing department. The sky-light and the sidelights have to be furnished with curtains, in order to soften or modify the light, which has access according to the circumstances of the case or the taste of the artist. The backgrounds are placed in the space beneath the flat roof; on the southern side, and so far back as to cut off, as much as possible, the direct rays upon the head of the sitter. The northern end must be papered with a grayish-colored paper--the more uniform the better--so as to keep this part as feebly lighted as possible. It is even advisable to have the part where the camera is situated entirely curtained off from the remaining space; by such an arrangement, the operator requires no focussing-cloth, and the curtains being of some material such as wool, and of a deadened color, the sitter's eyes are never strained by looking in this direction.

It happens, however, very frequently, that photographers can not direct the construction of their rooms, and that the sky-light is inserted directly into the slanting side of the roof. In this case, if the light comes from the north, the room will have a direction from east to west, the sitter being placed at either end, according to circumstances. Here only one side-light can be used; to compensate the want of a southern side-light, a screen, movable on an axis, is placed in its stead, which, receiving light either from above or the opposite side, can be made to reflect the same in the direction required.

Where the ridge of the roof of a building is directly north and South, and a sky-light has to be constructed on the slanting roof, there seems to be no alternative but to make two skylights, one on either side, furnished with thick curtains within, and on the outside with a tall partition between them, as also one on the southern side, to exclude the direct rays of the sun; or to construct a suite of rooms, by raising one of the side-walls of the building as nearly in accordance with the plan first proposed, with those exceptions only which the nature of the building would demand. For instance, if the building were somewhat wide, there would be only one side-window, and the facilities for printing would not be so great, unless some room could be fixed up with a southern aspect. The illumination of the background by the light from the sky-light, just described, is uniform, because the construction of the frame admits an equal quantity at the top as well as at the bottom. The ordinary mode of erecting the southern part of the frame, which supports the sky-light in a position perpendicular to the horizon, excludes much of the light, and forms a shadow on the upper part of the background, unless a contrivance of reflection overhead causes the illumination to be equally and uniformly distributed.

The screens or backgrounds for placing behind the model are various. If the background is to be quite white, the screen must be white; if intermediate between black and white, the screen may be gray, grayish-blue, blue, and violet. A red, orange-red, yellow, and black screen will produce a dark-colored background, from the fact that light, impinging upon such surfaces, reflects scarcely any but three colors, and absorbs almost all the rest; but these colors are known by experience to be possessed of little or no actinic influence. Screens with graduated tints, shading off from one color into another, or gradually shading off from a deep to a light color, are to be highly recommended to an artistic operator. Other screens again represent landscapes, castles, shipping, city scenery, etc., in dark-colored outlines and shading, on a gray or bluish-gray foundation. Such



representations are very pleasing to the uneducated taste; the true artist sometimes seems to regard them as finical. If such backgrounds are in true perspective, are correct representations of natural objects and scenery, and can be well focussed on the ground-glass, I would not hesitate to pronounce them legitimately artistic, and as such they must enhance the value of a card-picture or other photograph. On the contrary, if the productions are rude, faulty, and carelessly shaded, their images on the collodion-film will be equally so, and even more so, by distortion from the lenses, and will tend to communicate to the photograph a vulgar appearance.

On the subject of light, a few words more will suffice in this section. Place the model in a very easy and graceful manner, either standing or sitting, leaning on a pillar, balustrade, or small stand, in such a manner that every part is nearly equally in focus, but especially the hands, face, and feet, (if the latter are to be visible.) Avoid as much as possible that silly clinging to uniformity in the position of the sitter, which some operators fall into, as of laying the hands folded together on the lap, or of fixing the thumb in the armhole of the vest. Such sameness becomes a characteristic of the gallery, and renders the specimens that proceed from it ridiculous. Old and young, handsome and ugly, the grieved and the joyous, have all been invested in the same exuviae, have all been grouped or posed amid the same accoutrements. Above all things, endeavor at least to produce a variety of position and paraphernalia in the respective members of one and the same family; otherwise, your photographs will be no better than the painting of Dr. Goldsmith's family in the *Vicar of Wakefield*, in which is beheld an orange in the hand of each figure. As soon as the figure or group is fixed in a pleasing, an easy, and artistic position, the next and a very important business presents itself, which consists in illuminating this figure or group in such a way as to obtain a clear and distinct image on the ground-glass of the camera. If the light falls too much on the head, prevent this by means of the curtain on the skylight; if the shadows are too strong, and apparent beneath the eyebrows, nose, or chin, correct this defect by means of the side-light or the movable screen, recollecting the first law of reflection of light, which teaches that the angle of incidence is equal to the angle of reflection, so that, if the screen be inclined to the horizon at an angle of forty-five degrees, rays that fall upon it through the slay-light will pass off from it in a direction parallel with the horizon, and in a good condition for destroying those horrid black specks of shadow wherever there exist prominences or cavities. The great art in photography is to simplify the light to the very utmost, to use if possible light from two directions alone, and only that sort of light which is endowed with actinic influence on the sensitized plates. It will frequently happen that, with the most brilliant illumination, no other but a hazy image of the model can be obtained on the ground-glass; and where this image is thus indistinct and fuzzy on the ground-glass, it is utterly impossible to obtain any better result on the film of collodion. The haziness in question is caused by a multiplicity of reflections of light, by which rays interfere, cross each other, and are jumbled together in a very irregular and heterogeneous manner, and also by the impure and unequally dense layers of air and vapor set in motion in the room, which produce an atmosphere in front of and around the sitter similar to those dazzling ascending columns of air visible at the sides and on the top of a stove. To avoid the first cause, it is recommended to glaze the skylight with glass containing cobalt, which communicates to it a blue or violet tinge. Such glass excludes all superfluous light, allows only actinic rays

to penetrate, and subdues the illumination to such a degree as to render the image on the ground-glass quite distinct and agreeable to the eye. Although the room, by such glazing, is considerably darkened, the operations in photography are incomparably superior in result, and the time of exposure is not lengthened. The second cause is obviated by preserving a uniform temperature in the room, and by having the currents of ventilation proceeding to their exit at some distance from the sitter. Let me finally impress upon every photographer the absolute necessity he is placed in of learning to *manage the light*, before he can ever hope to be successful in the subsequent operations with chemical materials. An imperfectly lighted picture can never be metamorphosed afterward into a respectable production.

## **Chapter IV.**

### **SPECIALTIES CONTINUED.--THE CAMERA AND LENS.**

THE second most essential thing after a good light, and a successful illumination of the object, is a compound lens, so far corrected for spherical and chromatic aberration as to reproduce on the ground-glass an image in which straight lines are exhibited straight, and all the parts, both in the central and peripheral portions, are clearly defined and free from spectral colors. No single lens can be practically ground and polished so as to be free from spherical aberration; which means that no lens can be constructed so that, with the whole opening, the rays both through the center and all the way to the edges shall be refracted to one point. The focus of those rays which are transmitted through the lens near the periphery, is nearer to the lens than of those which pass through the center. Hence exist a multiplicity of foci, thus converting that which ought to be a point into a circular space; and that which ought to be a line, into a rectangular or curvilinear space; hence the origin of indistinctness and haziness in the photograph-the picture is devoid of sharpness and fine definition. If the optician were able to grind lenses with ellipsoidal surfaces, then a single lens might be constructed so as to be totally free from this sort of error or aberration. This, however, is manifestly a practical impossibility. The form of lens which distorts the least, that is, which has the least spherical aberration, is the one which is well known as the *crossed lens*, whose radii of curvature are in the proportion of one to six. Spherical aberration may be corrected partly by a combination of lenses and partly by the use of diaphragms, the latter of which exclude all but the central rays, or all but the peripheral rays.

Chromatic aberration arises from the difference in the refrangibilities of the colored rays in the spectrum, and the decomposition of white light into the colored or spectral light, whenever it is transmitted through a homogeneous transparent medium whose two surfaces are not parallel. But the two surfaces of a lens are never parallel; therefore every simple and homogeneous lens must decompose light into the spectral colors of which the violet on one side is much more refrangible than the red on the other. On this account the focus of the red light will be more remote from the lens than that of the violet light. This sort of aberration, therefore, has the same tendency as spherical aberration to convert points and lines into circular, rectangular, or curvilinear spaces, with an additional

inconvenience arising from the different colors, which it is well known are possessed of very different degrees of actinism. Now, when both these causes of distortion and indistinctness exist in a lens or in a combination of lenses, it is not in the power or skill of the photographer to obtain a well-defined, sharp, and actinically well-developed picture. Some sorts of glass refract light more than others; again, some decompose light into the spectral colors differently, so that the angle between the extreme rays, the red and the violet, where the refracting angle of the prism or lens is the same, but the material different, is not a fixed quantity. Combining these angular differences, the differences in the refracting powers of transparent media and the varying radii of curvature, mathematicians are now able to devise a variety of combinations of lenses which are practically free from the aberrations in question. Generally crown-glass and flintglass are combined in accordance with the principles just alluded to. Such a combination corrects partially; it is a decided improvement over any single lens as regards fine definition; but what it gains in definition it loses in magnifying power. A triplet, or a combination of three lenses, properly constructed, is an improvement upon the doublet; and a pair of doublets whose radii and distances are mathematically and optically calculated, can be made to produce more correction than it is possible to obtain from a triplet. Three pairs, too, will effect more than two; but, unfortunately, whatever is now gained in focal sharpness is diminished in value by the absorbing power of the different lenses; so that when the combinations increase in number, the light which finally emerges, however much corrected, becomes more and more actinically weak. For photographic purposes, a pair of compound lenses can be constructed and adjusted so as to be practically perfect. We are indebted to Dolland for the first achromatic combination. Doublets and triplets are decidedly the best arrangements for landscape photography; whereas two pairs of

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*To find the Equi-distant Conjugate Foci of a Lens or Combination.*--Adjust the object, as, for instance, a cardpicture, in front of the lens or combination in the camera, until the image on the ground-glass is of an exactly equal size with the object when in perfect focus. Measure the distance from the image to the object and divide this distance by two; the quotient will be the quantity required.

*To find the Comparative Value of Two Lenses or Combinations which produce the same Sized Image of an Object at the same Distance.*--Take the difference between the equidistant conjugate focus and the principal focus of either lens; the smaller this difference the better the lens, because the focal depth or penetration is greater; that is, objects farther apart can be brought into focus consentaneously and with more facility when this difference is small than when it is large. If this difference were zero, a lens would be perfect.

*To find the Magnifying Power of a Lens or Combination.*--On a sheet of card-board, in the middle, construct a circle one inch in diameter, for instance; place this sheet on a table. Insert the lens or tube into a piece of wood placed horizontally over the circle, and raise or depress it by blocks or books until the circle is seen most distinctly when viewed with one eye. Now, by a little practice, with both eyes open, one looking through the tube and the other on the side upon the paper, marks can be made on the board at the extremities of a diameter of the magnified circle; because the eye which is free can, by sympathy, see the magnified image which the other eye beholds, and the pencil at the same time. After this, measure the distance between the pencil-marks, and divide this distance by the diameter of the real circle; the quotient will indicate the number of times the image is larger than the object, which number is the magnifying power.

*To find the Comparative Magnifying Power of Lenses or Combinations.*--Measure the distance in either between the lens and the ground-glass when the moon is in focus, or measure the size of the image; the greater this distance or image, the less the magnifying power. The quotient arising by dividing one distance with the other will give the amount of magnifying power in favor of the lens, whose distance is the shorter.

*To find a Single Lens equivalent in Power to a Compound Lens.*--If a compound lens and a single lens be placed so that their centers are at the same distance from the moon or a distant object, for instance; then, if they produce the same sized picture, one will be equivalent to the other. (For further information *vide* chapters on Microphotography and Microphotography.)

*To ascertain whether a Combination is corrected for Spherical Aberration.*--Draw two parallel straight lines, exactly an inch apart, and two or three inches long, on a piece of card-board. Move the slide until they are correctly in focus on the ground-glass, and until the width between the lines is two inches. If this distance remains the same, that is, if the lines do not deviate from straight lines and from parallelism, the combination is aplanatically correct; if, on the contrary, the images of the straight lines are curves, the spherical aberration has not been corrected. Apply a diaphragm of small opening in front of the combination; it will be perceived that the curvature of the lines will diminish as the

aperture diminishes. If with a very small aperture the lines are still curved, the combination is worthless; whereas, if the lens or combination can be used without a diaphragm and still produces straight and parallel lines in the Images, such a magnifier will be very valuable.

*To ascertain whether a Lens or Combination is corrected for Chromatic Aberration.--* Adjust the slide most accurately, so that the image of an object is very clear and distinct. Next see that the surface of the collodionized plate is exactly coincident with the ground-surface of the glass, that is to say, at the same distance from the nearest surface of the lens. Sensitize the collodion film and take a picture. If, when developed and fixed, this picture is as sharp and well-defined as it was on the ground-glass, the lens is achromatic; if, on the contrary, the contrast between light and shade is imperfect, and the definition and sharpness feeble, the combination has been either over-corrected, under-corrected, or not corrected at all. The actinic rays are on the violet side whose refrangibilities are greater than those of the red rays; their focal distance, therefore, is shorter. Focus again, and after this has been accomplished draw the slide containing the ground-glass outward about one sixteenth part of an inch, insert the sensitized plate, expose, develop, and fix, as before. If the picture is better than before, it shows that the actinic focus is longer than the luminous, and that the combination has been over-corrected. By proceeding in this way, it can be ascertained exactly how much the slide has to be drawn out in order to produce a picture as sharp as that on the ground-glass. After this distance is found, the groundglass has to be advanced or sunk deeper in its frame by this amount, whereby the camera becomes adjusted to the tube. Should it happen that the slide has to be pushed in after focussing in order to obtain sharp definition on the collodion, it is an indication that the lens is under-corrected or not corrected at all. Where a lens requires no adjustment of the ground-glass, it is said to be achromatically correct, or that the actinic and luminous foci are coincident. The value of a lens in this respect is inversely proportionate to the amount of adjustment required; that is, the greater the amount of adjustment, the less its value.

Other methods have been proposed to test the coincidence of the actinic and luminous foci. One consists in pasting a newspaper on a flat board, and erecting the latter perpendicular to the horizon and in front of the opening of the lens, so that the axis of the lens passes through the center of the newspaper and at right angles to it. The operator next obtains a sharp focus upon the central parts, and afterward obtains a positive of the object. If the central parts are still in focus in the picture, the combination has been achromatically corrected; if the parts intermediate from the center to the periphery are in focus, the lens has been over-corrected; and more so if the marginal portions alone are in focus; whereas, if the picture is nowhere sharp, it is probable the lens has not been sufficiently or not at all corrected for chromatic aberration.

A second method is to focus first in the ordinary way; then, placing a piece of violet-colored glass in front of the lens, to focus again; if the two foci coincide, the actinic and luminous foci coincide.

A third method is that proposed by Claudet, which consists in placing printed cards at short distances apart, as, for instance, of one tenth of an inch, in grooves on an inclined

plane resting on a table in front of the tube. Let there be five cards so arranged, and focus upon the middle one. If the first or second is in focus, the lens is under-corrected; if the middle one is sharp, the lens is unexceptionable; and if the fourth or fifth is well defined, the combination is overcorrected.

For an over-corrected lens or combination the ground-glass has to be set back by introducing thin pieces of card-board between it and the ledge of the slide in which it rests; and where the correction has been defective, the glass has to be sunk deeper as before mentioned.

If a combination has been thoroughly corrected, I throw aside the ordinary ground-glass slide entirely, and focus upon a piece of glass of the same size as the collodionized plate, and introduced into the self-same aperture which is to contain the negative. In this way the collodion-surface and the ground-surface must necessarily coincide.

*How to buy a Good Lens.*--Do not purchase a secondhand tube of any one, if you are a *beginner* in the art of photography; but throw yourself implicitly and in full confidence into the hands of a photographic house of *decided reputation*, who will furnish you with a lens and camera in perfect adjustment and in working condition. The tubes manufactured in this country by two or three different firms, are not inferior to the best from abroad; and the advantage you have in dealing directly with them or their immediate agents is, that if by chance a lens turns out in any way defective, you can immediately obtain redress by an exchange. As soon as an operator is sufficiently skilled in optics and their application to the heliographic art, he will be in a condition to rely upon his own judgment, and to make his purchases where pecuniarily they are the most advantageous. The best criterion by which to ascertain whether, after purchasing an adjusted tube and camera, the actinic and luminous foci coincide, is to take the plate-holder containing a plate of glass with the slide drawn and place it upon a table, collodion side uppermost; by the side of this place the groundglass slide with the ground-surface uppermost. Placing a rigid flat ruler over either of these, it will be easy to measure the distance from each glass surface to the edge of the ruler. Where these two distances coincide, there has been no need of adjustment; and the lens may be regarded as good. If the difference is well marked, I would recommend you to return the tube and get a better.

Supposing, furthermore, lenses to be aplanatic and achromatic, there exist special differences by which their relative values can be distinctly estimated. The value of such instruments depends upon the extent of picture in perfect definition which can be obtained by them, with a given opening, focal distance, and diaphragm, and on the velocity with which this work can be accomplished. If of two lenses of equal opening and equal focal distance, the one will produce as sharp and large a picture without a stop as the other can with a diaphragm; the former is very much superior, because, with much more light, the operation of actinism will be relatively quicker. In like manner, if of two lenses whose three parts, as enumerated above, are all equal, but the picture of one is considerably larger than that of the other, and in every respect as well defined, the comparative value is easy to determine. Wherever this difference in the size of the picture exists, other things remaining the same, it will be found that the lens which produces the

larger picture will likewise comprehend a larger angular space containing objects. Drawing imaginary lines from the two extremities of the landscape, for instance, through the center of the lens or combination, to the corresponding extremities of the picture, two isosceles triangles are formed with their vertical angle at the center. This angle or opening of the two outside rays constitutes what is denominated the *angular aperture* of the lens. The greater this angle, the other values remaining the same, the greater the practical worth of the lens. For the purposes of portraiture, the lenses in general have but a small angular aperture, and produce a picture but little more in diameter than half the focal distance. The relation between the opening of the lens, the aperture in the diaphragm, the focal distance and the diameter of the picture, as given in the *Chimie Photographique*, are as follows: Calling the focal distance unity, then the diameter of the lens will be  $\frac{1}{5}$  of this unity, that of the stop  $\frac{1}{40}$ , and that of the picture  $\frac{3}{5}$ . If the diameter of the distinct picture is equal to the focal distance, the angular aperture will be about  $53^\circ$ ; and if this angle be  $90^\circ$ , the diameter of the picture will be about twice as great as the focal distance. It is asserted that the new globe-tubes, the invention of C.C. Harrison, have an aperture of ninety degrees, and that they are free from spherical and chromatic aberration; they will therefore be in a condition to produce large pictures with a small focus. The only disadvantages which they probably possess will be a deficiency of light, owing to the smallness of the aperture in the stops; an inequality of action from the center to the peripheral parts; and the production of what is denominated the "ghost" on the center of the picture, owing to reflections between the lenses of the combination. For architectural and landscape photography they must be inestimable, if the assertion of their merits is true.

The firms in this country that have gained a well-earned reputation for the manufacture of portrait, etc., lenses are those of C. C. Harrison & Co., and of Holmes, Booth, and Haydens; in Great Britain, those of Ross, Dallmeyer, Grubb, etc.; in France, of Jamin, etc.; in Germany, of Voightlaender, etc.

## **Chapter V.**

### **SPECIALTIES CONTINUED.--THE CAMERA.**

THE *camera obscura* was the invention of Porta,\* a Neapolitan; this instrument is, in fact, a miniature glass-house, a conjugate glass-house, which admits no light but that which passes through the lens. The ground-glass is the screen, which must be at right angles, and slide at right angles with the axis of the lens. The model, therefore, or sitter, must likewise be so arranged that the various component parts that have to appear in the picture shall be as much as possible in a plane perpendicular to the optical axis. In this case, it becomes the duty of the photographic artist, as soon as his model is gracefully and compactly arranged, to fix upon the point which is to be the center of the picture, as, for instance, the eye of the sitter, then to reconnoiter the ground, and examine the inclination of the different parts of the figure forming the visible surface, and to ascertain the direction of a line drawn from the eye at right angles to this surface; now bring the camera, raise it and incline it until the axis of the lens coincides with this previously determined direction. In this position, it will be possible to obtain a picture in which the

different parts are almost equally in focus. Before you begin to obtain the focus on the ground-glass, fix the lens in its brass slide in the middle of its motion by the rack and pinion. Next move the bellows slide of the camera until the image on the glass is distinct, and clamp the slide; finally obtain a sharp focus by means of the thumb-screw on the pinion-wheel. With a quick motion backward and forward of the lens, the point of sharpest definition can easily be descried with the naked eye, as long as the image is much smaller than the object; but in copying photographs or engravings, where the picture is to be of equal size with the original, it is not easy to obtain the exact focus; in this case the microscope is called into requisition. The first thing to be done, where this difficulty exists, is to hunt about upon the original photograph or engraving for some distinct landmark, as a very minute circle, or a couple of lines in apparent juxtaposition, or the opening in the letter a or o, or the extreme lines on the sides of a blade of grass; the space between these will become very manifest under the microscope, and by a sweep of the lens backward and forward, the boundary-lines can be designated when most sharp. It requires much practice to focus well in copying; hence it is that few photographers are good copyists. The microscope suitable for such purposes may be a common magnifying-glass, the front lens of one of the stereoscopic tubes, or a compound microscope of low power. An error in the focal distance of one sixteenth of an inch, in portraiture, is scarcely perceptible; whereas the same amount of error in copying will produce a total failure in the negative or positive. In taking a view, and in copying, it is frequently a plan to be recommended, to focus a point midway between the center of the picture and the outside. This is said to equalize the definition; it is essentially a means of dividing the error of spherical or chromatic aberration, where either exists. The eye of the sitter may regard some fixed point on a level with its direction; care must be taken that it is neither raised nor depressed nor in any way strained. By looking at some point on the camera, which is situated in the darkest part of the glass-house, the eyes will be able to remain quite at ease, even whilst steadfastly gazing at this point; if, however, the sight were directed to a point brilliantly lighted, the eyelids would involuntarily close, and the pupil contract, by which the picture would be impaired.

The photography of architecture and of landscapes requires absolutely that the camera be *horizontal*, and so does that of card-pictures, when the whole figure is comprehended, in order to avoid the pyramidal inclination of parts which in nature are parallel. This pyramidal distortion is the consequence of the obliquity of the rays as they are thus made to enter the lens, and for which obliquity the lens has not been corrected. On account of the large angle which a card-picture must necessarily comprehend, a long-focussed lens is preferred, much longer than is required for taking a portrait at the same distance. It is a frequent occurrence to those who occupy themselves with out-door photography not to be able to comprehend certain very desirable elevations within the compass allotted to the photograph without inclining the tube upward; but the tube must remain horizontal; therefore the only alternative remaining is to raise the camera upon a platform or to place it on a window-sill, on the roof of a house, on the branch of a tree, or on the spokes of two ladders, tied or hinged at the top, and with the feet drawn out so as to form a large base between them. Lenses with large aperture are exceedingly useful in such cases, as, for instance, in taking views of churches, public buildings, etc., from the opposite side of the street. The great desideratum has been to find a lens of short focus and large angle for



such sort of work, which can not be performed with lenses of long focus and small aperture.

If the objects in the foreground of a view, as is the case with a stereograph, are to be the principal items of attention, the lens will have to be focussed either upon the central object or upon one intermediate between the center and the edge. In this case, unless the difference between the focus of parallel rays and the focus at an infinite distance be exceedingly small, almost all remote objects will be slightly out of focus, and the picture in the distant background will be defective. To counteract this effect, a much larger lens is employed, which is carried to some distance from the principal objects, until the picture be of the same size as was intended to be taken with the lens of shorter focus. The camera, too, in such a case, must be raised above the horizon, but focussed parallel to it. The scenery in close proximity can be thus excluded, and the distant view will be nearly equally well defined and in true perspective. A small view taken in this manner can be enlarged afterward either into a negative or positive, as may be required, by the method which is fully explained hereafter.

There are certain rules to be observed in field-photography in reference to the light, as in room-photography.

The first is, not to place the axis of the camera in the same straight line with the sun and the object. This means that a picture is not to be taken in the direction of the sun's rays, where the front and central objects are equally illumined, and consequently must be very flat in the photograph; it would be equally absurd to attempt a picture in the shade, whilst the sun is shining, as it were, into the camera through the lens.

An inclination of the axis of the camera with the direction of the sun's light, to the amount of forty-five degrees, will produce an agreeable contrast of light and shade. It is very possible and very probable that such an illumination from the unobscured rays will produce too strong a contrast, and thus give rise to a very hard picture. The best effects are attained when the sun is obscured by a white cloud; the lights and shades still exist with the addition of decided middle tints, giving the photograph the appearance of an artistic production.

With these recommendations in view, the photographer must visit the ground previously to his taking a picture, in order to ascertain at what time of the day the light falls upon it, or can fall upon it, so as to produce the best photographic illumination; this sort of proceeding distinguishes the artist from the operator, and gives the same distinction to his work. It may happen that the principal object in a landscape, which it is required to photograph, is so situated as not to receive the direct light of the sun, as is the case with many northern aspects. The artist, in such a case, will have to wait for a cloudy day, when the direct light of the sun can produce no real shadows, and when perhaps a white cloud in the north-east or north-west may be found to make sufficient contrast.

Cameras for lenses of short focus can be roughly adjusted to focus by means of the bellows-slide, and afterward finely adjusted with the thumb-screw on the lens; but when

the focus is long, the thumb-screw is useless, unless attached to a long lever, as was formerly used in the Lucernal microscope; in such cameras, the bellows-slide has a rough or quick motion, and a slow or fine motion by means of a thumb-screw in front of the operator or on the posterior part of the slide. Such cameras, too, by reason of their length, have to be supported on two camera-stands, in order to make them rigid.

## Notes

\* Porta, Giovanni Battiste Della, was born at Naples, in 1540.

## Chapter VI. SPECIALTIES CONTINUED.--DARK-ROOM.

THE chamber intended for all operations of sensitizing, commonly called the Dark-Room, ought to lie contiguous to and open into the common operating or work-room of the photographer; and both these rooms ought to open directly into the glass-house. As before recommended, they can be constructed on the northern aspect of the gallery, each being seven and a half feet wide-that is, half the width of the glass-room-and about ten or twelve feet long. The work-room may be that on the left, whilst the remaining chamber is on the right, with a door in the middle of the partition between them. A single pane of orange-yellow colored glass on the northern end is all that is needed; this window may be about four feet from the ground, in order that, when the operator is standing, the light whilst developing may come from below and through the negative. This mode of admitting light permits the progress of development to be distinctly watched much more effectively than by reflected light. The elevation of the pane of glass above the floor must be regulated in accordance with the stature of the operator and his habits of standing or bending during the process, so that sometimes an elevation of two or three feet above the floor of the room will be found sufficient. The size of the pane will be adequately large, if its sides are eight inches by six, and a dark-colored curtain is adjusted over this, so as to render the room almost dark in case of need. On the north, east, and south sides a shelf is constructed twelve inches wide, and three feet from the floor. In the north-west corner the pail or barrel is placed to contain water for washing the negatives; this pail or barrel is supplied with a brass stop-cock, such as is used for beer or wine; beneath the stop-cock, and on the floor, is placed the large wash-tub or sink for containing or carrying off the refuse dirty water. Beneath the north-west and the north-east corner there will be found abundance of space for the gutta-percha developing and fixing dishes, as also for the respective solutions used in these processes, and for intensifying, as, for instance, protosulphate of iron, pyrogallic acid, cyanide of potassium, hyposulphite of soda, solution of iodine in iodide of potassium, tincture of iodine, nitrate of silver, bichloride of mercury, and sulphide of potassium. Each of these solutions must be legibly labeled, always placed in the same position, and always carefully corked. As regards the solution of the sulphide of potassium, the necessity for accurate closing of the bottle which contains it is absolute, because the fumes of hydrosulphuric acid, if allowed to escape into the room, would decompose the sensitizing-bath, and injure the prints and negatives. As soon as a negative or positive is complete, the developing and fixing solutions are

poured back into their respective vials. Care must be taken here also not to interchange dishes; for the cyanide of potassium decomposes the iron-salt into what soon becomes Prussian blue by oxidation of the iron, and thus renders it a difficult task to clean the dish afterward. The first things in order on the eastern shelf are the plate-holders, leaning in their respective places against the wall; after this comes the sensitizing-bath, on an inclined frame fixed upon the shelf. The inclination may be about fifteen degrees from the perpendicular; if it were more than this, the light particles of the undissolved iodide of silver, and of other insoluble substances, would be apt to settle upon the tender surface of the collodion, and give rise to apertures in the negative. To avoid this calamity of photographers, it is preferable to have some arrangement by which the collodionized plate can be introduced into the sensitizing-bath with its collodion surface downward. For this purpose flat dishes are used with a glass or porcelain ledge on the right side to support one end of the plate, whilst the other end rests on the bottom of the dish on the left side. In this way the left end of the collodionized plate is introduced first into the bath, whilst the right end is gradually and quickly lowered, by means of a silver or glass hook, until it comes in contact with the elevated ledge which is to support it. The plate is to be completely covered with the nitrate of silver when thus lowered upon its support, which need not be more than a quarter of an inch above the bottom of the dish. Naturally, when the plate is in this position, the collodion is nowhere in contact with the vessel which contains it, excepting at the upper and lower edges. By making the above-mentioned ledge still more shallow, a very small quantity of the silver solution will suffice to cover the plate, and the solution can be filtered, if necessary, after each operation; whereby there can be but small risk of any damage from the deposition of particles of undissolved matter upon the film of collodion. In this country, the vertical or slightly inclined sensitizing baths are preferred, and consequently in most general use; in France and Germany, the horizontal baths are frequently to be met with, and are certainly to be recommended in order to avoid the trouble above alluded to.

To the right of the silver-bath for collodion-plates is the appropriate place of the horizontal dish to contain the sensitizing solution for the chloridized paper. This dish will have a capacity to meet the requisitions of the establishment, and may contain a whole sheet, a half-sheet, or even less, as the case may be. On a small shelf two feet above this dish are placed, in separate bottles, the plain silver and the ammonio-nitrate of silver solutions, a small filtering stand and funnel, ammonia, alcohol, and distilled water; and running from the dish to the southern side is constructed an inclined plane with a semicircular groove covered or lined with plates of glass or porcelain, each one overlapping its fellow like tiles. The first one just projects over the edge of the dish. This grooved inclined plane is screwed to the eastern side of the room, and being thus tiled, is situated in the right position for receiving the droppings of nitrate of silver from the sensitized sheets when removed from the dish, and attached by pins through an upper angle to a soft wooden slip immediately above. The first sheet that is taken from the bath is fixed at the most distant point, and so that the lowest angle is just in contact with the uppermost inclined glass tile; the next is pinned close to it, until the row is complete. If the lower corners or angles of the silvered paper touch the glass, the superfluous fluid will easily flow off and down the inclined plane into the dish; if the corners curl up, it will then be necessary, with a small pad of cotton-wool or a glass rod, to remove the

accumulated solution, by bringing the corner in contact with the grooved channel. By this arrangement the photographer is able to economize his time and his solution. As soon as one row is thus filled with sensitized papers, those first pinned up will probably be sufficiently dry for removal to another slip situated on the southern side of the dark-chamber, thus making room for a fresh quantity of papers.

The semicircular grooves of glass can be manufactured as follows: Take, for instance, a piece of iron plate about fifteen inches long and two inches wide, and get it hammered longitudinally into a hollow groove; next cut up slips of glass of the same length, and about an inch and a half wide. Place one of these slips of glass in the iron channel so that it lies uniformly in the middle. Now heat the iron carefully red-hot, when it will be found that the glass will soften, sink, and assume the shape of the mould. When this has succeeded, allow the iron to cool gradually, in order that the glass may be properly annealed. By arranging these cylindrical glasses so that they overlap each other about half an inch, in the form of tiles, there is no need of applying cement.

## **WORK-ROOM.**

The collodion can be kept on a small shelf in the darkroom, close by the door, in a very convenient place to seize when occasion requires. With this convenience, the plates are flowed in the doorway between the two rooms. At the north end of the work-room there is a good, large window, with the lower part about two feet from the floor, flush with the upper part of a shelf or table constructed right across, from side to side. On the sides of the window-frame, on nails or hooks, hang the various-sized mats for cutting albumen, etc., papers or photographs, as well as the different-sized plate-holders, diaphragms, pliers, scissors, diamonds, rulers, brushes, pencils, etc., used in mounting, printing, etc. On the left side of the table, on small shelves, are kept acetic acid, nitric acid, hydrochloric acid, sulphuric acid, protosulphate of iron in crystals, distilled or rain-water, citric acid, pyrogalllic acid, alcohol, pestle and mortar, stirring-rods of glass, weights and scales, graduated measure for drachms and ounces, another for minims and drachms, cyanide of potassium, hyposulphite of soda, gun-cotton, iodide and bromide of cadmium, iodide and bromide of ammonium, nitrate of silver, ammonia, chloride of ammonium, gum-arabic, gelatine, solution of gum-arabic, etc., brush, spatula, and burnishing-tool, carbonate of lime, chlorineted lime, acetate of soda, phosphate of soda, iodine, iodide of potassium, bromide of potassium, bichromate of potassa, and other chemical materials for experimentation. The preceding articles have to be arranged on narrow shelves in the order in which they can be most conveniently laid hold of, according to their respective merits as necessary or accessory ingredients. On the right side of the window arrange the various-sized glasses, already cut, bath for negatives and positives, the patent plate-holder or vice for cleaning glass plates, rotten-stone, alcohol, solution of salts of tartar, dilute solution of nitric acid, cotton or linen rags, patches of Canton-flannel, silk cloths, broad camel-hair pencil for dusting off particles or fibers from the polished glasses, triangular file, alcohol-lamp, shell-lac for mending the glass-corners, box of pins, box of tacks, small hammer, large and thick glass plate for cutting out photographs, etc., scale and compasses, vignette-glasses, the different-sized printing-frames, varnish, mats,

preservers, cases, transfer-liquid, leather, black paper or velvet, etc., mounts of various sizes.

The sides of this room are furnished with wooden strips to which photographs can be attached by pins in order to dry them after fixation and washing. The toning and fixing dishes are situated on the shelf on the west side; as are also the chloride of gold, test-paper, nitrate of uranium, acetate and phosphate of soda, rain-water, alcohol, and hyposulphite of soda. Beneath the shelf place the tubs for washing prints. In drawers preserve the different sorts of paper in use. Have one drawer for dry but uncut positives, one for the cut positives, one for uncut stereographs, one for the right stereographs and one for the left, one for card-pictures not cut, and one for the prepared card-pictures. One writing-desk near the door and between the door and the window, for containing the day-book, etc. Photographic stock can be stored away on shelves on the southern end and oil the sides of this room. Both these rooms are to be supplied with stoves or other means of warmth and ventilation. On the entrance-door affix the sign forbidding all intrusion. Keep all visitors in the antechamber, which must be made comfortable, and somewhat artistically furnished for their reception. The photographer can not perform his duties with ease if crowded with inquisitive, meddling, and talking parties; the lenses do not operate well if the air is saturated with vapor, and the health is impaired in the midst of the mixed effluvia arising from degenerate lungs.

## **Chapter VII.**

### **COLLODION.**

IN 1851 Legray first suggested the application of collodion for the receptacle of the photographic picture; and in the same year Messrs. Archer and Fry published a detailed account of the practical mode of its application. Collodion is a solution of gun-cotton in ether and alcohol; and guncotton, of which there are several varieties, is cotton or linen fiber (that is, cellulose or lignine) altered by combination with peroxide of nitrogen and probably with nitric acid. Cotton consists chemically of carbon, hydrogen, and oxygen; whilst gun-cotton contains an additional element, namely, nitrogen, which communicates explosive tendencies to several of the metalloids. The altered cotton employed for photographic purposes is not the same as gun-cotton proper; in the first place it is not so explosive; It is, secondly, almost perfectly soluble in alcohol and ether, which is not the case with gun-cotton. It is denominated *pyroxyline*. Pyroxyline is soluble also in acetic ether. When this soluble cotton is dissolved in a mixture of ether and alcohol, and afterward poured upon a piece of glass, it leaves on evaporation, when of a normal condition, a transparent film; whereas gun-cotton so dissolved, or *xyloidine*, (another form of altered cotton,) leaves an opaque film after evaporation.

Cotton or ligneous fiber is transformed into pyroxyline by immersing it in' a mixture of nitric acid and sulphuric acid; the latter seems necessary only to concentrate the nitric acid; for neither sulphur nor any of its oxides are found in pyroxyline by analysis. This, although the accepted theory, is not satisfactory, because it is found necessary to add water to certain specimens of nitro-sulphuric acid. Another reason for the use of sulphuric

acid arises from the fact that pyroxyline is soluble into a gelatinous form in nitric acid, but not in the mixture of nitric and sulphuric acids. Gun-cotton may be precipitated from its ethereal and alcoholic solution into a fibrinous mass like the original, almost. This curious fact exhibits quite an analogy between solutions of salts and the mineral kingdom, and the gelatinous solutions in the organic kingdom. In the former the precipitate is either amorphous or crystalline, as in chloride of silver and carbozotate of potassa; whilst in organic solutions the precipitated ultimate atoms seem to exist, even in solution, in the form of fiber. This peculiar fibrinous deposit is thrown down by adding water to the mixed ethereal and alcoholic solution of pyroxyline, because this substance is insoluble in water. For this reason the necessity of using only Concentrated ether and alcohol is apparent; another deduction is equally apparent from this circumstance, which consists in the employment of such iodizing materials in the preparation of sensitive collodion, as are soluble in ether and alcohol, and in discarding those which are soluble principally in water, or only partially in ether and alcohol. Collodion containing a small proportion of water is thick and *flows* unevenly, and when dry is not quite transparent; whilst the film from anhydrous collodion is very thin, transparent, and uniform, and *flows* on the surface of glass very easily.

*Preparation of Pyroxyline.*--For this purpose the finest cotton or the best Swedish filtering-paper, or old white cotton rags are procured. These materials, especially the first, are not quite pure; a sort of resinous cement adheres with great tenacity to its fibers, and must first be dissolved before the cotton is fit for transformation into pyroxyline. The cotton is therefore boiled in a solution of carbonate of potassa in the following proportion: take one hundred parts of rainwater, two parts of cotton, and one of carbonate of potassa. These materials are maintained at a boiling temperature for a few hours, after which the cotton is taken out and thoroughly washed in several waters, and then left in clean rain-water for at least twenty-four hours, stirring the same from time to time, until every trace of the alkali is removed. It is then taken out, pressed, and dried in thin layers spread upon clean sheets of paper in the sun or on a steam-bath. Care must be taken that all moisture be entirely expelled. In this condition it is ready for the action of nitric acid. Certain rules have to be minutely observed in regard to the temperature of the nitric acid, the quantity of water which it contains, the length of time of immersion, and the intimate mixture of the ingredients; for as these conditions vary so will the pyroxyline. If, for instance, the acids are too strong, or the temperature too low, the pyroxyline will be much heavier than the weight of the cotton used, without apparently having, undergone any other outward change. Such gun-cotton will produce a thick and gelatinous collodion, giving rise to streaks in the film. If, on the contrary, the resulting pyroxyline is less in weight than the cotton introduced, or about equal to it, this indicates that the acids are too weak or the temperature too high, whereby a portion of the pyroxyline is dissolved. Such a species of gun-cotton is not wholly soluble in a mixture of ether and alcohol; it yields, however, a collodion which *flows* easily over the plate, is very adhesive to the glass, and yields a soft negative. Any little particles of dust that may fall on the plate are liable to produce with this collodion transparent specks on the positive or negative. The rule, therefore, on the whole is to steer between these two results, in order to obtain a pyroxyline in which the cotton fiber shows an incipient gelatinization in the acids. When

the operation is successful, the weight of the dry pyroxyline will be somewhere about twenty-five per cent heavier than the cotton from which it was formed.

*No. 1. Formula for the Preparation of Pyroxyline.*

Commercial sulphuric acid, spec. grav., 1.843 at 60 Fahr.,.	24 fluid ounces
Commercial nitric acid, spec. grav., 1.457 at 60 Fahr.,.	8 fluid ounces
Water,	7 fluid ounces
Cotton,	1 ounce.

The vessels used in the preparation of pyroxyline may be large porcelain or glass evaporating-dishes, sitting closely in the cover of a water-bath, maintained at a temperature of 150° Fahrenheit. Each dish is furnished with a pane of glass, fitting upon it as a lid or cover. Let the water-bath be first raised to the indicated temperature; then pour the sulphuric acid into one of the dishes, add to this the water, and mix intimately by stirring with a glass rod with a rounded end; finally pour in the nitric acid, and perform the same operation to insure an intimate mixture. The temperature of this mixture will rise from 15 to 20 degrees above the point required. Remove the dish, therefore, from the bath until the temperature falls to 150°. The temperature can be lowered by stirring the mixture with cold stirring-rods or spatulas of porcelain or glass. Whilst the acids are cooling the cotton can be divided into about a dozen lots, and each lot must be gently separated into a loose condition. As soon as the proper temperature has been attained, the dish is reinstated in its position in the water-bath, and the cotton is introduced one lot at a time, so that each is carefully pressed down beneath the surface by the glass rod. As soon as all the cotton has been introduced and completely covered by the acid mixture, the lid is placed on the dish for six or eight minutes.

The thermometer used on such occasions for ascertaining the temperature of the water or mixed acids, must be strongly made, so that the bulb can be moved about in the fluid with some degree of briskness without any liability to break; it is furnished with a hinged back, which allows the lower portion to be reflected on itself, and the bulb and the lower part of the stem to be exposed. Such thermometers are manufactured for the chemist, and can be purchased at the photographic establishments.

The acids are now poured into another dish close by, allowing the largest portion to drain off, and preventing the cotton from falling out at the same time by the cover which is retained in its place. The dish containing the pyroxyline is then quickly immersed in a large tub of water, and the cotton is well stirred about so as to part with the largest portion of its acidity; it is then taken out with a pair of glass rods and plunged into fresh water in another tub, and again thoroughly washed. After this operation the pyroxyline is placed in a wooden chamber through which a current of water is kept running for twenty-four hours or more, or at least until every trace of acidity has been removed. During this time the agglutinated or adherent portions are carefully separated, so that the stream of

water can more easily act upon each fiber. When blue litmus paper is no longer turned red by the water as it proceeds from the cotton, the latter is taken out, again carefully separated and placed in thin patches on sheets of paper in the sun to dry; or it may be dried on zinc plates, being part of a hot-water bath, whose temperature is maintained at about 120° Fahrenheit. At this temperature pyroxyline will not explode. In the hot days of summer, however, it can be dried quite efficaciously when placed out in the sun.

Pyroxyline, when exposed to the air, absorbs moisture; it undergoes decomposition, too, in an air-tight vessel, if light reaches it; the products of decomposition being nitric acid, peroxide of nitrogen, and probably other compounds. It has not yet been thoroughly ascertained by what means it can be preserved in a normal condition permanently; absence of moisture and of light have been found to assist in this preservation.

If a specimen of pyroxyline by keeping manifests an acid reaction, it is advisable to wash the cotton in several waters, as before, and again to dry it. To neutralize the cotton by an alkali, or a carbonated alkali, is scarcely to be recommended, because they both have a tendency to decompose it; and especially if any trace of these should be left in the fiber, decomposition is likely to ensue in the drying.

*No. 2. Formula for the Preparation of Pyroxyline.*

	<i>By Weight.</i>
Commercial sulphuric acid, spec. grav., 1.843, at 60° Fahr.,.	18 ounces,
Commercial nitric acid, spec. grav., 1.43, at 60° Fahr.,.	14 ounces
Cotton,	2 ounces

Proceed with these ingredients in all other respects as with those in Formula No. 1.

*No. 3. Formula for the Preparation of Pyroxyline.*

Commercial sulphuric acid,	40 ounces,
Pure nitrate of potassa,	20 ounces
Cotton,	1 ounce.

As soon as the mixture of acid and nitre has been thoroughly mixed, and almost cool, the cotton is introduced in small portions and well stirred. In about a quarter of an hour the whole mixture is thrown into a large tub full of water; in this way the pyroxyline is freed as much as possible from the acid; after this it is washed in warm water, and finally in a running stream, as in Formula No. 1.



*No. 4. Formula for the Preparation of Pyroxyline.  
Disdéri's Pyroxyline.*

Sulphuric acid,	4000 grains.
Pulverized pure nitrate of potassa,	2000 grains

Place these in a glass vessel provided with a close-fitting cover, and stir them intimately together with a glass rod. Next add 150 grains of fine cotton-wool, in small flocks at a time, and immerse them thoroughly with the glass rod. When all the cotton has been introduced, close the vessel and set it aside for ten or fifteen minutes. After this, the pyroxyline is withdrawn by means of a pair of glass rods, and well washed, as before recommended, and dried.

In all these formulas the acids, when once used, can not be employed a second time; by distillation, the nitric acid that has not been decomposed might be obtained and used over again, if other combinations and decompositions did not result from the application of so high a temperature. In general the mixture is regarded as useless, and thrown away.

## **Chapter VIII.**

### **ETHER AND ALCOHOL.**

THE next ingredients employed in the manufacture of plain or normal collodion are alcohol and ether. Both these substances belong to a group of hydrocarbons whose basic compound radical, although hypothetical, is denominated *ethyle*, consisting of four equivalents of carbon combined with five of hydrogen, and represented in symbols by  $C_4 H_5$ . Ether is the oxide of this base, and alcohol the hydrated oxide; that is, chemically regarded, the only difference between ether and alcohol is, that the latter contains one equivalent of water, constitutionally combined, which is wanting in ether. The hypothetical compound base, ethyle, enters into combination with several of the alkaloids and acids, giving rise to distinct chemical combinations. This fact will lead us to seek a clue for various untoward and, as yet, unaccountable phenomena in the constitution of sensitized collodion, and its frequent want of permanency.

*Ethyle Group*

Ethyle Symbol Ae,	$C_4 H_5$	Cyanide of ethyle	Ae Cy.
Oxide of ethyle, (ether,)	Ae O	Nitrate of the oxide of ethyle,	Ae O, NO <sub>5</sub> .
Hydrated oxide of ethyle, (alcohol,)	Ae O, HO.	Nitrite of the oxide of ethyle	Ae O, NO <sub>3</sub>

Bromide of ethyle,	Ae Br.	Oxalate of the oxide of ethyle,	Ae, O C <sub>2</sub> O <sub>3</sub>
Chloride of ethyle,	Ae Cl.	Hydride of ethyle,	Ae H.
Iodide of ethyle,	Ae I.	Zinc ethyle,	Ae Zn, etc.

Some of the compounds of the ethyle series are crystallizable salts; but the most of them are volatile aromatic fluids, denominated *ethers*.

Although an equivalent of water is the only difference between alcohol and ether, yet no direct means have yet been discovered whereby an atom of water can be so combined with ether as to form alcohol, nor abstracted from alcohol constitutionally so as to leave ether. It is supposed, therefore, that the elements that enter into the formation of ether, and water and ether, owe their difference to a differ. Once in the grouping of the elementary atoms.

## ETHER.

Ether, sometimes denominated, but very wrongly, sulphuric ether, is obtained by decomposing alcohol by means of sulphuric acid. One method consists in the distillation, of equal weights of rectified alcohol (spec. grav. .835 and sulphuric acid. As soon as ebullition commences, a colorless and highly volatile liquid passes over and is condensed into a receiver surrounded with ice or snow. This method is far from being a profitable one; for at a temperature below 260° Fahr. alcohol distils over; and, if the heat be greater than: 310°, another of the numerous hydrocarbons, olefiant, gas, is generated, together with other gaseous and liquid bodies. By a second method the sulphuric acid is maintained at a temperature of about 300° Fahr., and a, stream of alcohol is made to enter the acid gradually. lit this way a large quantity of alcohol becomes converted into ether. There are two stages in the preparation of ether; by one an impure and crude ether is the result; by the latter the ether is rectified. The minutia; are as follows

Take of alcohol, four *pints*- sulphuric acid, *one pint*; potassa, six *drachmas*; distilled water, *three fluid ounces*. Add gradually fourteen fluid ounces of the acid to two pints of the alcohol in a tubulated retort, and drake frequently in order to produce an intimate mixture. Connect the retort, when placed on a sand-bath. with a proper condensing apparatus, furnished with. a long connecting-tube, so as to remove the vapors, if any should escape, as far as possible from the flame. Explosions are very apt to take place in the preparation of ether, unless great caution be taken. The temperature *is* now raised quickly until ebullition commences. As soon as half a pint of ether has distilled over, the remainder of the alcohol previously mixed with two fluid ounces of the acid is allowed to enter gradually through the tubulated aperture by means of a tube dipping beneath the mixture in the retort, and in quantity as near as can be equal to that which distills over. In this way continue the distillation until about three prints have passed over into the condenser.

The product thus obtained contains sulphurous acid, *sulphuric acid*, *sulphovinic acid*, and other impurities. By rectification most of these are removed as follows:

Add to the ethereal contents in the condenser the solution of the potassa in the distilled water, and shake them frequently during the twenty-four hours they are kept together in a stoppered bottle. After subsidence separate the supernatant ethereal solution by means of a syringe, and distill off two pints of this solution at a low and gentle heat. The specific gravity at this stage will be about .750. By further rectification over newly burnt quicklime and chloride of calcium, ether may be obtained of a specific gravity of .720, or even lower. When perfectly pure its specific gravity is .713, and it boils at 95°. The sulphuric ether of commerce is not sufficiently concentrated for photographic purposes; and none can be relied upon excepting that which is obtained direct from establishments that prepare chemical ingredients for the photographer. When the specific gravity is .720, ether boils at 98°; this is the kind which is generally used in the preparation of collodion. When too long kept it undergoes decomposition, being converted partially into acetic acid. It is a very important solvent of oils, resins, and alkaloids, and certain metalloids, as iodine, bromine, sulphur, and phosphorus. It does not dissolve potassa and soda, a very distinct characteristic from alcohol. It unites in all proportions with alcohol and with one tenth its volume of water. The impurities, as before, mentioned, are acids, alcohol, water, and oil of wine. The presence of acids are shown by litmus; alcohol combines with water when added in excess, and settles and forms the lower stratum; by decantation the upper stratum is removed, which now contains one tenth its weight of water; water is removed by distillation from fresh chloride of calcium; the acids by distillation from lime or potassa; the oil of wine is shown by the production of a milky emulsion when mixed with water.

Alcohol is the rectified spirit of wine of the specific gravity of 0.835, containing eighty-five parts of anhydrous alcohol and fifteen of water. When pure and anhydrous it, is the hydrated oxide of ethyle, (Ae O, HO.) It contains six equivalents of hydrogen, four of carbon, and two of oxygen ( $H_6 C_4 O_2$ ). All saccharine substances undergoing vinous fermentation give rise to the vapors of alcohol, which by distillation are obtained in a separate and more concentrated form. By the vinous fermentation sugar is converted wholly into alcohol and carbonic acid; and it is only from sugar, or substances which by chemical processes are converted into sugar, that the vinous exhalation can be obtained. The ordinary alcohol of commerce is not sufficiently concentrated for the purposes of the photographer, because the water which it contains would precipitate a solution of pyroxyline, or produce an opaque solution. Like ether, therefore, it has to undergo a process of concentration. Whisky is the spirit from which the first alcohol is obtained, which contains water, a peculiar oil, and extractive matter. By distilling a hundred gallons of whisky, between fifty and sixty gallons of alcohol are received in the condenser of a specific gravity of 0.835. By a second distillation, taking care to collect only the first portions and cautiously managing the heat, so as not to allow it to rise to the temperature of boiling water, alcohol may be obtained of a specific gravity of 0.825, which is the lightest spirit that can be received by ordinary distillation. At this stage it contains eleven per cent of water and some small portions of fusel oil.

The process by which most of the remaining water is separated from the alcohol is as follows"

Take *one gallon* of the alcohol of commerce; chloride of calcium, (freshly made,) *one pound*. Throw the chloride into the alcohol and, as soon as it is dissolved, distill off seven pints and five fluid ounces. Or, take of rectified spirit *one pint*, (imp. meas. ;) lime, *eighteen ounces*. Break the lime into small fragments, mix with the alcohol in a retort properly connected, and expose the mixture to a gentle heat until the lime begins to slake; then withdraw the heat until slaking is finished. Now raise the heat gently and distill off seventeen fluid ounces. Alcohol thus obtained will have a density, when the operation is carefully managed, of 0.796.

Neither of the preceding fluid, taken separately, dissolves pyroxyline, a mixture of the two is required to perform this operation; the proportion in which they exist to this mixture, in order to attain to the maximum degree of photographic excellence, is a problem which has not yet been absolutely solved. When there is a large excess of ether over the alcohol, the former menstruum will easily dissolve from one to one and a half per cent of the prepared cotton; and this proportion will scarcely exceed, under the most favorable conditions, from two to three per cent without producing a precipitate in the solution. On the contrary, if the, alcohol, in its purest state, exists in the, mixture in greater quantity than the ether, three per cent of pyroxyline is easily dissolved, producing a collodion of the proper consistency; the mixture, however, will dissolve from eight to ten per cent without producing any deposit in the collodion.

The property of ether in collodion is to communicate tenacity to the film, which, owing to the excess of this fluid, frequently peels off from the glass in one adherent sheet; beside this, ether is more liable to decomposition than alcohol, and is perhaps one of the causes of the want of permanency in collodion, although most probably pyroxyline is the principal cause. This want of stability, even in normal collodion, is increased by the quantity of air contained in the same vessels, giving rise to an ethereal effluvia which it did not possess before. This decomposition is much more rapid when the collodion is exposed to light.

*Decomposition of Collodion.*---The decomposition of normal) or plain collodion is a fact that can easily be verified; but experience shows also that the iodides and bromides when dissolved in pure alcohol and ether are not decomposed, or at any event in a very trifling degree, when properly protected to accurately closed bottles; the fluid does not change color materially, nor does it allow the presence either of free iodine or bromine; furthermore the solutions in question, when kept for any length of time, produce the same sensitive effects on plain collodion as if they were freshly made. The decomposition in collodion does not seem, therefore, to be superinduced by ether, alcohol, the iodides, or the bromides; for each, taken separately or in combination, when pure and properly protected, is not liable to any perceptible decomposition. But Van Monckhoven maintains, and all photographers are aware of the fact, that there is a very perceptible difference between freshly-made plain collodion and old plain collodion. The difference is this: if a plate be coated in newly-made plain collodion and then immersed in a solution

of nitrate of silver and exposed before an object, and afterward submitted to the action of the developing fluid, no traces of the picture will appear; on the contrary, if the plain collodion be old, and a plate be treated with this as in the preceding case, the film will be whitened by the sensitizing solution, and will be sensitive to the action of light when exposed before an object, and will yield a picture. A second difference is this: the collodion, before thick and consistent, becomes thinner and exhales an odor of nitric ether as it grows older.

Such being the case, it seems evident that the pyroxyline is the cause of the decomposition, or that the pyroxyline contains sometimes extraneous matter that produces this decomposition; and when the change has once set in, the newly formed bodies may react upon the iodides or bromides when introduced, and tend to produce a variety of decompositions according to the facility or difficulty with which they undergo change.

But the next question is: What are the differences between freshly-made iodized collodion and an iodized collodion that has been kept long? They are as follows

Firstly. New collodion is more sensitive to light than old collodion.

Secondly. Although more sensitive, it produces images which are much less intense than those produced by old collodion, that is, the shadows are not so deep or black. The images are mere surface-pictures when developed with the sulphate of the protoxide of iron.

Thirdly. If the plates be washed after sensitizing, (in the dry process,) when *freshly-made* collodion is used, no image will appear; on the contrary, with old collodion the washing does not prevent the picture from appearing.

Fourthly. The shadows of the picture developed by the protosulphate of iron are *entirely soluble* in nitric acid when a *freshly-made* collodion is used; and are not entirely soluble with an old collodion.

Fifthly. New collodion is colorless, or nearly so; whereas old collodion sometimes is as deeply red as a strong solution of burnt sugar.

Sixthly. New collodion has the odor only of alcohol and ether; but old collodion has a peculiar ethereal smell resembling that of nitric ether and aldehyde.

We are indebted to Van Monckhoven for the summation of these differences in juxtaposition, and many photographers will recognize the truth of them.

The third question to be asked is then the following: What substance in solution will communicate to recently prepared iodized collodion the properties of old collodion? Hardwich says that grape-sugar, glycyrrhizine, and nitroglucose will render fresh collodion much more intense, but that they diminish its sensitiveness. Such is also the

action of the substance, be it what it may, contained in altered collodion, it renders collodion more intense but less sensitive.

Furthermore Hardwich remarks, that, if these substances be employed to increase the intensity of the shadows in the

image, they ought to be added cautiously because they deteriorate from the keeping properties. But nitro-glucose is said to be an impurity in pyroxyline; it is analogous in several respects to pyroxyline; and it is prepared with sulphuric acid, nitric acid, and *sugar*; but lignine or cellulose yields sugar when treated with sulphuric or nitric acid; hence in the preparation of pyroxyline grape-sugar is formed at the same time, and by the further action of the acids, nitro-glucose is produced. That there exists a duplex compound in collodion may be shown by adding water to it; a precipitate will be formed, of which one part is fibrous and the other gelatinous.

But the identity between the unknown substance and nitro-glucose is apparently shown by the identity of properties. If nitro-glucose be dissolved in alcohol, it forms a colorless solution with an odor of alcohol, which has no *effect* at this stage on collodion, nor on an alcoholic solution of nitrate of silver; but, after the expiration of a few days, it assumes a *rose-colored* tinge and the odor peculiar to old collodion; furthermore, at this second stage, it now communicates to fresh collodion all the properties of old collodion, and forms a precipitate in nitrate of silver in alcohol. Van Monckhoven in addition has convinced himself that the precipitate formed in old collodion by an alcoholic solution of nitrate of silver is six times as bulky as that which would be the result from the iodide of silver, and that its properties were the same as those in the precipitate formed by mixing the rose-colored nitro-glucose with alcoholic nitrate of silver.

*Preparation of Glycyrrhizine.*--*This substance* is obtained by boiling liquorice-root in water for some time, and adding sulphuric acid to the concentrated syrup. A white precipitate is formed, containing glycyrrhizine, albumen and sulphuric acid. The albumen is removed by washing the precipitate, first in acid-water, then in water, and afterward by solution in alcohol. Carbonate of potash is then added to decompose the alcoholic solution, and to precipitate the sulphuric acid. By evaporating the liquid, glycyrrhizine remains as a yellow, transparent mass.

*Preparation of Nitro-glucose.*--Add one ounce of powdered sugar to a mixture of two fluid ounces of sulphuric acid, one of nitric acid. Stir the mixture for a few minutes with a glass rod; a tenacious mass may thus be collected from the fluid, and washed in warm water by kneading it until every trace of acid is removed.

Collodion iodized with the ammonium salt is the least stable; whilst a cadmium collodion is the most permanent. Collodion in which the alcohol is in larger abundance than the ether is more stable, and at the same time more fluid; it adheres well to the glass, forms no rides in flowing, and is in fact quite structureless.

## **Chapter IX.**

# **COLLODION SENSITIZERS--IODIDES AND BROMIDES**

THE salts employed for sensitizing plain collodion for the reception of the actinic impression, are the iodides and bromides of different metal, as of potassium, sodium, ammonium, lithium, zinc, iron, calcium, cadmium, etc.

Iodides and bromides, which are soluble, in ether and alcohol, can alone be employed in the preparation of sensitized collodion, in order to produce, by decomposition in and on the film, an iodide and a bromide of silver, which are insoluble. In so extensive a choice of materials it is a difficult matter to collect all the advantages of a given iodide or bromide over its neighbors; so that it has not yet been decided which is the most appropriate iodide or bromide.

If each soluble iodide or bromide were equally applicable in a photographic sense, then the choice would be influenced by pecuniary considerations of cost and the quantities required; and if by weight the iodides and bromides were equal in price, the selection would fall upon that iodide and bromide whose chemical equivalent is the least; for the less the combining proportion of a given chemical substance, the less the quantity required to produce a given effect. Guided by this consideration. of the subject, the iodide and bromide of lithium would claim our first attention; after lithium come magnesium, ammonium, calcium, sodium, iron, zinc, potassium, cadmium, etc. The solubility of the respective iodides and bromides in a mixture of ether and alcohol. will naturally form a second consideration; and, thirdly, a very important property must have its due weight in the scales, and that is the stability of the given salt in the ethereal solution. The alkaline iodides and bromides are all soluble, so that lithium stands, perhaps, quite as high as the rest in this respect. In absolute alcohol. the iodide of potassium is not soluble to the same extent as iodide of ammonium. The latter iodide is the most easily decomposed. On this account it is regarded as a more sensitive iodizer; it is also quicker; but on the same account it is unstable and undergoes spontaneous decomposition. The iodide of ammonium, as well as that of potassium, is very capricious.

The bromide of silver is sensitive to light as well as the iodide and the chloride; but the spectral rays have not the same influence on either of these three salts. The actinic impression on the iodide and bromide of silver is invisible or latent, and requires the aid of some developing agent to make manifest the effect of light; whilst the impression made on the chloride of silver becomes manifest in proportion to the intensity and duration of light.

The photographed image of the solar spectrum is much broader on the bromide of silver film, than on the iodide film. In the former case, the violet, the indigo, the blue, and partially the green produce actinic action; whilst in the latter the blue part is but partially represented. Equal portions on the violet side and external to the violet color produce an equal impression on either of the films. The greater capacity of the bromized film has

induced photographers to attribute to bromine qualities specially adapted to landscape-photography, where the greens occupy so large a space. By the introduction of the bromides into collodion, together with the iodides, much discussion has arisen to determine the precise action of the former. Certain collodions with certain baths are acknowledged to undergo an improvement when a bromide is a part of the sensitizer; the picture is softened, that is, the middle tints are more pronounced, or the lights and shades more agreeably graded with the bromo-iodizer, than with the simple iodizer. On this account, probably, bromides have been regarded by many as accelerators, or substances which render collodion more sensitive to light. On this ground alone the deduction would be false. The capacity for comprehending a greater range of colors is possessed by the bromo-iodized collodions. This, perhaps, is the only true and legitimate deduction that can be drawn in the case; they are considered by very high authority, on the contrary, as deduced from experiments carefully conducted, to be retarders of the actinic action. In consequence of the greater comprehensiveness, as regards colors, of the bromides over the iodides, it may be concluded, that there are very few cases in which the bromo-iodized collodion can not be appropriately preferred to the simply iodized collodion; the exceptions being the copying of engravings, plain or uncolored photographs, maps, letterpress printing, etc., where the iodized collodion alone possesses all the capacity required.

A peculiarity has been discovered in reference to iodized collodion. Some sorts of collodion are suited for one iodizer, and some for another. As a general rule, a cadmium iodide glutinizes collodion; whereas an alkaline iodide liquefies it. The natural deduction from these circumstances is this: a glutinous or tenacious collodion is suited for sensitizing with iodide of ammonium, or iodide of potassium; for it becomes thereby less tenacious, and flows better. Such collodion soon attains its maximum amount of sensitiveness, and almost with the same facility begins to deteriorate; it is very unstable, and not permanent in any degree of sensitiveness. On the other hand an alcohol collodion, which is in a condition to flow easily, is, in fact, thin and liquid, can be rendered more glutinous by a cadmium iodide. Collodion thus iodized is much more stable than when iodized with the alkaline iodides, but it attains its maximum degree of sensitiveness very slowly, that is, it takes a longer time to ripen than the first-mentioned collodion; but when ripe, it retains its sensitiveness much longer, is in fact a stable collodion. Coupling these two facts together, attempts have been made to combine the iodide of cadmium with an alkaline iodide in such proportions as to comprehend the peculiar advantages of either, that is, the stability and permanency of the one with the quick sensitiveness of the other, and the mutual tempering of either toward a medium glutinosity or liquefaction. The result of such experiments indicates that the cadmium salt must exceed the alkaline salt in quantity. As soon as the highest degree of sensitiveness and stability can be established by means of the iodides alone, it remains then to combine with these a certain proportion of a bromide to communicate to the collodion a greater capacity for colors. Notwithstanding that this is, in my opinion, the view we have to take of the matter, it must be confessed that the best working quantities of the iodides, or of the bromo-iodides have not yet been satisfactorily determined. The difficulty that stands in the way of this determination is increased by the peculiar condition of the nitrate of silver bath, whether it be acid, neutral or alkaline; and furthermore whether it be rendered acid by nitric acid or acetic acid; or whether it contain carbonate of soda or acetate of soda. A cadmium



iodized, or bromo-iodized collodion sensitized in a bath of nitrate of silver rendered slightly acid with nitric acid, produces irreproachable pictures, but not more rapidly than a bath containing acetic acid, acetate of soda, or carbonate of soda, when these happen to be in a happy mood; but the latter are very unstable, whilst the former remains for a long time constant, and is regarded accordingly the proper bath for the cadmium collodion. It must not be forgotten that acids are retarders of sensitiveness, and that consequently a bath that yields a picture without spots, stains, or foginess is preferable in the ratio as it approaches neutrality. A bath containing either acetate of soda or carbonate of soda is, when in its best condition, an accelerator; but it is very unstable, deteriorates very quickly, and at present no means are known to rectify the evil and preserve or restore the sensitiveness.

The iodides and bromides most generally employed by the photographer are those of lithium, potassium, sodium, ammonium, cadmium, and silver.

## **Chapter X.**

### **PREPARATION OF THE IODIDES.**

SEVERAL of the iodides are formed by the direct contact of the elements, as, for instance, the iodide of iron and the iodide of phosphorus. Others by double decomposition, as iodide of silver from a soluble iodide and nitrate of silver. And, finally, others are obtained by combining chemical equivalents of hydriodic acid with the carbonates of the bases required., as, for example, iodide of potassium from hydriodic acid and carbonate of potassa, iodide of barium from hydriodic acid and carbonate of baryta, etc. Iodine or hydriodic acid is the material from which the iodides may be and are prepared.

#### **Iodine.**

Symbol, I. Chemical Equivalent, 127 1/10; Specific Gravity, 4.948.

Iodine was discovered in 1812, by Courtois, a chemical manufacturer in Paris. This substance exists in nature combined with metals, such as calcium, magnesium, and sodium; and these are found in many saline springs and mineral waters, as also in sea-water. These salts are absorbed by several marine plants and animals; and it is from such plants that iodine is obtained in considerable abundance. The sea-plants are collected, dried, and burned in large pits, the ashes of which are called *kelp*. Formerly this kelp was collected on account of the carbonated alkali which it contains; its value now is enhanced on account of the iodides and chlorides which are found in it. The powdered mass is dissolved in cold water, which is afterward evaporated until a scum forms on the surface. The solution is then set aside to cool, when a quantity of crystals will be deposited. By a further evaporation, more crystals may be obtained, until finally the mother-liquor ceases to yield any more. The dark-colored liquid contains the iodides, which may be precipitated by a mixture of five parts of sulphate of iron and two parts of sulphate of copper. The precipitate is subiodide of copper, which, by treatment with

sulphuric acid, the deutoxide of manganese and heat, yields iodine in violet vapors, which by condensation form the metallic-looking crystals of iodine. There are other methods of separating the iodides.

## **Properties.**

Iodine resembles plumago or black lead, in outward appearance; it is a crystalline substance, soft and brittle. It melts at  $224^{\circ}$ , and sublimes at  $347^{\circ}$ . Its taste is very acrid and astringent; its smell is somewhat like that of chlorine. Water dissolves about one part in seven thousand parts, and receives a brown color. Alcohol and ether dissolve it abundantly; and so do iodide of potassium and hydriodic acid, forming brownish red solutions. Iodine in solution, as tincture, or in iodide of potassium preferably, has very valuable medicinal properties. It is regarded as a specific in the reduction of glandular swellings, and in scrofulous diseases. It is said to cause the pustules of small-pox to abort. In photography, it is impossible to estimate its value; for without it, the art could not exist in its present state.

The impurities in iodine are plumbago, sulphide of antimony, and iodide of cyanogen. If by evaporation on a piece of porcelain there be any residue, one or both of the former impurities may be present; the latter impurity is of rare occurrence.

Tests: *Free* iodine is easily recognized by the formation of a deep blue color when mixed with a solution of starch; and this blue color is volatilized by heat. The iodine in an iodide has first to be set free before it can be thus tested. To effect this, either a current of chlorine is passed through the solution, or nitric acid is added to it; by boiling the solution afterward, the fumes may be obtained and thus tested.

## **Preparation of Hydriodic Acid.**

Hydriodic Acid.--Symbol, I H. Combining Proportion,  $128 \frac{1}{10}$ , Specific Gravity, 4.43.

This substance is a condensable gas; at a temperature of  $59.8^{\circ}$ , it solidifies into a transparent, colorless mass; and water absorbs a large quantity. The strongest liquid hydriodic acid has a specific gravity of  $1 \frac{7}{10}$ , when it boils at a temperature between  $257^{\circ}$  and  $262^{\circ}$ . It is not a stable compound; oxygen from the air is absorbed, and iodine is liberated and dissolved by it. Chlorine and bromine decompose it.

Hydriodic acid may be obtained by several methods. From the property which iodine possesses of abstracting hydrogen from several of its compounds, as from phosphide of hydrogen, hydrosulphuric acid, ammonia and organic compounds, methods have been devised to obtain hydriodic acid by their mixture. Thus, by diffusing iodine in powder through water, and then passing a current of hydrosulphuric acid through the solution as long as iodine is thus taken up and the fluid is rendered colorless. By this process, sulphur is deposited and iodine takes its place. By filtration, the sulphur is removed; by heat, the superfluous hydrosulphuric acid is driven away. The remaining transparent solution is hydriodic acid.

A solution of iodide of barium may be decomposed by an equivalent proportion of sulphuric acid, and by filtration from the insoluble sulphate of baryta, hydriodic acid is obtained in solution.

Phosphorus combines very vividly with iodine, and the iodide of phosphorus, when it comes in contact with water, is decomposed into hydriodic acid and phosphoric acid. Liebig has availed himself of this property in the preparation of the iodide of lithium, barium, calcium, potassium, sodium, etc.

Lithium: Symbol, Li.	Combining Proportion, 6 5/10
Barium.--Symbol, Ba.	Combining Proportion, 68 5/10, Specific Gravity, 4.
Calcium.--Symbol, Ca.	Combining Proportion, 20.
Potassium.--Symbol K.	Combining Proportion, 39.
Sodium.--Symbol, Na.	Combining Proportion, 23. Specific Gravity, 0.97.
Ammonium.--Symbol nh <sub>4</sub> =Am.	Combining Proportion, 18.
Cadmium.--Symbol, Cd.	Combining Proportion, 56. Specific Gravity, 8.6.

Take one part of phosphorus, twenty-four parts of iodine, and forty of warm water; mix them intimately in a Wedgwood mortar by means of the pestle. The color of the fluid is at first dark brown, but becomes transparent as soon as the decompositions are effectuated. The heat of a water-bath and friction will soon complete the action. By this operation, iodine and phosphorus combine, so as to form iodide of phosphorus, which becomes resolved into *hydriodic acid* and *phosphoric acid* by the decomposition of the water. A little free iodine added to the transparent solution prevents the formation of phosphorous acid.

### **Iodide of Barium.**

To the transparent solution above obtained, by decantation from any remaining phosphorus, add, in the first place, carbonate of baryta as long as effervescence ensues, and afterward a little water of baryta, so that the mixture becomes slightly alkaline. By this decomposition phosphate of baryta is formed from the phosphoric acid and the carbonate of baryta; and from the hydriodic acid, and the carbonate of baryta, iodide of barium is the resulting formation; and carbonic acid is liberated as gas. The iodide of barium, being soluble, is separated from the insoluble phosphate by filtration. A current of carbonic acid is now passed through the filtrate, in order to combine with any remaining solution of baryta, and the mixture is again filtered.

## **Iodide of Calcium.**

This salt is obtained precisely in the same way as the preceding substituting only milk of lime for the barytic salt. Both these salts crystallize, when slowly evaporated; they are, too, both deliquescent. Froth either iodide of barium or iodide of calcium the alkaline iodides are easily formed.

## **Iodide of Lithium.**

Add two ounces of carbonate of lithia to the iodide of either barium or calcium solutions produced from seven ounces of iodine by the preceding manipulation. The carbonate is previously levigated in water to an impalpable consistency. The mixture is frequently stirred during the twenty-four hours it is allowed to stand, in order to effect the complete precipitation of baryta or lime. The solution of iodide of lithium is now separated by filtration from the insoluble carbonate of baryta or lime. If the iodide of barium or of lime has not been thoroughly decomposed, add a cold solution of carbonate of lithia as long as any precipitate is formed.

## **Iodide of Potassium.**

Digest a hot solution of sulphate of potassa in a solution of iodide of calcium in the proportion of their equivalents for six or eight hours. Double decomposition ensues, the sulphuric acid and oxygen of the potassa combine with the lime to form sulphate of lime, whilst the iodine and potassium enter into combination to form iodide of potassium. By filtration through cloth these two salts are separated. The liquid, containing probably still some iodide of calcium and solution of sulphate of lime, is evaporated and then treated with pure carbonate of potassa as long as any precipitate is produced. The insoluble lime is again separated, and the filtrate is evaporated to crystallization. The mother-liquor is afterward evaporated to dryness.

## **Iodide of Sodium and Iodide of Ammonium.**

These two salts may be prepared in like manner, either from the iodide of barium or of calcium, by the substitution in one case of sulphate and carbonate of soda, and in the other of sulphate and carbonate of ammonia. The results are better with the iodide of barium, owing to the more perfect insolubility of the sulphate of baryta after decomposition. Both of these iodides, as well as that of potassium, may be obtained by the direct action of iodine on the caustic alkalies. In this way iodine is added to a solution of potassa, for instance, until the latter becomes slightly colored; the solution so obtained contains iodide of potassium and iodate of potash; it is evaporated to dryness, and then heated to redness, in order to convert the iodate of potash into iodide of potassium by driving off its oxygen. The fused mass is afterward dissolved and crystallized. Sulphuretted hydrogen is sometimes used to decompose the iodate.

Another method, similar to the first, consists in first obtaining either the iodide of iron or of zinc, by mixing iodine, water, and iron-filings, or iodine, water, and zinc-filings,

together, and then heating the mixture until the combination is complete, which is indicated by its becoming colorless. The filtered solution is next decomposed completely by adding solution of carbonate of potassa as long as any precipitate takes place. The precipitate, which is either carbonate of iron or of zinc, is removed by filtration; and the filtrate is evaporated to crystallization.

### **Iodide of Cadmium.**

This very important iodide is formed precisely in the same way as iodide of iron or of zinc, by gently heating a mixture of the filings of cadmium, water, and iodine, until the solution becomes colorless.

### **Impurities of the Iodides.**

The iodides which are formed by the direct contact of the two elements are quite pure if the materials are pure; whereas, if the iodides arise from double decomposition, the combination may sometimes fail in accuracy, in which case carbonates and sulphates of foreign ingredients and iodates of the same base may be found in such iodides; chlorides may be present, too, in the decomposing carbonates and sulphates, so that we may sometimes expect to find them with the other impurities.

### **Tests of the Purity of the Iodides.**

No precipitate is produced in a pure iodide by solution of *chloride of barium*. If a precipitate results from the introduction of this test, one or all of the following acids are probably indicated: carbonic, iodic, and sulphuric. Other acids might be indicated, but not probably, because materials are not used in the preparation of the iodides containing the acids hinted at, as, for instance, oxalic, sulphurous, silicic, chromic, hydrofluoric, phosphoric, and boracic. Supposing, however, a precipitate is formed when the test is added, then a carbonate, iodate, or sulphate may be one or all present. The next test is to find out which or how many of the three are present. Add, therefore, *nitric acid* to the precipitate; if it becomes dissolved, there is no sulphate in the iodide. Carbonic acid or an alkaline carbonate added to lime-water produces a milkiness caused by the formation of the insoluble carbonate of lime; and an iodate in solution is recognized by the addition of chlorine-water, or citric, or tartaric acid, which liberates free iodine, afterward made manifest by solution of starch. The chlorides are tested for as follows: in a given quantity of the iodide precipitate with solution of nitrate of silver, until nothing more falls as sediment; dissolve this sediment in ammonia, and then add nitric acid; if a chloride is present, a white flocculent precipitate will be produced, which is chloride of silver.

## **Chapter XI.**

### **BROMINE.**

Bromine.---Symbol, Br. Combining Proportion, 80. Specific Gravity, 2.966.

THIS peculiar substance was discovered in 1826 by Balard, of Montpellier. It was originally obtained from the uncrystallizable mother-liquor of sea-water, called *bittern*. It occurs in sea-water in small quantity as bromide of magnesium, or of an alkali; but in much larger quantities in several mineral springs, as, for instance, at Kreuznach, Cheltenham, etc., and is naturally found in many marine plants and animals.

### **Preparation of Bromine.**

The solution of the bromides obtained by evaporation of sea-water, spring-water, or from the ashes of certain plants and animals, is submitted to a current of chlorine, which takes the place of the bromine in the salts. When the liquid ceases to assume a deeper color from the introduction of chlorine, (and great care must be taken not to add too much, because it combines with the bromine as soon as there is no base present for it to combine with,) it is well shaken with ether, which, taking up the bromine, ascends and swims on the surface. This film is then decanted, or otherwise separated, and mixed with a strong solution of potassa, by which both bromate and bromide of potassium are formed; the ether may now be removed by distillation, and the remaining solution is evaporated to dryness. The residual mass is then fused, whereby the bromate of potassa is converted into bromide of potassium, analogously with the iodate or chlorate under similar circumstances. By distilling the resulting bromide with sulphuric acid and peroxide of manganese, bromine passes off as vapor, and a sulphate of the base remains in the retort together with the manganese in a lower state of oxydation.

Bromine thus obtained contains water and bromide of carbon. The water is removed by a second distillation over recently fused chloride of calcium. Bromine is a brownish-red liquid, which solidifies at  $-7^{\circ} \frac{2}{10}$ , volatilizes very rapidly when exposed to the air, and boils at about  $145^{\circ}$ . Its smell is very disagreeable and pungent. A drop on the cuticle destroys it and produces a sore. It is soluble in  $33 \frac{3}{10}$  parts of water, and this solution is decomposed by exposure to light into hydrobromic acid.

Test: Chlorine liberates bromine from all its soluble compounds. Ether combines with it and collects it; solution of starch produces a yellowish-red color with it; it distills as a liquid.

### **Hydrobromic Acid.**

Symbol, Br H. Combining Proportion, 81. Spec. Grav., 2.73.

This acid is very analogous in its formation and reactions to hydriodic acid. It can be prepared by mixing directly phosphorus, water, and bromine, or from a mixture of six parts of crystallized sulphite of soda, three parts of bromine, and one of water, and by distillation. It can be obtained also by transmitting a current of hydrosulphuric acid through water, holding in solution or suspension a small quantity of bromine; sulphur is deposited; the hydrogen combines with the bromine. By a gentle heat the fumes of hydrosulphuric acid are expelled; and by filtration the hydrobromic acid is obtained in solution.

## **Bromides.**

These binary combinations can be obtained, as a general thing, by manipulating precisely as in the preparation of the iodides, with the single substitution of bromine for iodine. They contain in like manner, and for the same reason, the same impurities which may be manifested by the same tests, with the exception of bromic acid instead of iodic; the former of which is decomposed by chlorine.

## **Preparation of the Chlorides.**

Chlorine.---Symbol, Cl. Combining Proportion, 35.5. Spec. Grav., 2.47.

This substance was discovered in 1774 by Scheele. Its affinity for other elements is very great, so that it does not exist free or uncombined. The great geological formation of rock-salt is a chloride of sodium, to which the ocean owes its saline taste. It combines with most of the metalloids as well as the metals, giving rise to some of the most important and interesting combinations in chemistry. Chlorine, iodine, bromine, and fluorine form analogous binaries with

hydrogen and the metals; but chlorine has greater affinities for bases than any of the others; it is, therefore, employed in separating iodine and bromine from their combinations.

## **Preparation.**

Chlorine may be obtained from any of its binary combinations by double decomposition. Thus hydrochloric acid is a binary consisting of chlorine and hydrogen; now by adding to hydrochloric acid a material in which oxygen is loosely combined, hydrogen and oxygen unite to form water, chlorine is liberated, and a chloride of the base is at the same time formed. Take, for instance, four parts of hydrochloric acid, one part of the binoxide or black oxide of manganese, and the same quantity of water. Mix these ingredients in a flask or retort connecting with a jar filled with warm water and inverted over the pneumatic trough, or by a tube dipping to the bottom of a large tumbler. By applying heat, either from a lamp or sand-bath, an effervescence is produced, being the result of the decomposition just alluded to. The gas as it passes out displaces the water in one case and the air in the latter.

The mode by which it is procured from a chloride consists in first obtaining from the chloride hydrochloric acid, And then proceeding as before. But the two operations are combined in one, that is, they take place consentaneously by mixing all the materials together which are required in their separate formations as follows: take three parts of common salt, five of sulphuric acid, five of water, and four of binoxide of manganese, and apply heat as before; the same result will ensue as in the first case.

## **Properties.**

This substance is a heavy gas of a greenish-yellow color, and exceedingly suffocating odor. Under a pressure of four atmospheres this gas is condensed into a liquid of a bright yellow color, whose specific gravity is 1.33. It is soluble in water, which takes up and dissolves about two volumes of this gas, and receives the taste, odor, and other properties of the gas. With very cold water chlorine enters more abundantly into combination, forming a crystalline hydrate. Chlorine in solution, when exposed to the light, soon decomposes the water, giving rise to hydrochloric acid. Chlorine has an exceedingly great affinity for hydrogen, and removes this latter body from many of its combinations, as, for example, from ammonia; still dry chlorine and hydrogen, when mixed and kept in the dark, do not combine; if brought into the full blaze of the sun, they combine and explode; if exposed to diffused light, they combine silently into hydrochloric acid. Its action upon metals in a state of fine division is in many cases very energetic; if a piece of bronze or gold-leaf be injected into a tumblerful of the *moist* gas, the combination is so energetic as to produce flame. The moist gas combines with the hydrogen of organic colors and bleaches them; these colors can not be restored, because the hydrogen can not be restored organically; hence we say in such an instance that the color has been destroyed. In like manner *moist* chlorine removes the hydrogen from putrid and miasmatic substances, as from fish, meat, and offensive localities. It is, therefore, denominated a disinfecting agent. Its combination with the hydrate of lime is the form in which it is used both for bleaching and disinfecting.

## **Chloride of Lime, Chlorineted Lime, etc.**

This substance is prepared by passing chlorine through sets of chambers or compartments of wicker-work containing layers of hydrate of lime. The lime absorbs a large quantity of the gas, and probably combines with it in the formation of a hypochlorite of lime. Chloride of lime is soluble to some extent in water, giving to it an alkaline reaction; its bleaching powers are more effectual when an acid is added, which liberates the chlorine. This substance is now used in photography in the preparation of the gold-toning bath. When added to chloride of gold, which is slightly acid, it renders it alkaline, and at the same time chlorine is liberated, which assists in producing pure whites on the paper, and in furnishing a chloride of gold which is more effectual in toning.

## **Chapter XII.**

### **NORMAL OR, PLAIN COLLODION, IODIZED COLLODION, BROMO-IODIZED COLLODION.**

NORMAL or plain collodion is a solution of pyroxyline in a mixture of ether and alcohol, ready for being iodized or bromo-iodized. This sort of collodion when preserved in well corked bottles becomes clearer with age, and the sediment occupies continually less space. After it has stood for a week or two, the clear supernatant solution is decanted by means of a syphon, syringe, or stop-cock from the residue of undissolved pyroxyline beneath, and again put aside to settle. There is no fixed rule, arising from chemical



equivalents or combining proportions, by which to institute a fixed formula for the preparation of normal or plain collodion. I have selected those which may be relied upon.

Take of ether, specific gravity, .715	1000 parts by weight.
Take of Alcohol, (absolute,)	1000 parts by weight.

In another vessel shake together thoroughly--

Alcohol, (absolute,)	850 parts.
Pyroxyline	45 parts

As soon as the pyroxyline is completely covered and saturated with the alcohol, add the mixture of alcohol and ether, and shake well until the cotton has completely disappeared. Cork the vessel carefully, which is supposed to be full, and put it aside in a cool, *dark* place for a week or two, as before directed.

If a glutinous collodion, or a collodion with more body be desired, such as is required in the transfer of the collodion film upon glazed leather, etc., as much as fifty parts of pyroxyline may be dissolved in the above proportions of alcohol and ether; on the contrary, if a thin collodion be required for the flowing of large plates, the proportion may be as low as thirty-six or forty parts of the prepared cotton. Normal collodion for present use may be filtered; but it is far from being as pure by filtration as by subsidence. Filters for such purposes may be procured of the photographic establishments, by which the filtration proceeds without the contents coming in contact with the atmosphere. The above proportions are for the preparation of what is denominated alcohol collodion, which produces a soft, short, and structureless film on the glass plate.

*Bromo-iodizing Solutions for the same.*

Take of Alcohol, (absolute,)	100 parts.
Take of Iodide of sodium,	8 parts
Take of Iodide of cadmium,	3 parts
Take of Bromide of cadmium,	4 parts

Or,

Take of Alcohol, (absolute,)	100 parts.
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Take of Iodide of lithium,	10 parts
Take of Bromide of lithium,	5 parts

Or,

Take of Alcohol, (absolute,)	100 parts.
Take of Iodide of lithium,	6 parts
Take of Iodide of cadmium,	6 parts
Take of Bromide of cadmium,	2 parts

Or,

Take of Alcohol, (absolute,)	100 parts.
Take of Iodide of cadmium,	10 parts
Take of Bromide of ammonium,	5 parts

Dissolve the salts in each case in the given quantity of alcohol, shaking the mixture frequently, and preserve it in well-closed bottles and in a dark place.

Collodion for photographic purposes is prepared from a mixture of plain collodion, and one of the bromo-iodizers above given, in the proportion of *ten* parts of the former to *one* of the latter. The mixture requires to be placed aside for a day or two, before it arrives at its maximum sensitiveness.

Many operators prepare their collodion directly with the requisite quantity of iodizing and bromo-iodizing materials, of which the following selection contains some of the best formula.

*Formula of Lieut.- Colonel Stuart Wortley.*

Ether,	1 ounce.
Alcohol, .802,	2¼ ounce.
Iodide of lithium,	15 grains.
Bromide of lithium,	6½ grains.

The pyroxyline is first steeped in the bromo-iodized alcohol, and the ether then added. These proportions produce a very fluid collodion, which is quite an advantage in coating large plates, where a very even film is required. It is said to be well adapted for instantaneous pictures. The sensitizing bath, which is used with this collodion, will be found amongst the list of silver baths given hereafter.

*Ommeganck's Formulas for Portraits and Landscapes.*

*For Portraits of short exposure.*

Ether	667 parts.
Alcohol	333 parts
Iodide of ammonium	6 parts
Iodide of cadmium	6 parts
Bromide of cadmium	3 parts
pyroxylin	12 parts

This collodion is sure to be thick enough; if too thick, however, it can be rendered more fluid by the addition of an appropriate quantity either of ether or absolute alcohol. If more than one tenth of the original volume be added, it will be necessary to mix with this the corresponding quantity of the bromo-iodizers.

*For Landscapes, Views, and Direct Transparent Positives.*

Ether	667 parts.
Alcohol	333 parts
Iodide of zinc	6 parts
Iodide of cadmium	6 parts
Bromide of cadmium	3 parts
Pyroxyline	12 parts

In this, as also in the preceding formula, weigh out the salts first; put them into a bottle of the proper capacity; add the alcohol, and dissolve them by frequent shaking; next add the ether and mix; finally introduce the pyroxyline in small flocks at a time, and shake until the cotton is dissolved. After the solution is effected the collodion is put aside in a cool,

dark chamber, and allowed to settle for a couple of weeks. The first collodion will keep for a long time; the latter is less stable, but more sensitive to certain colors of foliage.

*Formulas of Disdéri.*

NO. 1.---COLLODION FOR WINTER.

*First Formula.*

Alcohol--spec. grav. .813	4000 grains.
Ether, spec. grav. 720	6000 grains
Pyroxyline	110 grains
Iodide of ammonium	60 grains
Iodide of cadmium	40 grains
Bromide of ammonium	6 grains
Bromide of cadmium	4 grains
Iodine	5 grains

*Second Formula.*

Alcohol--spec. grav. .813	4000 grains.
Ether, spec. grav. 720	6000 grains
Pyroxyline	110 grains
Iodide of ammonium	50 grains
Iodide of potassium	50 grains
Bromide of ammonium	10 grains
Bromide of potassium	10 grains
Iodine	5 grains

The iodide and bromide of potassium are dissolved in the smallest quantity of water. A quarter of the prescribed quantity of alcohol is poured into a clean bottle; the pyroxyline is then introduced, and the mixture is well shaken. After this operation the ether is added.

The salts of iodine and bromine are next weighed and dissolved in the remaining quantity of alcohol, and then mixed with the solution containing the cotton. The collodion is put aside for a day or two, and then either decanted or filtered.

COLLODION FOR SPRING.

Alcohol, (as before,)	5000 parts.
Ether,. (as before,)	5000 parts
Pyroxyline	100 parts
Iodide of ammonium	50 parts
Iodide of cadmium	50 parts
Bromide of ammonium	10 parts
Bromide of cadmium	10 parts
Iodine	5 parts

*Second Formula.*

Alcohol and ether, of each	5000 grains.
Pyroxyline	100 grains
Iodine of ammonium and of potassium of each,	50 grains
Bromide of ammonium, and bromide of potassium of each,	5 grains
Iodine	5 grains

COLLODION FOR SUMMER.

Alcohol, (as before,)	4000 grains.
Ether, (as before,)	6000 grains
Pyroxyline	80 grains
Iodide of ammonium	50 grains
Iodide of cadmium	30 grains

Bromide of ammonium	5 grains
Bromide of cadmium	2 grains
Iodine	2 grains

For copying engravings, etc., all that is required is a very simply iodized collodion, without any bromide.

*Formula for Copying Collodion.*

Alcohol, (absolute,)	5000 grains.
Ether, .720	5000 grains
Iodide of cadmium	100 grains
Pyroxyline from	75 to 100 grains
Iodine	2 grains

The collodion film, whether iodized or bromo-iodized, is rendered sensitive by immersion in a bath of nitrate of silver, which will be described in the following pages.

(Owing to the instability of collodion when once iodized, it has been proposed to invert the operations, and to mix with the collodion an equivalent quantity of the nitrate of silver, instead of the iodizers or bromo-iodizers, and then to sensitize the film in a bath as follows:

Distilled water	100 parts.
Alcohol	25 parts
Iodide of ammonium	2 parts
Iodide of cadmium	4 parts
Iodide of zinc	2 parts
Bromide of zinc	2 parts

As soon as withdrawn from this bath, the collodion plate is washed in distilled water, and either used immediately by immersing it in a weak solution of nitrate of silver, or put away to dry. This process is due to Ch. D'Orma, and remains to be tried.) Whatever may be the difference of the composition of the collodion, arising from the variety of formulas

that exist-for there is scarcely a single operator that does not boast of his own formula- each collodionized plate, when the film has sufficiently dried, is submitted to the chemical influence of a solution of nitrate of silver, in order to obtain by double decomposition in and on the film an iodide, or a bromo-iodide of silver, which is sensitive to the actinic influence of light. If the film contained a pure iodide, or a pure bromo-iodide of silver, without the presence of a nitrate, the results would not be satisfactory. The nitrates, or nitrogenized organic substances seem to be essential as accessories in the photographic operation of producing collodion positives and negatives. The most important salt in photographic chemistry is nitrate of silver; it is the salt from which most of the other silver salts are obtained, and is besides a very costly article, and deserves therefore to be treated with all due respect. Hence the following chapter is devoted to its service chiefly.

## Chapter XIII.

### SILVER-SALTS OF SILVER.

Silver.-- Symbol, Ag.	Combining Proportion, 108. Spec. grav., 10.474.
Oxide of Silver.--Symbol, Ag O.	Combining Proportion, 116.
Chloride of Silver.--Symbol, Ag. Cl.	Combining Proportion, 143.5.
Iodide of Silver.--Symbol, Ag. I.	Combining Proportion, 234.36.
Bromide of Silver.--Symbol, Ag. Br.	Combining Proportion, 188.
Sulphide of Silver.--Symbol, Ag. S.	Combining Proportion, 124.
Cyanide of Silver.--Symbol, Ag Cy.	Combining Proportion, 134.
Nitrate of Silver.--Symbol, Ag O. NO <sub>5</sub> .	Combining Proportion, 170.
Hyposulphite of Silver.--Symbol, Ag O. S <sub>2</sub> O <sub>2</sub>	Combining Proportion, 164.
Sulphate of Silver.--Symbol, Ag O. SO <sub>3</sub> .	Combining Proportion, 156.
Nitrite of Silver.--Symbol, Ag O. NO <sub>3</sub> .	Combining Proportion, 154

#### Silver.

SILVER, like gold, is found in a native state; frequently too it occurs as an alloy containing gold, which is recognized, when the silver is dissolved in nitric acid, as the black sediment or oxide of gold. Arsenic and antimony are found also alloyed with it. Several of the ores of lead and copper contain silver.

AS an ore, the sulphide is the most abundant; *horn silver*, or the chloride, occurs native, as also the carbonate in small quantity.

Native silver, and the silver in the native sulphide, are separated in one case from the investing rocky materials, and in the other from sulphur by a process called that of *amalgamation*. The ores and the rocky mass are reduced to powder, and then roasted in a reverberatory furnace with about ten per cent of chloride of sodium, which converts the silver into chloride of silver. The pulverized mass is next put into barrels, hung horizontally and capable of being rotated by machinery. It is mixed with a certain quantity of *water, iron and quicksilver*. By being kept in continual agitation for eighteen or twenty hours, the chloride of silver becomes decomposed by the iron, whereby chloride of iron is formed, and the silver set free. Coming in contact with the mercury, an amalgam is formed, which flows off out of the barrel when the contents are made fluid by the addition of water, and by rotating the barrels very slowly. The amalgam is then subjected to pressure through chamois leather, which allows the mercury to permeate through its pores, but retains the amalgam. By distillation, the mercury can be expelled from the silver residue. Copper and lead ores, containing silver, are treated in the same way.

In certain ores of copper and lead, silver exists in small quantities, and is melted or separated by amalgamation along with them. If the quantity is sufficiently great, the silver is separated by a process called *cupellation*, which is practised in the mint in the assay of metals containing silver. A *cupel* is formed out of well-burnt and well-washed bone ashes, kneaded into a thick paste with water, and forcibly pressed in an iron ring. Cupels vary in size from one to two inches in diameter or more, and from a quarter of an inch to three fourths of an inch thick, hollowed on one side in the concave form of a watch-glass. They are afterward dried by a gentle heat, as on a stove, when they are ready for use. The metal, consisting of copper, silver and a large excess of lead, to be assayed, or the silver to be purified, is placed in the concavity of the cupel, which rests on a muffle in a furnace, over which a current of air can flow with some force. It soon melts, and by the access of the draft of air, the surface becomes covered with a film of oxide; this, as it forms, is removed. Lead oxidizes first, and finally the copper is induced to oxidize by means of the oxide of lead, and forms with it a fusible compound, which sinks into the pores of the cupel. As soon as the foreign metals are nearly removed, the silver assay assumes a rounder shape, and when the last trace of oxide disappears, there is a beautiful play of prismatic colors, and finally the silver button becomes very brilliant, and exhibits a bright *flash* of light, indicative of the completion of the operation.

A second process of purifying silver, and one which will be found better adapted to the wants of the photographer, consists in dissolving the silver of commerce, or of the coinage of the country, in pure nitric acid. Take one ounce and a half of silver, in thin famine, or in filings, one fluid ounce of nitric acid, and two ounces of pure rain or distilled water. Mix the acid and the water in a glazed porcelain dish, or in a glass dish; then add the silver., and place the vessel with its contents in a sand-bath, and apply a gentle heat. The silver will soon disappear in the solution. By this operation, the nitric acid is easily broken up into its combinations, one portion oxidizes the silver and



liberates peroxide of nitrogen; whilst a second combines with the oxide so formed, and produces the nitrate of the oxide of silver. If the metal was impure, as is most likely, and it contained copper, the solution will be tinged blue according to the quantity of impurity. A small drop at the end of a glass stirring-rod, will give rise to a brilliant blue color, in a wine-glass full of water, made alkaline with ammonia, if there be any copper present; or a steel knitting-needle, dipped in the solution, becomes coated with a film of copper, on the same conditions.

Supposing the solution, therefore, contains copper, we may proceed as follows to separate it from the silver. Add to the solution of the nitrate, a small quantity of common salt dissolved in water, drop by drop, as long as a flocculent precipitate is formed. When flakes of the chloride of silver, thus produced by double decomposition by means of the chloride of sodium, no longer appear on the addition of the salt solution, the precipitate is allowed to subside in a dark room, or it is poured directly on a filter, and the fluid containing copper, etc., is thrown away. The precipitate is now well washed by repeatedly filtering pure hot water over it, until a drop no longer produces a blue tinge with ammonia. The chloride is now dried. Next weigh the chloride, and take twice its weight of carbonate of potassa, and fuse the latter in a crucible; when fused, add gradually to it the dry chloride of silver, which will be decomposed, as well as the carbonate of potassa. The chloride leaves the silver and gives rise to chloride of potassium, whilst the carbonic acid and oxygen escape, and the silver remains diffused through the mass. By raising the temperature, the silver sinks into a button at the bottom, and the fused chloride of potassium swims on the surface. The melted mass may now be poured out into a pail of water, or upon a hollow stone. The silver thus obtained and washed, will be quite free from copper, and all other metals, excepting lead or mercury, which might be present. If lead were present in the nitrate, the addition of sulphuric acid would produce a precipitate; and the presence of mercury is easily shown by introducing a piece of polished copper wire into a small quantity of the nitrate in solution, by which it will be covered with a film of mercury when the latter is present.

Chloride of silver may be reduced, also, by fusing it with seventy per cent of chalk, together with four or five per cent of charcoal.

A third method of reduction of the chloride, is one which is very convenient for those who do not possess a furnace, or have the convenience of fusing ores or residues. Moisten the chloride with dilute hydrochloric acid, and immerse a plate of zinc in the moistened mass for several hours. Decomposition will gradually take place, the silver being deposited, whilst the soluble chloride of zinc is formed. After the chloride has been thus completely decomposed, the remaining zinc is withdrawn, and the precipitate is washed with dilute hydrochloric acid, until there is no longer any precipitate formed in the decanted fluid by means either of ammonia or of sulphide of ammonium. The precipitate is next well washed with warm water. It is now in a condition for being dissolved in nitric acid.

Instead of precipitating the silver as chloride, in order to separate it from the copper, the solution is evaporated to dryness, and then heated nearly to redness. By this process the

nitrate of silver is fused, but suffers no other change; whilst the nitrate of copper is decomposed, yielding up peroxide of nitrogen and oxygen, and leaving the insoluble black oxide of copper mixed with the fused silver salt. By dissolving a small portion of the fused mass from time to time in water, and testing the solution, after filtration, with ammonia, it can easily be ascertained whether it be free from copper or not. As soon as no copper is indicated, the fused mass is dissolved in pure water and separated from the insoluble residue, evaporated and crystallized.

The oxide of copper may be separated from the nitrate of copper in the solution by substitution of oxide of silver. This oxide of silver is obtained by precipitating a quantity of the given solution by a solution of potassa. The collected precipitates of oxide of copper and of oxide of silver, are then well washed, and afterward boiled with the remaining parts of the impure nitrate. The solution is then finally separated from the residue, evaporated and crystallized.

Finally, the mixed solution may be treated with plates of copper, whereby the silver is precipitated in a state of very fine division, which is afterward obtained on the filter, and thoroughly purified by washing. This silver is then treated with pure nitric acid until dissolved; the solution is then evaporated to dryness, redissolved, evaporated and crystallized.

In every case where the salt thus obtained is intended for photographic purposes, the crystals when thoroughly dried are dissolved in pure water, and again crystallized; or the solution of the crystals is boiled for some time in a glass flask containing fragments of pure silver, or perfectly well-washed oxide of silver, (procured as just indicated.) In this way the nitrate of silver, after evaporation and crystallization, can be had in an absolute neutral condition.

The mother-liquor remaining after the crystals have been removed, is evaporated to dryness, fused and poured into cylindrical moulds of the size of a quill. In this form it is denominated *lunar caustic*, and used principally by surgeons for cauterizing erysipelatous, ulcerated, etc., surfaces. From this mode of its manufacture, it can not always be relied upon by the photographer as pure. In fact it frequently blackens by exposure to light, whilst pure crystallized nitrate of silver, does not change by a similar exposure. In addition to impurities of an organic nature, it frequently contains, besides, *nitrite* of silver, produced by the decomposition of the nitrate by the heat of fusion.

## **Properties.**

Nitrate of silver crystallizes in colorless square tables; it is an anhydrous salt, and neutral when carefully prepared. This salt may be fused, as before mentioned, into lunar caustic; but if the heat be too great, it is decomposed into nitrite of silver, oxygen being liberated; and by a still greater heat the nitric acid is entirely removed, and pure silver left behind. Nitrate of silver dissolves in one part of cold water, and in less of boiling water. It is soluble also in about four parts of alcohol. The oxide of the nitrate of silver, is precipitated by any of the alkalies or alkaline earths. In ammonia, added in excess, the

oxide is redissolved, forming a definite compound of the formula  $\text{AgO}, \text{NO}_5, 2\text{NH}_3$ , denominated *ammonio-nitrate* of silver, which by evaporation is obtained in the crystalline form.

### **Photographic Properties of the Nitrate of Silver.**

Collodion iodized with a solution of iodide of silver in iodide of potassium does not produce a picture when exposed and developed by the ordinary process; nor is a collodion film, when sensitized in the bath of nitrate of silver, and carefully washed in the dark-room after the operation of sensitizing, any longer as sensitive to the actinic influence as before; or supposing it to be so, it no longer yields a picture 'by ordinary development. It is, therefore, not the iodide of silver *alone* which undergoes the actinic impression, but the iodide in connection with the nitrate of silver, or the nitrate of the new base, and probably with free nitric acid, which is easily broken up or decomposed, and yields thus its oxygen to produce or induce further decompositions. Whatever the theory or the true explanation of the photographic impression on the iodides or bromides may be, whether physical, chemical, electrical, or mixed, that is, physico-chemical, etc., one thing as yet is quite certain, (and this is certainly the beginning of knowledge,) that the rationale of actinism on any substance or surface is a *mystery*, has not been hitherto explained on unexceptional grounds, is not satisfactorily deduced from experiments. It is useless then to give a long dissertation on a mere hypothesis. But we do know, if not with certainty, at least nearly so, by what conditions the best results can be obtained in reference to the nitrate of silver bath in combination with the iodized or bromo-iodized collodion. For instance, collodion containing, amongst other chemical ingredients, free iodine, indicates at once that the silver-bath may be *neutral, even slightly alkaline*; whilst if the collodion be new, contain no free iodine or bromine, be colorless, then the bath appropriate for producing a good picture must be the very contrary of the preceding, it must be *slightly acid*. We know that acids *retard* the action of development, limit this action to the parts impressed actinically, prevent in consequence what is denominated fogging. We know, moreover, from repeated experiments, that it is immaterial whether the collodion or the silver-bath be slightly acid, the result is the same, the production of a clear picture accompanied with the disadvantage of lengthening the time of action. But we do not yet know the exact conditions of collodion and bath by which clearness and sensitiveness can be attained in a maximum degree in the shortest time without exception.

The iodide of silver, whether produced by the decomposition of iodide of cadmium, of lithium, or of any other base, is, in all probability, equally sensitive; but this sensitiveness is found to be materially changed by the presence of the other salt in the decomposition. From experiments in this direction it is known that the greatest degree of sensitiveness is arrived at when the collodion contains *iodide of iron*, and this probably because the proto-nitrate of iron is very unstable and easily broken up. With such an iodizer, however, the silver-bath would soon be entirely deteriorated by the continual introduction of a developing material; so that many points have to be taken into consideration before normal conditions can be isolated or legitimate deductions drawn.

## Preparation of other Salts of Silver.

*Other Salts of Silver--Sulphate of Silver--*This salt is obtained by dissolving silver in concentrated sulphuric acid by the aid of heat; or by double decomposition of nitrate of silver with sulphate of soda. Sulphate of silver is soluble in eighty-eight times its weight of boiling water, from which it crystallizes on cooling. Like the nitrate it is anhydrous, and forms in like manner a distinct and definite combination with ammonia, whose equivalent is  $\text{Ag O. SO}_3 + 2 \text{NH}$ , in fine transparent crystals.

*Hyposulphite of Silver.--*This combination is obtained by the double decomposition of an alkaline hyposulphite and nitrate of silver. For instance, add a dilute solution of hyposulphite of soda to a similar one of nitrate of silver; a white precipitate is formed which is soon dissolved in the menstruum; after a while, when the hyposulphite of soda has dissolved the newly formed precipitate to saturation, a flocculent substance is formed of a dull gray color, which is permanent. This second precipitate is hyposulphite of silver in an isolated state. But the hyposulphite of soda contains a large quantity also, thus giving rise to a soluble double salt, which has a very sweet taste. Hyposulphurous acid has a very powerful affinity for silver, so that hydrochloric acid or a soluble chloride produces no precipitate in the solution of the double salt of hyposulphite of silver and of soda. In such a solution, containing a large proportion of waste silver, the best way to obtain or separate the silver is to pass a current of hydrosulphuric acid through the solution, in order that the silver may be precipitated as sulphide of silver. Hyposulphite of silver undergoes spontaneous decomposition into sulphate and sulphide of silver; on this account the fixing-bath is found to contain in general a large quantity of black sediment, which is sulphide of silver. This sulphide, when a sufficient quantity has been collected, is reduced by heat into sulphurous acid and metallic silver.

*Iodide of Silver.--*This salt is found native, and sometimes in the form of hexagonal prisms. It may be formed artificially by allowing the vapor of iodine to play upon polished plates of silver, as in the Daguerreotype process, or by double decomposition. When excess of nitrate of silver in solution is added to a solution of iodide of potassium or to hydriodic acid, a yellow precipitate is produced; this is iodide of silver; whereas if the iodide of potassium be in excess, the precipitate is nearly white, its soluble and yellow part having been dissolved by the alkaline iodide. The yellow precipitate is that form of the iodide which is best adapted for photographic purposes. It is insoluble in water and in dilute nitric acid; almost insoluble in ammonia; and is not so soon colored by the action of light as the chloride. It is very soluble in the alkaline iodides, in cyanide of potassium, and hyposulphite of soda, and by evaporation may be crystallized out of them as double iodides, etc. When silver is dissolved in hydriodic acid, crystals of the iodide of silver may be obtained in the solution by spontaneous evaporation. Iodide of silver may be reduced in the same way as the chloride by means of zinc. Hydrochloric acid converts it into chloride of silver. It is decomposed by both chlorine and bromine which liberate iodine. It is soluble to a small extent in solution of nitrate of silver.

*Iodide of Silver for the Silver-Bath.--*Add to a small quantity of iodide of potassium in solution a larger quantity of dissolved nitrate of silver; allow the canary-yellow colored

precipitate to subside; decant the supernatant liquid; wash with water and again decant, and repeat the washing several times. Let this operation be performed in the dark-room. The yellow precipitate, whilst still moist, is added to the bath of nitrate of silver in proper quantity as long as it is dissolved by the same; the solution is then filtered; and as regards saturation with the iodide of silver, is ready for use.

*Bromide of Silver.*--This salt is found native in Mexico and in Bretagne, sometimes in an amorphous condition, and sometimes crystallized of a greenish-yellow color. It is formed artificially by exposing plates of silver to the vapor of bromine, or by decomposing nitrate of silver by an alkaline, or any other soluble bromide. The precipitate is white at first, but becomes yellow afterward. It may be fused, and when cool its color is intensely yellow. Bromide of silver is very sensitive to light, but the color when so acted upon by light is very different from that of the chloride. It is soluble in strong ammonia and in chloride of ammonium, as also in hyposulphite of soda and cyanide of potassium. The bromides are decomposed by chlorine, whereby bromine is liberated, and may be collected by ether, which, by agitation, collects the bromine and carries it to the surface, from which it may be decanted.

*Chloride of Silver.*--Next to the nitrate of silver, the chloride is perhaps the most important combination of this metal. It occurs native as horn-silver in translucent cubes or octohedra of a grayish-white color; its specific gravity in the native form is 5.55. Like the iodide and bromide of silver, it may be obtained by exposing plates of silver to the vapor of chlorine. The surface of the plates soon becomes covered with a chalky film, which is the chloride in question. It is obtained as an insoluble white powder by decomposing nitrate of silver, or any other solution of silver excepting the hyposulphite, by means of hydrochloric acid or a soluble chloride, by which a complete interchange takes place, and a dense curdy precipitate falls gradually to the bottom. After subsidence the liquid is poured off, and the residue is well washed in several waters. This operation must be performed in the dark-room, because the chloride of silver is very sensitive to light, and soon changes from a white to a violet color in the sun or in diffused light. This violet-colored substance is a sub-chloride or an oxy-chloride, and may be formed directly by chemical means as follows: dip a plate of polished silver into a solution of sesquichloride of iron, or of bichloride of mercury; the surface becomes stained black; the iron or mercury parting with a portion of its chlorine, is reduced to a lower chloride, whilst the silver film becomes converted into a sub-chloride of silver. Chloride of silver is insoluble in water; it is very soluble in ammonia, in cyanide of potassium, in hyposulphite of soda, as also in concentrated and boiling solutions of chloride of potassium, chloride of sodium, and chloride of ammonium, from which may be obtained, by evaporation in one case and by cooling in the other, crystals of double salts of chloride of silver and the other substances in the solvents. Hydrochloric acid in a very concentrated state dissolves a minute quantity of chloride of silver, which crystallizes on evaporation of the acid. It is precipitated from all solutions of silver salts, as before mentioned, except from hyposulphite of silver, by means of hydrochloric acid. At a temperature of 500° Fahr. it fuses into a transparent yellowish fluid, which when cool may be cut with a knife like a piece of horn, and has beside some other resemblance to horn; it hence received the name of horn-silver by the older pharmacutists. Chloride of silver can not be volatilized like

the protochloride of mercury. The mode of its reduction into pure silver by two or three different processes has already been given under the head of Silver. It may be reduced also by a mixture of carbonate of potassa, cane--sugar, or starch--sugar and water.

Tests: Chloride of silver is distinguished from all other precipitates, having the same color, by the property which it possesses, when exposed on a white saucer or evaporating-dish, of becoming changed into a violet-colored substance. Its insolubility in nitric acid, and solubility in ammonia, is also an excellent test when combined with the preceding.

### **Photographic Properties of Chloride of Silver.**

There is quite an analogy in the application of iodide of silver and chloride of silver; the former being essentially in combination with a nitrate or free nitric acid, the sensitive collodion film; whilst the latter, in combination likewise with a nitrate or free nitric acid, forms the sensitive film on gelatine, albumen, arrow-root, resinized, gutta-percha, or plain paper. These papers have first imbibed, or have been invested with, certain soluble chlorides, as of ammonium, sodium, etc., by floating or otherwise, and then dried. By double decomposition afterward these chlorides are converted, by floating the papers on a solution of nitrate of silver, into chloride of silver. Organic salts of silver are formed simultaneously, such as the albuminate, etc., which assist in, or detract from, the photographic operation. Of this I shall speak more extensively when I have to discuss the theory and practice of Positive printing on paper.

Other Uses of Chloride of Silver.--The solution used in galvano-plasty, or electrolysis, for plating with silver is made by dissolving in a saturated solution of cyanide of potassium the moist and undecomposed chloride of silver to saturation, and then diluting this solution by four or five times its bulk of water.

The grayish-colored powder used for dry-plating or for silvering dial-plates, thermometer-scales, etc., consists of one part of chloride of silver, five parts of cream of tartar, and four of common salt, rubbed on with a piece of flannel or sponge dipped in solution of salt.

## **Chapter XIV.**

### **REDUCING AGENTS-DEVELOPERS.**

As already remarked in a preceding chapter, the actinic impression of an object on the prepared collodion film is invisible or latent; it is like the impression of the finger on a plate of copper, or of a warm piece of metal on a glass mirror; after the removal of the finger, or of the metal, the eye can not distinguish the spot where the impression was made; but, as Moeser first illustrated, breathing upon the glass will make the impression manifest, will show that the image was there in a latent or invisible condition. In like manner a plate of polished silver may be substituted for the glass mirror, and excised

metallic figures be placed when warm on its surface; the impression is quite invisible, but becomes visible when the silver plate is exposed to the vapor of mercury.

Furthermore, if the glass mirror, or the polished metallic plate be exposed in the camera before an object, and the former be breathed upon, and the latter exposed to the vapor of mercury, in either case the picture becomes visible; but the picture in either case is a *mere breath*, an evanescent shadow. It gives us, however, a distinct idea of what is meant by a developer, it is the prototype of a reducing agent. In chemistry is understood by a reducing agent, a substance, which, when applied to a combination, properly speaking of a metal, will decompose the compound in such a way as to leave the metal in the reguline condition, isolated from the other combining materials. Hydrogen and carbon are the best chemical reducing agents. Pass a current of hydrogen through a glass tube containing oxide of copper heated to redness; in this state the hydrogen has more affinity for the oxygen of the oxide than the copper possesses; the two metalloids therefore pair and pass off in combination as the vapor of water, leaving the copper *reduced* to the metallic state. A solution of nitrate of silver, impressed by blocks upon silk, is reduced to a bright film of silver when exposed to hydrogen gas. Heat a mixture of charcoal and oxide of lead in a crucible, carbonic acid results from the combination of charcoal and oxygen, whilst the metal lead is reduced. Electricity, Heat and Light are all reducing agents. Fill a tumbler with the solution of chloride of silver in cyanide of potassium, just above mentioned. Next take two copper wires, to the end of one solder a quarter of a dollar, to the other attach on a hook any clean and well-polished article of brass or copper; the other end of the latter wire is now fastened to the negative or zinc side of a galvanic battery, whilst the end of the other copper wire is fixed on the positive or platinum side of the battery. Insert the piece of silver and the brass, etc., object in the tumbler, but not in contact; the silver in the solution will immediately begin to be reduced, and by the electrical current, will be carried to the negative side and deposited on the object to be plated.

By heat alone several of the oxides are reduced to the metallic state, as for instance, oxide of mercury, of silver, etc. Some are reduced by light, as those of gold.

Many of the salts of the metals are reduced by the superior affinity of other metals. Immerse a piece of copper wire in a solution of nitrate of mercury; nitrate of copper will be formed and mercury precipitated on the copper. Mercury precipitates silver from nitrate of silver; zinc precipitates lead from the acetate of this metal, and iron precipitates copper from its nitrate.

Potassium and sodium by their very superior attraction for oxygen are regarded as among the best reducing agents; cyanide of potassium unites the properties of carbon and potassium in the way of reduction. The protosalts of iron are easily changed into the persalts when brought into contact with oxides in which the oxygen has been loosened in its affinities, or when in contact with chlorine or nitric acid; and the metallic base is precipitated. Tannic acid, gallic acid, pyrogallic acid and formic acid are all excellent reducers. The last substances enumerated are those in general use as reducers or developers in photography; but the substance reduced or precipitated by them is not always a pure metal; in some instances it appears pure and metallic, in others black and

free from metallic lustre, as if it were mixed with organic material. The act of reduction in photography consists in reducing a silver compound; this reduction is, aided by the *presence of nitric acid or a nitrate; without nitric acid or a nitrate the development in question seems impossible, and it is equally impossible without the previous action of light.* Now let us see what the action of the protosulphate of iron is upon the oxide of silver in solution, as also of nitric acid upon the protosulphate of iron. In the first place dissolve a crystal of green vitriol in a drop or two of nitric acid: decomposition ensues; the nitric acid is broken up into parts, fumes of the peroxide of nitrogen are liberated, and a reddish colored persulphate of iron is produced from the absorption of oxygen. Secondly, dissolve a small quantity of the oxide of silver in nitrate of ammonia, and add solution of the protosulphate of iron to the ammonio-nitrate. The mixed solution becomes colored and turbid, and a deposit subsides, which is found to be *pure silver.*

By experience we know that the film on a collodion plate, after development with protosulphate of iron, is also pure silver, soluble in nitric acid. Now coupling the two facts together that both light and *nitric acid* are required before: the reduction can take place, and also that there must be present the oxide of silver in solution, (for the reduction is ineffectual with the iodide of silver,) it seems as if we were indicated to believe that the *action, of light* produced an oxide in all those parts where. it struck, or loosened the oxide of the nitrate of silver present on the film, wherever the actinic rays made an impression. This loosening of the oxide of silver from its connection with the acid may be effectuated by the conjoint action of light and iodine or bromine, whereby a double decomposition is instituted the very reverse of that which ordinarily takes place, that is, iodide of silver and nitrate of potassa are reconverted by light into iodide of potassium and nitrate of the oxide of silver in the act of formation, or properly speaking, into nitric acid and oxide of silver, held in abeyance by some power (light or electricity) which prevents their union. If this were so, it seems to me, we have an assemblage of materials in the right condition for producing the effects which in reality take place. With such circumstances and conditions it is easy to see how a solution of protosulphate of iron would reduce the oxide of silver into a film of pure silver, whose thickness would vary as the intensity of the actino-chemical action. There is no absurdity in supposing the possibility of the inversion alluded to. The vapor of water, by passing through an iron or porcelain tube heated to a white heat, is decomposed into its elements; whereas if the heat of flame be applied to a mixture of these gases, they recombine instantaneously and reproduce the vapor of water. Other analogous inversions of chemical affinity are known to the chemist.

### Iron Developer.

Iron.--Symbol, Fe.	Combining Proportion., 28. Spec. Grav., 7.8.
Protoxide of iron.--Symbol, FeO.	Combining Proportion 36.
Sesquioxide of iron.--Symbol, Fe <sub>2</sub> O <sub>3</sub> .	Combining Proportion 80.

With iron, as with some metals, we have two classes or salts, the *protosalts* and the *persalts* that is, the salts of the protoxide and the salts of the peroxide. The two classes



are not equally permanent, sometimes the protosalts being the stable salts, and sometimes the other. Those salts which are not stable are liable to part with their oxygen, or to take up more oxygen, according to their condition of stability. Thus it happens with the iron compounds. The protonitrate, for instance, is changed by boiling into a salt of the sesquioxide; and the proto-sulphate is apt to undergo decomposition and assume a coppery appearance, by changing into the persalt. This property in salts and acids of communicating to, or of abstracting oxygen from other chemical substances in contact with them is made available in various reactions; as, for instance, in toxicological investigations, arsenic acid is reduced by *sulphurous* acid into arsenious acid; on this account sulphurous acid is properly called a reducing agent. In photography, as already remarked, the sulphate of the protoxide of iron passes easily into the sesquisalt, by abstracting oxygen from somewhere, whereby a picture on the collodion film becomes visible.

### **Nitrate of the Protoxide of Iron.**

Symbol,  $\text{FeO}, \text{N O}_5$ .

This substance is obtained best by decomposing the sulphate by means of nitrate of baryta. The solution has a green color, like all the protosalts; it can not easily be crystallized, because a high temperature decomposes it into a sesquisalt.

### **Sulphate of the Protoxide of Iron.**

Symbol,  $\text{Fe O}, \text{S O}_3, \text{H O} + 6 \text{ Aq}$ . Combining Proportion, 139.

Sulphate of iron is obtained by dissolving iron to saturation in a dilute solution of sulphuric acid, decanting the supernatant liquid, evaporating and setting aside for crystallization. These crystals have a slightly bluish-green color. When exposed to the air the crystals become colored of a brick-red color, by decomposition; and if the crystals be exposed to a temperature of  $212^\circ$  Fahr., or a little upwards, they part with the six equivalents of the water of crystallization, and crumble into a grayish-white powder; at a higher temperature the remaining equivalent of water may be expelled. It is from the anhydrous salt now left that anhydrous sulphuric acid is obtained, or at least the very strong and fuming sulphuric acid of Nordhausen. In the preparation of this acid from the residual salt above mentioned, a high temperature is required, by which the affinity of the acid for the base is destroyed, and is expelled, leaving in the retort a pulverulent red mass, the *colcothar* of the alchemists, or sesquioxide of iron. Sulphate of iron is soluble in two parts of cold water and three fourths of a part of boiling water; the solution is neutral. This salt is not soluble in alcohol; if alcohol be added to a solution of sulphate of iron, the salt is precipitated in a white granular form, which is very convenient for photographic purposes; by this process it is purified from any superfluous acid which it may contain.

## **Double Sulphate of Iron and Ammonia.**

It has been proposed by Meynier to substitute this double salt for the protosulphate of iron, because of its permanency when exposed to the air, or its less liability to decomposition. This double salt was described by Mitscherlich.

### **Preparation.**

Take equivalent proportions of sulphate of iron and sulphate of ammonia, that is, 139 parts of the former to 75 of the latter, and dissolve the salts in four or five parts of water; when the solution is complete, filter and evaporate, and afterward set aside to crystallize. The solution for photographic purposes can be prepared in quantity, and it keeps well without undergoing much change. The formula for development with this double salt does not differ from the simple protosulphate; it contains alcohol, water, and acetic acid.

## **Sulphide of Iron.**

Symbol, Fe S. Combining Proportion, 44.

This substance is not used directly in any photographic operation; but for the chemist and experimental photographer it has great value, because it assists in the formation of hydrosulphuric acid, which is by far the most valuable reagent in chemistry.

### **Preparation.**

Heat a bar of iron in a blacksmith's forge to a welding heat, and then rub it on a stick of sulphur; combination will take place very, vividly, and the new compound will drop off like melted wax. When cool it has a dark gray, color and metallic appearance. Pulverized and thrown into dilute sulphuric acid, it gives rise to hydro-sulphuric acid, which may be collected or used immediately by passing it through a given fluid, as for instance, an old hyposulphite bath, in order to reduce the silver in the form of the sulphide of silver.

## **Tannic Acid-Gallic Acid-Pyrogallic Acid.**

The first substance exists in the vegetable kingdom, and is obtained from the astringent materials in various plants, but especially from oak bark and nutgalls, which are excrescences on the leaves of an oak (*quercus hafectoria*) produced by an insect. The second does not exist naturally, or at least in very minute quantity, but is rather a production arising from tannic acid when exposed to moisture and the atmosphere; and the third is obtained from the second by sublimation at a given temperature. The peculiar property of the astringent principle in various barks, is to *occasion a precipitate* in solutions of gelatine, and in several metallic salts. It produces in solutions of the persalts of iron a dark blue or dingy green color, according to the bark from which it is extracted. From the property of acting upon gelatine, by which skins are converted into leather, it is denominated tannin; and from its power of combining with metallic bases, and forming precipitates, etc., it is regarded as an acid, and termed *tannic acid*.

The tannin extracted from the wood, the bark, the leaves and the galls of oak, the twigs of the black currant and of the sumac, the petals of the pomegranate, etc., and from the roots of several plants, produces in solutions of the sesquisalts of iron, a *deep blue* color, the foundation of writing-ink.

Whereas the tannin from horse-chestnuts, the different varieties of tea, from catechu and kino, cinchona bark, cinnamon, cassia, etc., yields a *green* precipitate with solutions of the persalts of iron.

Tannic Acid.--	Symbol, $C_{54}H_{22}O_{34}$ .
Gallic Acid.--	Symbol, $C_{14}H_6O_{10}$
Pyrogallic Acid.--	Symbol, $C_6H_3O_3$ .

### Preparation of Tannic Acid.

Tannic acid is prepared by a process suggested by Pelouze. Take an elongated glass funnel, terminating at the upper orifice like a bottle, which can be closed by a cork. The lower orifice is loosely closed by a plug of cotton-wool, or a piece of sponge; the body of the funnel is then half filled with powdered nutgalls, over which is poured a quantity of commercial ether, so as to fill the remaining part of the funnel. The cork is then replaced loosely, admitting a little air as the filtration proceeds. The liquid that passes through the funnel, and accumulates beneath, forms two layers; the upper one light and very fluid, and the lower heavier and of a yellowish tinge. Ether is added above the galls, from time to time, until the lower stratum of the filtrate no longer increases in depth. The funnel is then removed from the vessel beneath, and the lower stratum is separated by means of a glass syringe inserted to the bottom; or the whole contents can be placed in a funnel, of which the lower aperture is closed by the finger. In this way the dense fluid is allowed to flow off, and when the whole has been thus removed, the aperture is again closed with the finger, and the light fluid is poured into a retort, and distilled at a gentle heat. It consists principally of ether. The dense fluid is then washed with concentrated ether, from which it is separated as before, and afterward evaporated at a low temperature to dryness. The resulting substance is light and spongy, of an ochreous color. It is pure tannin or tannic acid, in quantity about thirty-five per cent of the galls employed. It has a slightly acid reaction, is very astringent, not bitter. It is soluble in water and alcohol, but sparingly soluble in ether. With mineral acids, albumen, gelatine, salts of the alkaloids, mineral bases, it forms precipitates. Salts of the protoxide of iron are not changed by tannic acid; but those of the sesquioxide give a deep bluish-black precipitate.

Tannic acid is used extensively in photography in the preparation of the dry plates by the Tannin Process of Major Russell. This process is fully described in a subsequent chapter.

## Preparation of Gallic Acid.

As before observed, gallic acid exists in minute quantity in nutgalls; but it is rather a product of the decomposition of tannin, than a naturally existing substance. Mix powdered nutgalls into a thin paste, and expose it to the air for two or three months, taking care to replace the water as it evaporates. The mass becomes mouldy, and darker in color by this exposure; it is then pressed in a cloth; afterward, the residue is boiled in water and filtered whilst hot. On cooling, crystals of gallic acid are deposited, which are purified by boiling in eight parts of water and one fifth of their weight of animal charcoal. After filtration and cooling, pure crystals of gallic acid are deposited, in the form of long silky needles. During exposure to the atmosphere, moist tannic acid absorbs oxygen, and liberates carbonic acid, so that gallic acid is altogether a definite and distinct compound. When quite purified, it has no effect upon a solution of gelatine; it has an acid and astringent taste. The solution is soon decomposed. Gallic acid is soluble in one hundred parts of cold water, and in three of boiling water. It has no effect upon the solution of salts of the protoxide of iron, but upon those of the sesquioxide, it produces a deep bluish-black precipitate, which disappears when the liquid is heated, the sesquioxide being converted into the protoxide by the decomposition of the gallic acid. Gallic acid meets with an extensive application in photography, in various processes, as in the Tannin Process of Major Russell, the Dry Process of Taupenot, etc., and in the process of Positive Printing by Development.

## Preparation of Pyrogallic Acid.

The etymology of the word indicates the origin of this substance. When gallic acid is heated to the temperature of 410° Fahrenheit, and kept at this temperature, in an oil-bath, a volatile substance sublimes of a beautiful white color, in crystalline plates. This is *pyrogallic acid*, which is soluble in water, alcohol, and ether. The solution of pyrogallic acid soon turns brown when exposed to the air, by becoming oxidized. It communicates a blackish-blue color to the solutions of the salts of the protoxide of iron, and reduces those of the sesquioxide to the state of the protoxide. When mixed with an alkaline solution, it absorbs a large quantity of oxygen from the atmosphere, and has been used in the analysis of air for this special purpose. When gallic acid is raised to a higher temperature than 410° Fahrenheit, that is, to 480° Fahrenheit, it is decomposed into carbonic acid, water, and a new substance denominated *metagallic acid*, being the black shining residue left in the retort. Pyrogallic acid, at the proper temperature, is in like manner decomposed into metagallic acid and water.

Owing to the property possessed by pyrogallic acid of absorbing oxygen from bodies with which it is in contact, it is as yet the second best developer of the latent image in the collodion process; and taking into consideration the nature of the image produced, where the time of exposure is not important, it certainly is the most easy and reliable developer. There is no doubt that a solution of protosulphate of iron acts more quickly; or, what is meant, requires a much shorter time of exposure. From the experiments in ordinary landscape photography, I have frequently observed a difference of three to one in the time in favor of the sulphate of the protoxide of iron.

## Acids in Developing Solutions.

The solution of protosulphate of iron, or of pyrogallic acid, is frequently much more energetic in reduction than is manageable, and proceeds, after the image has been thoroughly developed, to act upon those parts on which the actinic influence has been but very feeble or almost imperceptible. The difficulty in such a case is two-fold. It consists in flowing the plate *uniformly grad instantaneously*; otherwise lines of demarkation will be quite visible at those edges where the fluid was momentarily retarded; and secondly, in stopping the progress of development *uniformly and instantaneously*. Many excellent negatives have been ruined by the misfortunes arising from the difficulties alluded to; and yet Instantaneous Photography has to search in this direction for the surest means of success, rather than upon any fortuitous advantages in the collodion. The operation of light is, practically speaking, instantaneous, because its velocity is greater than conception. A certain time always elapses between the opening and closing of the shutter, before the lenses, in the operation of instantaneity; and in this time light has traveled thousands of miles, or rushed with its thousands of miles' momentum on the sensitized plate. The picture, therefore, is already there; because the impression has been made. It remains, consequently, to find a reducing agent so refined and energetic as to effectuate the proper reduction. With the ordinary quantity of acids in our developers, we can scarcely hope for success; but with their diminution, and a proportionate increase of velocity in the manipulation of flowing the plates, and of stopping the further advance of reduction, instantaneous photography has, in my opinion, to seek a clue for its reliable performance. As a general rule in practice, the photographer requires less acid in the developer according as the time of exposure is less; consequently, the positive on glass, or prepared iron plate, called the ambrotype and the melainotype, requires a much less acid developer than the negative, where the time of exposure is much longer. In like manner, two photographers may be in the habit of operating, the one with short exposures, and the other with long exposures; but it will be found that the developer of the former is much less acid than that of the latter. Now it may be asked: What is the reason that the same developer can not be used for the two kinds of pictures? Because, in the case of ambrotypes, if the developer be acid as is the case for negatives, the reduction will be *very slow*, and *most likely ineffectual*; whilst in the case of a negative, the non-acidified developer would be *too rapid* and *too unmanageable*.

The temperature is a very influential item in modifying the operation of development. The higher the temperature the greater the quantity of acid required to preserve the exact equilibrium between fogging on the one hand and deficiency of development on the other.

The principal acids used for this special purpose are acetic acid, tartaric acid, citric acid, and formic acid. The latter may be regarded at the same time a developer from its power of reducing metallic salts, and from its analogy to acetic acid as a check upon development.

## Acetic Acid.

Symbol, C, H<sub>3</sub> O<sub>3</sub> HO. Combining Proportion, 60. Specific Gravity, 1.063.

Acetic acid belongs to a small group of which *acetylene* is the base or compound radical derivative from ethylene by the oxidation of two equivalents of its hydrogen in the formation of water. When alcohol and ether burn in the air the products of combustion are carbonic acid and water. But sometimes the oxidation of the hydrogen alone takes place, and water only is formed, together with a small series of new bodies containing the same number of equivalents of carbon. Some of the substances arise from the decomposition of collodion, such as aldehyde, etc. This acid may be formed directly from the oxidation of alcohol or by substituting two equivalents of oxygen in the place of two of hydrogen. Platinum-black acting upon the vapor of alcohol will produce this reaction; or a small quantity of yeast, or almost any other nitrogenized organic material undergoing putrefactive decomposition, added to dilute alcohol and exposed to the air induces the same reaction. In this manner vinegar and alecar arise from the slow acetic fermentation, as it is denominated, of weak wines and beer. When hard dry wood or twigs, or oak, beech, etc., are submitted to destructive distillation at a red heat, acetic acid is one of the products of the distillate. The first part of the sour liquor which distills over by a second operation is not acetic acid; the second, however, contains the acid, but is impure. It is now saturated with hydrate of lime or carbonate of lime, by which process acetate of lime is formed. Sulphate of soda is then added in solution to the acetate of lime as long as any precipitate of sulphate of lime falls. The resulting acetate of soda is filtered from the lime salt, and evaporated to its crystallizing point and then set aside until crystals are formed. The latter are drained as much as possible from the water and adhering tarry liquor, and then heated cautiously to fusion, by which the tar is decomposed and expelled. The fused mass is again dissolved and crystallized. By decomposing this salt by means of an equivalent of sulphuric acid and by distillation we obtain strong acetic acid, which, by rectification over red oxide of lead, can be concentrated so as to yield crystals at a low temperature. This is denominated glacial acetic acid, and melts into a colorless liquid above 60° Fahr. It boils at a temperature of 240°; its vapor is inflammable. It mixes in all proportions with water, alcohol, and ether. The acetates are very numerous; all of them are soluble; those of silver and mercury the least so.

Its photographic uses are, as above described, to check the vehemence of reduction by the developers; it is used also to acidify the nitrate of silver bath in connection sometimes with acetate of soda, and with this connection it is said to yield much sensitiveness and intensity with a plain iodized collodion.

## Formic Acid.

Symbol, C<sub>2</sub> HO<sub>3</sub> HO. Combining Proportion, 46. Specific Gravity, 1.235.

This acid is so called because it is found in ants, from the Latin of which the word is derived. It bears the same relation in the methylene group as acetic acid does in the ethylene series; acetic acid being formed by the substitution of two equivalents of oxygen for two

of hydrogen in the formula for alcohol, whilst formic acid arises from the substitution of two equivalents of oxygen for two of hydrogen in the formula for *wood-spirit*, a substance very analogous to alcohol. This acid can be obtained by distilling ants in water. It is an organic acid, however, which can be formed artificially by heating organic substances, such as sugar, starch, etc., with oxidizing agents. Thus: mix one part of starch or sugar or tartaric acid with four of the binoxide of manganese, four of water, and four of sulphuric acid. By this mixture carbonic acid will be liberated with effervescence. As soon as this is over the materials are subjected to distillation until four parts and a half have passed over. The acid liquor thus obtained is impure formic acid, which is purified by neutralizing it with carbonate of soda, and evaporating the solution so as to obtain *formiate of soda* in crystals which may be freed from all impurities in the same manner as acetate of soda in the preceding paragraphs. From the pure formiate of soda, any other formiate, or formic acid, may be obtained by neutralizing the formiate with sulphuric acid and by distillation. Hydrated formic acid is a limpid, colorless fluid, of an intensely pungent odor; it fumes slightly; at a temperature below 32° Fahr. it crystallizes in brilliant plates; it boils at 212°. It produces a blister on the skin when concentrated. In very many respects it is very similar to acetic acid, but may be distinguished from the latter by its comportment with oxide of silver or mercury, in which, when heated, it reduces the metal after a while and liberates carbonic acid. This acid is obtained, and perhaps most easily, by the decomposition of oxalic acid in contact with glycerine and by distillation.

### **Photographic Uses of Formic Acid.**

From the similarity between acetic and formic acid it may easily be inferred that either might be substituted for the other in the developer, but the reader will have remarked a decided difference in their action on silver salts; and it is just on these salts that the acid is brought into action; it is in fact an excellent reducing agent, and when heated is used by several distinguished photographers in their developing solutions, of which the formula will be given in the proper place.

### **Citric Acid.**

Symbol,  $C_6H_8O_7 + 3 H_2O + 2 Aq.$

This acid is obtained from the juice of limes, lemons, orange, currant, quince, cranberry, red whortleberry, and other fruits. The juice is imported in the liquid state from the West-Indies, and being in connection with much mucilage and other organic impurities, it is liable to undergo decomposition on the way, and to yield in the preparation of citric acid other acids endowed with different properties. On this account it is advisable in many instances for the photographer to prepare his own citric acid.

### **Preparation.**

Take ten ounces of expressed lemon juice; boil the juice for a few minutes, then add to it after it is cool the whites of three eggs, and stir the mixture so that the albumen is intimately broken up and mixed with the juice. Boil the mixture again, stirring it all the

while, and allow the coagulum to settle. When cool, filter the sour liquor and boil it again, adding to it gradually powdered chalk as long as effervescence is produced; citrate of lime is formed, which is but sparingly soluble in water. The dark-colored mucilaginous liquor is filtered off; the residue is well washed, and afterward decomposed by a quantity of sulphuric acid equal in weight to the chalk employed in the previous decomposition. The sulphuric acid is diluted with about seven times its weight of water; and the mixture is stirred about for some time until the citrate of lime is completely decomposed. By filtration the citric acid is separated from the insoluble sulphate of lime, and is afterward evaporated until a pellicle forms on its surface; it is then set aside to crystallize. The dark-colored crystals are removed from the supernatant liquid by a strainer and again dissolved in pure water; the liquid is again evaporated as before, until the formation of a pellicle takes place, and is again set aside to crystallize. By repeating the operation several times the crystals become quite clean and purified. Citric acid has an agreeably sour taste; like phosphoric acid it is tribasic, and gives rise to three classes of citrates. It is soluble in less than its own weight of cold water, and in half its weight of boiling water; it is not very soluble in alcohol.

### **Citrate of Soda.**

This salt is prepared by dissolving citric acid in pure water and throwing into the solution, by degrees, pulverized carbonate of soda as long as effervescence is produced. The liquid is afterward evaporated to a crystallizing consistency and then set aside. In this case, as well as in the preceding, the mother-liquor can be made to yield new crops of crystals by further evaporation or by a repeated decomposition and a repetition of the other proceedings arising out of it.

### **Photographic Uses of Citric Acid.**

This acid is frequently mixed with pyrogallic acid in proper quantity for solution in water instead of acetic acid. It is used as a check on the too rapid action of pyrogallic acid, and as a reducing agent. A frequent impurity in this substance is malic acid, and sometimes aconitic acid. Citric acid is recognized by its producing in a diluted state no immediate precipitate with *Chloride of Calcium*; but an immediate precipitate is formed when the solution is boiled.

### **Tartaric Acid.**

Symbol,  $C_8 H_4 O_{10} + 2 Aq.$

This acid exists in combination with potassa in most kinds of fruit, and sometimes in a free state. Its combinations in fruit are cream of tartar and tartrate of lime. The former exists in abundance in grape juice, and is denominated, in the crude state, *Argol* or *Tartar*, which is either red or white according to the wine from which it is deposited during fermentation.



## Preparation of Tartaric Acid.

This acid is obtained from argol, or from cream of tartar, which is a bitartrate of potassa, by two processes; one consists in abstracting One equivalent of tartaric acid from the bitartrate, and the other in decomposing the residual tartrate in the solution. Following the formula of the London College, and using the imperial gallon, which contains ten pounds of water, the method stands thus: take of bitartrate of potassa four pounds; boiling distilled water, two gallons and a half; prepared chalk, twenty-five ounces and six drachms; diluted sulphuric acid, seven pints and seventeen fluid ounces; hydrochloric acid, twenty-six fluid ounces and a half, or as much as may be sufficient. Boil the bitartrate of potassa with two gallons of the distilled water, and add, by degrees, the half of the chalk; when the effervescence is over, add the remainder of the chalk, previously dissolved in the hydrochloric acid, diluted with four pints of the distilled water. Then set aside until the tartrate subsides; after which pour off the liquor, and wash the tartrate of lime frequently with distilled water as long as it has any taste. Next pour on the diluted sulphuric acid, and boil for a quarter of an hour. Having filtered the liquor from the insoluble sulphate of lime, evaporate it by a gentle heat until a pellicle is formed on its surface; then set it aside to crystallize. By dissolving the crystals in pure water, filtering, and recrystallizing, and by repeating these three operations several times, pure tartaric acid may be obtained.

Tartaric acid is not volatile; wh

in the nitrate bath. It is true, as regards the introduction of injurious substances into the bath, all effects resulting therefrom can be avoided by using the solution of nitrate of silver only *once*. If this salt were not so expensive, this mode of avoiding trouble would be by far the wisest and the safest. In such a case the photographer would flow his plate with the silver solution in the same manner as with the developing or fixing solution, using just sufficient to cover the film and to sensitize it. All the residual part might be collected, decomposed, and fresh nitrate prepared. But because the silver salt is a dear material, we aim to economize by using the solution over and over again. For this purpose, glass, porcelain or photographic-ware baths are constructed for containing the fluid. They are made so as to accommodate the largest plate with the least quantity of the solution, a great mistake superinduced by false economy. In this country vertical baths seem to be the only ones employed; whereas in France and Germany, for economical and other special reasons already alluded to, horizontal dishes contain the solution, and the plates lie, as it were, collodion side downward in a thin layer of the same. Some of these baths are especially adapted for the tourist, admitting the fluid to be closed hermetically by means of India-rubber caps, screws and clamps. Nitrate of silver will permeate through the parietes of porcelain baths; the photographic-ware bath and the glass are not subject to this inconvenience.

### **Preparation of the Sensitizing Solution.**

An ounce Avoirdupois contains 437.5 grains; the druggists and photographic dealers retail all their chemicals according to this weight, and not, as many suppose, according to the Troy weight, of which the ounce contains 480 grains. The sensitizing solution is found by experience to be sufficiently strong if it contain from 35 to 40 grains to the fluid ounce of water, or from 8 to 10 per cent.

#### *Formula No. 1.*

Nitrate of silver, (recrystallized,)	3 ounces.
Distilled or pure rain-water.	36 ounces
Washed iodide of silver	6 grains.
Washed oxide of silver	6 grains.

Dissolve the nitrate of silver in half the water, then add to it the washed iodide of silver, prepared as directed on a preceding page, afterward add to the mixture the six grains of oxide of silver, which is prepared as follows: Take a solution of ten grains of nitrate of silver and drop into it a solution of *pure* caustic potash, as long as a brown precipitate is formed. Then filter and wash the brown oxide on the filter many times with cold water, and afterward with warm water, until the filtrate ceases to have any action on red litmus paper.

The mixture is now boiled in a large glass flask on a sandbath, and when cold the remaining water is added to it, and the whole of it is filtered through a double filter of Swedish filtering paper. The solution so prepared will be saturated with iodide of silver, so that it will not dissolve any of the iodide of silver on the collodion film; it will be besides perfectly neutral, if the oxide of silver has been thoroughly washed from any adhering alkali. With a collodion containing free iodine, either from decomposition or by insertion, this bath is exceedingly sensitive, and produces at the same time clear pictures. For colorless collodions it is not suitable, nor for collodions which are quite freshly made, without the addition of iodine, that is, for those which have not had time to ripen, as it is termed in ordinary language.

For such collodions, the colorless and pale colored collodions, containing, as they generally do, cadmium salts, the following bath will be found to be quite effective in producing good results

*Formula No. 2.*

Nitrate of silver, (recrystallized,)	3 ounces.
Distilled or rain-water	36 ounces.
Iodide of silver, (washed	6 grains.

Mix as before, and filter without boiling. For each ounce of nitrate of silver add one drop of nitric acid. This amount will probably be found sufficient to produce a clear picture; should the picture show any signs of fogging, add another drop, and so proceed until the details of the development appear without a universal cloudiness over the plate.

*Formula No. 3.*

Nitrate of silver, (recrystallized,)	3 ounces.
Distilled, or pure rain-water	36 ounces.
Iodide of silver, (washed,)	6 grains.

Prepare as before, and after filtration divide the quantity into two lots of 18 ounces each. Neutralize one of these with washed oxide of silver by boiling, and then filter. Add to the other 18 drops of a solution of acetate of soda, (containing 160 grains to the ounce of water,) and 10 drops of glacial acetic acid. Each of these baths may be used separately, or in mixture. The neutral bath is kept neutral without admixture; but to the second, containing the acetate of soda and acetic acid, a portion of the first may be added as required from time to time, if it is found to work too slowly. As a general thing the acetate of soda bath produces very vigorous pictures, and renders the collodion film quite sensitive.

In summer the bath need not be so strong in nitrate of silver as given in the preceding formulas. Six or seven grains of silver per cent of the water will be sufficient when the temperature is high; on the contrary, from eight to ten per cent may be used when the temperature is moderate or low. The sensitizing solution works quicker when warm than when cold.

When the sensitizing solution becomes weak by exhaustion, it can be restored to a good working condition by the addition of a stronger solution of nitrate of silver, containing 40 or 50 grains to the ounce of water. After a bath has been in operation for some time, it becomes saturated with a variety of impurities, such as ether, alcohol, acetic acid, aldehyde, the various nitrates in the collodion, and a variety of substances arising from the decomposition of this heterogeneous mixture. The best way to get rid of all volatile material is to subject the solution to distillation, until all the ether and alcohol, at least, have been expelled, and then to filter the residue in the retort, and to mix it with anew bath. Although such a restored bath will give good results for a while, it soon gets out of order, and can no longer be relied upon. In such a case it is far more expedient to set it aside for reduction, and to form a totally new bath, than to be at the trouble of a second distillation, because the fixed salts have accumulated to such a degree as to render the bath very capricious and unstable.

When a bath does not yield clear pictures when first formed, or ceases to do so after a given time with the same collodion, or happens not to do so with a new collodion, it is advisable not to trifle with the bath by adding either acid or alkali. It may be well to ascertain by test-paper whether the trouble is attributable to alkalinity or acidity. If no alkali has been added to the bath, it will probably have an acid reaction. In this case it is preferable to boil the bath with the washed oxide of silver, as before prescribed, and then to filter it. Should the bath turn out to be neutral to test-paper, it will be found in general a better practice to add a few drops of tincture of iodine to the collodion, rather than to acidify the sensitizing solution; because the iodine in the collodion liberates an acid by decomposition on and in the film of collodion, which rectifies the evil where the rectification is wanted, and at the proper time, without changing materially the conditions of the bath. Thus the operator will learn to use up a highly colored collodion by mixing it gradually, as it is wanted, with new and almost colorless collodions, in order to clarify his pictures, without resorting to methods of attaining to the same result by adding acid to the bath.

During the time the bath is in use, a quantity of insoluble material of a gray or violet-gray color is precipitated on the bottom and sides of the bath, and frequently floats about in the sensitizing fluid. The particles of this material, as well as of the acicular crystals of acetate of silver in a weak bath are apt to attach themselves to the moist collodion film on its immersion, and thus give rise to the innumerable small apertures sometimes exhibited on the developed negative. These particles are not the sole cause of this evil, so much dreaded; but they frequently cause it by their attachment to the film during the exposure, and owing to their opacity, prevent the actinic action from taking effect on the film beneath, and becoming loosened by the developing and fixing solutions, afterward expose the transparent parts on which they had rested. It is advisable, therefore, to expose

the bath in a glass vessel to the rays of the sun as often as possible, in order that the organic matter may be precipitated. The bath, too, ought to be filtered very frequently in the same filter, at least once a week; and if every evening, so much the better. After filtration the bath can be strengthened by an addition of fresh solution, in proportion to the daily work performed. See, during filtration, that the sides and the bottom of the vessel are perfectly clean before the solution is poured back again. A long thin wooden spatula, with a piece of sponge at the end, will be found very convenient for clearing away the adhering gray deposit. Use only rainwater for rinsing; rinse thoroughly; then turn the bath wrong side up, and rear it on one corner, in order that every drop of water may thus be removed. Wipe the edges before the sensitizing fluid is again introduced. This exposure to the rays of the sun, and frequent filtration will remedy in a great measure the trouble alluded to, and there is no fear of injuring the property of the solution, for nitrate of silver alone is not acted upon by light, does not change at all when pure.

By exposing the solution in a vessel, such as a glass evaporating dish, much of the superfluous ether and alcohol will pass off in vapor, and thus produce a remedy for another evil which an old bath invariably gives rise to, namely, that of causing oily-looking stains and streaks on the surface of the film.

Where the trouble of recrystallizing the nitrate of silver would be deemed too great, and neutral nitrate of silver can not easily be purchased, I would recommend that the photographer should fuse the nitrate of silver in a porcelain evaporating dish, at a gentle heat, and afterward pour out the fused mass on a silver or marble plate, as directed in the manufacture of lunar caustic. The same proportions of the fused nitrate are used as in the formulas for the recrystallized nitrate. Or a strong solution of the nitrate may be boiled with the washed oxide of silver, filtered, and evaporated to dryness, and used in the same way.

Towler, John. *The Silver Sunbeam*. Joseph H. Ladd, New York: 1864. Electronic edition prepared from facsimile edition of Morgan and Morgan, Inc., Hastings-on-Hudson, New York. Second printing, Feb. 1974. ISBN 871000-005-9

<http://albumen.stanford.edu/library/monographs/sunbeam/>