THE ELECTROCHEMISTRY OF LIGHT. IV

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The Problem of Solarization. Part I

The literature on the subject of solarization or the reversal of the photographic image is so scattered and to a certain extent so contradictory that it has seemed wise to give a pretty thorough idea of the problem in two papers and to postpone till a later paper the application of the theory of Grotthuss to this problem.

There is an excellent presentation of certain portions of the subject to be found in a lecture by Major-General Waterhouse,¹ which was delivered on April 14, 1901, and from which I quote extensively.

"The observation of the reversal or apparent destruction of the impressed photographic image was a very early one in the history of photography. Early in 1801, Ritter showed that silver chloride, which had already been darkened in the violet rays of the spectrum, became lighter again when exposed to the yellow, red, and especially the infra-red rays, and he attributed this to an oxidizing action of the less refrangible rays counteracting the deoxidizing action of the more refrangible rays.² Wollaston,³ on the other hand, shortly afterwards, in 1804, stated that about the same time as Ritter, he had found that while gum guaiacum became green by oxidation when exposed to the violet rays, it was deoxidized and brought back to its original yellow color by the red and orange rays. The same decolorizing effect could, however, also be produced by heat. Much later, in 1840, Sir John Herschel⁴ described a similar experiment in which, again, paper coated with the alcoholic tinc-

¹ Jour. Camera Club, **15**, 63 (1901).

² Phys. Chem. Abhandlungen, **2**, 90.

³ Nicholson's Journal, **8**, 293 (1804).

⁴ Phil. Trans., **130**, 35 (1840).

ture of guaiacum was first exposed to light, and then exposed in the spectrum, the result being that the part acted on by the more refrangible rays became of a darker blue than the original ground, while about the orange rays the original pale yellow color of the paper was restored.

"In 1842, J. W. Draper, by allowing daylight to fall along with the spectrum upon a Daguerreotype plate, found that the daylight and sunlight antagonized each other, and thus he succeeded in obtaining the first photograph of the red end of the spectrum showing the α , β and γ lines below A, these lines appearing positive.

"This bleaching action of the red and orange rays upon sensitive surfaces already darkened or affected by exposure is very remarkable when taken in connection with the opposite effect which can be produced on under-exposed Daguerreotype or paper prints prepared with haloid salts of silver containing an excess of nitrate, by continuing the exposure under a yellow or red glass. This continuing action of the less refrangible rays was discovered in 1840 by Edmond Becquerel, and led him to call the more refrangible rays *rayons excitateurs*, and the less refrangible *rayons continuateurs*. It can be shown quite well with P.O.P.,¹ or an iodized silver plate.

"It is noteworthy that Ritter, in discussing the nature of the difference between the action of the two ends of the spectrum, says that water is the chemical agent in all processes of oxidation in the wet way, and that it is decomposed in all processes of oxidation or deoxidation. In the first case, the oxygen combines with the oxidizable body, and the hydrogen is set free or combines with more oxygen to form water anew. In the second case, the hydrogen of the water combines with the oxygen of the body to form water, while the oxygen formerly combined with the hydrogen goes to the oxidizable body present, the deoxidation of which it usually only indirectly brings about. In some later

¹ [Printing out paper.]

researches he showed that perfectly dry silver chloride is not acted on by white light, or the violet rays.

"Some years, however, before Ritter announced this theory in connection with photographic action, our own countrywoman, "the ingenious and lively" Mrs. Fulhame, as Count Rumford calls her, had discovered, and published¹ in 1794, that the presence of water is essential to the reduction of metals (more especially the salts of gold and silver) by light, an observation which has been confirmed so far as most of our ordinary photographic processes are concerned. She held that when light reduces the metals, it attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state to the oxygen of the metal and reduces it, forming, at the same time, a quantity of water equal to that decomposed. Further, she says, water is decomposed in every instance of oxygenation.

"Ritter² wrote an analysis of Mrs. Fulhame's book and thus was well acquainted with her theories, some of which he seems to have adopted. He himself made a good many observations on the action of light, and intended to have devoted himself to the study of it, but was led to give most of his energies to the development of galvanism. This study led him to remark in one of his numerous papers that the result of a thorough practical investigation would be that the polarity of chemistry, electricity, magnetism, heat, etc., was due to a single principle common to all. He was also one of the first to recognize the electrical nature of sunlight. Eder says, however, that his hasty and unverified electrical hypotheses led him astray.

"Experiments made long after Ritter's, by Robert Hunt, also showed that the accelerating power of moisture in promoting the reduction of silver salt was due to the decomposition of the water and the formation of nascent hydrogen. Schönbein has also shown that, in all cases of oxidation, in presence of water, hydrogen peroxide is formed. It is well

¹ Essay on combustion.

² Phys. Chem. Abhandlungen, 1, 91

known that this substance is capable of acting both as an oxidizer and a reducer, and as Sonstadt has found traces of it when silver chloride is exposed to light in water, it is probable that it has to be reckoned with in most cases of photographic action.

"I have dwelt on these early researches of Mrs. Fulhame and Ritter, because the principles they enounced as to the action of moisture in the reduction of silver and gold from their salts by the action of light seems to be closely connected with the phenomena of photographic reversals, which it is generally agreed are due to oxidation, though they do not fully represent the complex actions that take place in our ordinary photographic processes.

"The lightening action of the less refrangible rays of the spectrum upon darkened silver chloride was confirmed in 1810 by Seebeck, who also recorded some interesting observations on the differences of tint taken by silver chloride exposed under colored glasses, corresponding with the color of the transparent medium under which it was exposed. With this aspect of the question we have, however, nothing to do.

"The next process of reversal to be noticed is one that appears to have been first published by Dr. Fyfe,¹ in April, 1839, though several similar processes for obtaining positive pictures direct in the camera were brought out all about the same time, in 1839 and 1840, by Bayard and Lassaigne in France, and by Herschel, Hunt and Talbot in England.

"In Fyfe's process, paper prepared with silver phosphate (in most of the other processes silver chloride was used) was first darkened by the action of light, then immersed in a solution of potassium iodide, and while still moist, exposed to light in contact with the object to be reproduced, and left until the whole of the paper exposed became yellow. It thus showed a positive image of the subject, dark upon a light ground. The prints were fixed by simple washing in water

¹ Phil. Mag. [3], 14, 463 (1839).

to remove the soluble iodide. He also stated that darkened silver chloride could be used, but with a weaker solution of iodide.

“Robert Hunt, in his *Popular Treatise on the Art of Photography*, published in 1841, has given a full account of this method, and has discussed the principles on which the action is based. He says, “If a dark paper is washed with an hydriodate (iodide in solution), and exposed to sunshine, it is first bleached, becoming yellow, then to light again darkens it. If, when quite dry, it is carefully kept from the light, it will be found in a few days to be again restored to its original yellow color, which may be again darkened by exposure, and the yellow color be again restored in the dark. The sensitiveness to the influence of light diminishes after each exposure, but I have not been able to arrive at the point at which this entirely ceases. If a dark paper, bleached by an hydriodate (iodide) and light, be again darkened, and then placed in a bottle of water, the yellow is much more quickly restored, and bubbles of gas will escape freely, which will be found to be oxygen. By enclosing pieces of hydriodated (iodized) paper in a tube to darken, we discover, as might have been expected, some hydrogen is set free. If the paper is then well dried, and shut up in a warm dry tube, it remains dark; moisten the tube or the paper, and the yellowness is especially restored.

“Take a photograph thus formed and place it in a vessel of water, in a few days it will fade out, and bubbles of oxygen will gather around the sides. If the water is examined, there will be found no trace of either silver or iodide; thus it is evident that the action has been confined to the paper.

“We see that the iodide of silver has the power of separating hydrogen from its combinations. In the process of darkening, the liberation of hydrogen is certain, but I have not in any instance been able to detect free iodine; of course it must exist, either in the darkened surface or in combination with the unaffected under layer; possibly this may be

the iodide of silver with iodine in simple mixture, which, when light acts no longer on the preparation, is liberated, combines with the hydrogen of that portion of moisture which the hygrometric nature of the paper is sure to furnish, and as an hydriodate again attacks the darkened surface restoring thus the iodide of silver. This is strikingly illustrative of the fading of the photograph.

"The picture is formed of iodide of silver in its light parts, and of oxide of silver in its shadows. As the yellow salt darkens under the influence of light, it parts with its iodine, which immediately attacks the dark oxide, and gradually converts it into an iodide. The *modus operandi* of the restoration which takes place in the dark is not quite so apparent. It is possible that the active agent *light* being quiescent, the play of affinities comes undisturbed into operation—that the dark parts of the picture absorb oxygen from the atmosphere, and restore to the lighter portions the iodine it has before robbed them of." Hunt then describes a series of experiments on silver iodide which more strikingly exhibit this remarkable peculiarity.

"He repeats the above in his later work published in 1859, and I have quoted it at length because it seems to give a very probable exposition of the reactions which take place in some reversals and carries on the theory enunciated by Mrs. Fulhame and Ritter of photographic action being to some extent dependent on the decomposition of water present either in the atmosphere or in the sensitive surface.

"On the same principle, Poitevin proposed in 1859 a method of obtaining reversed positives in the camera which seems to have been successful in his hands for making stereoscopic transparencies.

"A sensitive plate was prepared by the wet collodion process, with a collodion containing less iodide than usual for negatives. It was then exposed for a few seconds to direct light, the appearance of the plate being unchanged. After washing to remove the excess of silver nitrate, it was treated with a 4 percent solution of pure potassium iodide

free from iodine, all these operations being performed in the dark room. The plate was then exposed in the camera about three times longer than the ordinary exposure for negatives. It was next washed to remove the iodide solution, and having been treated with a weak bath of silver nitrate at 2.5 percent, was developed with pyrogallie acid, acidified with lactic acid. It was then blackened only in the parts acted on by light, and after the development had been carried to the usual extent, the image was fixed with a weak solution of hyposulphite or cyanide, or a mixture of the two. The image obtained in this manner was a positive by transparence.

“Poitevin¹ gives a list of substances which he found might replace the potassium iodide in bringing about this reversing action—among them those most active were: cyanide of potassium, also when saturated with silver iodide; solution of bichromate of potash acidified with sulphuric acid; dilute hydrochloric acid.

“Sir William Abney has given the rationale of this process in his *Treatise on Photography*, p. 305, and has shown that potassium or other simple bromide can be substituted for the iodide.

“He also shows that if a plate prepared with silver iodide have a preliminary exposure given to it, and then be given a prolonged exposure in the camera, reversal of the image will take place. If, however, such a plate, after washing, be treated with a solution of a deoxidizing agent, such as pyrogallie acid or potassium nitrate, the reversal will not take place, nor will it if the plate be exposed in a cell containing a hydrocarbon such as benzene, or in dry hydrogen. Consequently, the presence of oxygen in some form is necessary to obtain reversal, and it is not easily obtained if a substance readily taking up oxygen is in contact with the silver salt.

“In 1862, Dr. Sabatier² gave a description of a method

¹ *Traité de l'impression photographique sans sels d'argent*, p. 117ff.

² *Phot. News*, 6, 366 (1862).

of obtaining direct positives in the camera. A glass plate was coated with a bromiodized collodion, sensitized in a neutral silver bath, and given a normal exposure in the camera. The plate was developed with weak pyrogallie acid solution, acidified with glacial acetic acid. As soon as the details were out, the developer was poured off, and the plate washed. It was then treated with a 4 percent solution of silver nitrate, which was again poured off after a sufficient interval, and then the plate was redeveloped with the pyrogallie acid solution, the development of the positive image taking place quickly if the treatment with the silver solution had been prolonged—more slowly with a shorter treatment or a weaker silver solution. The plates were fixed in hypo or cyanide, and could be toned if desired.

“The most interesting feature of this process is Dr. Sabatier’s theory of the reversal of electrical action by the second silver bath. He says: “When no more pyrogallie acid remains on the plate, the formation of the negative must necessarily be interrupted, and to form a color different from the first with the exposed iodide not yet employed, it suffices to substitute for the electrical current which prevailed at the first combination, an electric current of the opposite nature.

“Many substances poured in solution upon a negative, the formation of which has been interrupted, possess the power of inverting the electrical current previously developed, and causing the positive combination to succeed the negative. Such are most of the alkalis, limewater, solution of ammonia, and especially nitrate of silver.” “The presence of strong acids in the bath or developing solutions was prejudicial, and, therefore, preference was given to pyrogallie acid with acetic acid which does not interfere with the transformation.

“The difficulty, of course, is in knowing when to stop the first development, but Dr. Sabatier says that, with the method he described, successful results were obtained. At any rate, the theory of the reversal of current working the

transformation from negative to positive is of interest, though rather vague. It was founded on some observations of the Abbé Despratz, which are given in the same volume. Another method of Sabatier's was by admitting light after the development was started; the light acting on the developed parts caused them to blacken at the expense of the already partially developed parts. Many similar methods with wet collodion will be found in the journals, and are referred to by Eder, in his *Ausführliches Handbuch*.¹

"Returning to the earlier periods, we note that shortly after the introduction of the Daguerreotype process it was found that if the exposure of the plates in the camera was unduly prolonged, the mercury was deposited irregularly over the plate, giving a pale blue image, with a partial or total reversal. Dr. J. W. Draper was, I think, the first to study this phenomenon, and he attributed it to an action of the rays of light analogous to those of heat acting on a mass of ice, the temperature rising gradually to 32° F, where it stops till the molecular change of liquefaction is accomplished, when it goes on rising again. In the same way, when the rays of light begin to act on a Daguerreotype plate, the silver iodide commences changing, and is capable of being whitened by mercury. This process goes on gradually with increased whiteness on the more exposed parts until a certain point is gained, when the iodide apparently undergoes no further visible change, but another point being gained, it begins to assume, when mercurialized, a pale-blue tint, becoming deeper and deeper, until at last it assumes the

¹ I find that in 1888 a series of experiments was made in the Photographic Office, S.I.D., Calcutta, with Poitevin's, Sabatier's, and other processes of making reversed positives with wet collodion, with the result that the only one likely to be of practical use was that described by Capt. Biny, in the *Bull. Soc. Franc. de Photographie*, **27**, 130. With gelatine dry plates, it was found hyposulphite of soda in the developer, or preliminary treatment of the plates with bichromate of potash seemed to have little influence in causing reversal. The best reversals were obtained by a simple over-exposure of about 1,800 times normal, or 30 minutes for an "ordinary" plate. This agrees with results lately obtained by Dr. R. Englich.

brilliant blue of a watch-spring, thus producing the effect called solarization.

"He gave no further elucidation on physical or chemical grounds at the time, but in a later paper¹ he maintained that the plate was polarized to light. He says, 'We know that iodine is not thrown off during exposure, but is absorbed by the underlying silver, while silver is liberated on the anterior surface of the plate. From the circumstance that iodine is evolved at the back of the film and silver at its front, the film itself remaining of the same thickness throughout, it is obvious that there is a strong resemblance between this phenomenon and that of the polar decomposition of water. The electro-positive and electro-negative elements are yielded up on opposite faces of the film, and its interior undergoes incessant polar changes, the opposite electrical particles sliding, as it were, on one another.'

"There is, I think, little doubt that some such action does take place; during the exposure there is a constant transference of atoms, till after a certain stage there is an excess of silver in the most exposed parts, and the mercury is deposited more readily upon the less exposed parts, or more or less equally all over the plate.

"Draper also found the Daguerreotype plates were acted on by the red and blue rays of the spectrum, in opposite ways, similarly to the action noticed by Ritter with silver chloride.

"Moser also examined the phenomenon of the solarization of Daguerreotype plates, and attributed the gradual change in the developable condition of the iodized silver surface to the action of atmospheric oxygen, which is ever present and cannot be gotten rid of. This agrees with Scholl's theory, referred to in my lecture on the *Teachings of Daguerreotype*, that there is a constant transference of atoms by the continual formation of silver oxide and silver iodide, their alternate decomposition and re-formation. The same prin-

¹ Phil. Mag. [3], 22, 367 (1843).

ciple probably applies to gelatine dry plates, in which, however, moisture diffusing through the colloid material, no doubt plays a very active part.

"During the course of recent work on Daguerreotype, I found that plain metallic silver exposed to light showed this reversed action by long exposure very distinctly when developed with mercurial vapor, and I had several instances of it, some of which I can show you. In this case, of course, there is no halogen or electro-negative element present except the atmospheric oxygen, together with the moisture of the air. How far the change in the molecular structure of the film may be due to their action I am not prepared to say, but, as far as I have been able to ascertain, metallic silver is not oxidized by exposure to light, and any action would more probably be catalytic, as in the case of the iodide, according to Scholl's theory.¹

"In 1875, during the course of some experiments in photographing the solar spectrum on dyed collodio-bromide dry plates, I constantly met with reversals in the red or blue end of the spectrum, often both simultaneously. Noticing that when the plates were quite clear of fog the reversal at the red end did not take place, while the direct action only extended as far as C, and recollecting Draper's principle of previous exposure of the plate, I was able to obtain a reversed negative picture of the whole of the red spectrum up to and some little distance beyond A. In this case the lines appeared black on a clear ground, and the plates were stained blue with a mixture of malachite green and methyl violet, known as "marine blue," but similar results were also obtained with plates stained with annatto, as well as with other coloring matters and aniline dyes.

"By another application of the same principle I found that very complete reversed negatives could be obtained by first exposing one of these stained dry plates for a short time to light, and then placing it in a printing frame under

¹ Wied. Ann., 68, 149 (1899).

a negative, over the face of which a red glass was placed. After an exposure in the sun for about twenty minutes and developing with alkaline pyro a very fair negative was produced.

“When exposed under blue glass, however, these plates gave quite a mixed result, half positive and half negative. It is not impossible that suitable gelatine dry plates treated in the same way would produce similar results, and such a method would have many practical uses. I am sorry I have no specimens of the method to show you, but I have brought with me two of the collodio-bromide plates of the spectrum, one stained with a blue dye and the other with naphthalene red.

“In April, 1876, when photographing the sun on similar blue-stained collodio-bromide plates, I had a case of recurrent reversal, but not to its full extent, of which an account is given in the *Phot. Journ.*, May, 1898. One of these plates showed, with an almost instantaneous exposure, an unreversed image; exposures of 5 to 10 seconds were fully reversed, and then as the exposures increased from 60 to 80 up to 200 seconds, the reversal was not observed except just round the limb. The reversed images were all quite clear and sharp. With an unstained plate, the reversed images were those exposed for the shortest time, and then they gained strength according to the length of exposure. With similar plates prepared with collodion containing annatto, the shorter exposures were well reversed, then, as the exposure increased, the images of the sun were not so clear, but cleared again as longer exposures from 100 to 200 seconds were given.

“In 1879, Bennett¹ stated that gelatine dry plates were very readily reversed by over-exposure, and showed this phenomenon of recurrent reversal very clearly, the image first gaining intensity up to a certain point, then losing it by over-exposure, to a point when the most exposed parts are perfectly clear on development, then increasing in den-

¹ *Phot. News*, 23, 139 (1879).

sity again, and then again losing it. Sir William Abney has shown that in this case, also, the tendency to reversal is destroyed by exposing the plate bathed with a solution of potassium nitrite, while a solution of potassium bichromate will favor it.

"In 1880, M. Janssen carried the observation of these recurrent reversals much further, and, by prolonged exposure, obtained six distinct stages.

1. The ordinary negative image.
2. The first neutral state, dark ground.
3. The positive image.
4. The second neutral state, clear ground.
5. The second negative.
6. The third neutral state, dark ground.

The second negative was calculated to require 100,000 times normal exposure."

From a paper by Draper¹ I quote the following paragraphs:

"The accompanying photographic impression of the solar spectrum, which I will thank you to give to Sir John Herschel, was obtained in the south of Virginia- probably you can make nothing like it in England, the sunlight here in New York wholly fails to give any such result. It proves, that under a brilliant sun, there is a class of rays commencing precisely at the termination of the blue, and extending beyond the extreme red, which totally and perfectly arrest the action of the light of the sky. This impression was obtained when the thermometer was 96° Fahr. in the shade, and the negative rays seem almost as effective in protecting, as the blue rays are in decomposing iodide of silver.

"The most remarkable part of the phenomenon is that the same class of rays makes its appearance again beyond the extreme lavender ray. Sir J. Herschel has already stated, in the case of bromide of silver, that these negative rays exist low down in the spectrum. This spectrum, how-

¹ Phil. Mag. [3], 21, 349 (1842).

ever, proves that they exist at both ends, and do not at all depend on the refrangibility. It was obtained with yellow iodide of silver, Daguerre's preparation, the time of exposure to the sun fifteen minutes.

"In this impression, six different kinds of action may be distinctly traced by the different effects produced on the mercurial amalgam. These, commencing with the most refrangible rays, may be enumerated as follows:—1st, protecting rays; 2nd, rays that whiten; 3rd, rays that blacken; 4th, rays that whiten intensely; 5th, rays that whiten very feebly; 6th, protecting rays.

"It is obvious we could obtain negative photographs by the Daguerreotype process by absorbing all the rays coming from natural objects, except the red, orange, yellow, and green, allowing at the same time diffused daylight to act on the plate.

"This constitutes a great improvement in the art of photography, because it permits its application in a negative way to landscapes. In the original French plan the most luminous rays are those that have least effect, while the sombre blue and violet rays produce all the action. Pictures, produced in this way, never can imitate the order of light and shadow in a colored landscape.

"If it should prove that the sunlight in tropical regions differs intrinsically from ours, it would be a very interesting physical fact. There are strong reasons to believe it is so. The Chevalier Fredrichstal, who traveled in Central America for the Prussian government, found very long exposures in the camera needful to procure impressions of the ruined monuments of the deserted cities existing there. This was not due to any defect in his lens; it was a French achromatic, and I tried it in this city with him before his departure. The proofs which he obtained, and which he did me the favor to show me on his return, had a very remarkable aspect. More recently, in the same country, other competent travelers have experienced like difficulties, and as I am informed failed to get any impressions whatever. Are

these difficulties due to the antagonizing action of the negative rays upon the positive?"

This paper of Draper's brings up two points, the reversing action of certain rays and the apparent necessity for long exposures in tropical countries. The second part was answered by Beck¹ in 1904, though no reference was made in the latter's paper to the question asked by Draper. Beck's observations are so interesting that I take the liberty of quoting them even though they have no direct connection with the problem of solarization.

"The first time I set up my camera in Egypt I was startled at the way in which the picture looked on the focusing screen. Instead of a beautiful harmonious image it looked like a harsh photograph. There were crude, bright lights and immediately adjoining them, almost without intermediate steps, were deep, black shadows showing almost no details. It was clear to me at once that, in spite of all theory, a short exposure was out of the question. In fact, on account of the deep shadows, it would be necessary to give a longer exposure than would be customary under the same conditions at home (Vienna).

"After thinking the matter over for a while I saw clearly what was the cause of the great contrasts and especially of the heavy dark shadows. I perceived that the purer air of the South—just because of its clearness and permeability to light—did not scatter the sun's rays so much as our own air does. Since the shadows were lighted so little by diffracted light, they were necessarily heavier and darker than they would have been in our latitudes.

"The phenomenon of the dark black shadows appeared in the most surprising way in the dry, crystal-clear, desert air of Upper Egypt.

"For three weeks, while I was partly on the Nile and partly in the desert, I had absolutely no chance to develop any plates, but I was nevertheless so convinced of the ac-

¹ Eder's *Jahrbuch der Photographie*, 18, 159 (1904).

curacy of my observations that in practically every case I made longer exposures than were permissible theoretically. The results were an eminently satisfactory confirmation of my views. In view of all this¹ and as a consequence of similar experiences in Africa, Spain, Greece and elsewhere, I should sum up my experiences in regard to length of exposure in southern countries as follows:

"In southern countries a relatively brief exposure is permissible only when practically all parts of the subject to be photographed are well lighted. If large or important portions are in shadow, a shorter exposure will not do and one must expose at least as long as, and in very clear, dry air up to twice as long as, one would do at home under equally favorable conditions of light. Of course, this is after taking into account variations due to the differences in the season, length of day, and height of sun, resulting from the difference between our latitude and that of the southern country."

Waterhouse referred to Abney's work on reversals, but Abney's paper² is of such fundamental importance that I quote it practically in full.

"It is well known, if a plate be prepared with silver iodide by the ordinary wet process, be briefly exposed to light, and after washing be treated with a solution of potassium iodide and then be exposed to an image in the camera, that, after dipping in the silver-bath and developing, a positive image is obtained. It matters not whether the potassium iodide be alkaline, neutral, or acid, the same effect will be noted; also that there is no difference if, after treatment with the potassium iodide, the plate be washed or not, the reversal of the image will still be shown. In this case the iodine is liberated as before, but the action is increased by the access of oxygen from the air; in fact it is a mixture of effects.

"If potassium bromide or any simple bromide be substi-

¹ Cf. Wiener Phot. Blätter, 1898, 267; Phot. Correspondenz, 1899, 45.

² Phil. Mag. [5], 10, 201 (1880).

tuted for the iodide, the same result obtains. Silver iodide, if prepared with an excess of soluble iodide, or if, after preparation with excess of silver, it be treated with a soluble bromide, is insensitive to light, and the explanation of this perhaps may be found in the fact already stated.

"It has been usually held that a soluble iodide, such as potassium, can destroy an invisible impression made by radiation, but this is not the case if it be treated with the iodide in the dark. If, however, any iodide, such as cupric or ferric, be employed, which readily liberates an equivalent of iodine, the destruction is accomplished in the dark. The least favorable iodides for such destruction, as I have already shown,¹ are the monads.

"If a plate prepared with silver iodide have a preliminary exposure given it, and then be exposed *for a considerable time* to the image formed in the camera, a reversal of the image will take place as before. If, however, such a plate, after washing, be treated with an aqueous solution of pyrogallie acid, potassium nitrite, or any other oxidizing agent, such reversal of the image will not be obtained; nor will it if it be exposed in a cell containing such a substance as benzene, or if exposed in dry hydrogen. From this we learn that, to obtain reversal, oxygen must be present in some form or other, and that if a substance readily taking up oxygen be in contact with the silver salt, a reversal cannot be readily obtained.

"An interesting corroboration of the above statement is to be found in the treatment of an exposed plate in a cell containing a dilute solution of permanganate of potash, bichromate of potash, or hydroxyl, when it will be found that the reversal takes place with the greatest facility. The same reversals may also be obtained by using any of the mineral acids in a diluted form.²

¹ Photographic Journal, 1878.

² It must, however, be remembered that the solutions must be very dilute, or the whole effect of the preliminary exposure will be destroyed, since these oxidizing agents are active in the dark, but act more readily in the light.

"The above experiments show, then, that a reversal may be obtained by the presence of the iodides or bromides (and in a more feeble manner I have also found, by that of the chlorides), and also by oxidizing agents and mineral acids, while the presence of a deoxidizing agent, or the exposure of the plate in a medium free from oxygen, prevents the occurrence of the phenomenon.

"We shall consider shortly as to whether the reversing action depends upon the sensitiveness of the salt of silver obtained by the preliminary exposure, or upon that of the agents employed in effecting such reversal.

"With the bromide of silver we have rather different phases of the phenomenon to consider. The development can be carried out with the alkaline or the ferrous oxalate developer, a mode which is more easy to carry out than the development by precipitation of metallic silver from an aqueous solution of silver nitrate. For experimental purposes, films containing silver bromide may be formed of collodion or of gelatine, and the behavior of the silver salt in the two vehicles is somewhat different, and has to be considered separately. Collodion is, or should be, a strictly neutral substance; that is, it is merely a medium in the pores of which the silver salt is entangled and kept in position, and has no effect on the progress of development or on the action of light, beyond that which may be due to its physical qualities, its chemical constitution remaining unchanged.

"A collodion film is essentially porous and not continuous, as may be seen by a microscopic examination, and free access of the atmosphere to the silver is thus obtained. Gelatine, on the other hand, is a substance readily acted upon by oxidizing agents and by the halogens; and consequently it may have an effect on the progress of development and on the action of light, its chemical constitution becoming altered. It is a homogeneous film, and not porous in the ordinary sense of the word, and is a protective agency against the atmosphere to those silver salts which may be embedded in it.

"The most convenient method of experimenting with silver bromide is in the form of emulsion, made either with collodion or with gelatine, but it is not to the purpose of the present paper to refer to the mode of preparation beyond stating that in the former case the emulsion is usually prepared with an excess of silver nitrate, and the latter with an excess of soluble bromide, both of which are eliminated as far as possible by washing.

"If a film containing silver bromide, whether in gelatine or collodion, have a preliminary exposure given to it, and then be treated with a soluble bromide of an alkali, such as of potassium, and be again exposed to light in the camera, it will be found that there is not such a rapid reversal of the image as with the iodide, but that longer exposure is required to effect it, the reason being that bromide of silver prepared with a large excess of soluble bromide is still sensitive to light. If, therefore, the light decomposes the soluble bromide on the plate, liberating enough bromine to form fresh bromide of silver with the subbromide formed by the preliminary exposure, that freshly formed bromide, being sensitive to light, is again reduced to the subbromide state by the same rays which formed it. It will be evident, however, that reversal should take place more rapidly with the soluble bromide present than without it, and such is the case.

"It is useless to treat a silver bromide film with a soluble iodide, since silver iodide is immediately formed, and the reactions that take place are similar to those already described.

"If bromide of silver in collodion be exposed to the image in the camera without the presence of any other substance, a reversal takes place. Roughly speaking, the reversal takes some sixty times more exposure to the light than is requisite to produce the maximum ordinary effect. To trace the cause of this reversal it is only necessary to treat the film with a 5 percent solution of potassium nitrate, when it will be found that the reversal does not take place. The

same holds true when the film is treated with any deoxidizing solution, or if the plate be immersed in benzene or hydrogen. The cause, then, of the reversal in this case is evidently an oxidation, and this may be further verified by treating the film, after a preliminary exposure, with bichromate of potash, hydroxyl,¹ etc.; it will then be found that the reversal takes place much more rapidly than when those oxidizing agents were absent. The same may be said of the mineral acids.

"If silver bromide be held in a gelatine film, the action of light is somewhat different. If the plate be exposed in the camera for a short time, say a few seconds, the image develops in the usual manner and we have a negative image; if it be prolonged to, say, a minute, the image is reversed on development; a further exposure causes a negative image to be produced, while one much more prolonged causes a positive image again to be formed on development. Here are four distinct phenomena² which need explanation. To solve the problem offered, plates should be exposed when saturated with a solution of potassium nitrite as before, when it will be found that the phenomena are absent, a reversal being almost impossible to obtain unless the length of exposure be such as to thoroughly oxidize the nitrite at the expense of gelatine. For ordinary purposes it may be said that a reversal is non-existent under these conditions.

"If a plate be exposed in benzene, however (a liquid which does not permeate through gelatine), the phenomena are still existent. If a plate be exposed to such an extent that there is a marked image apparent before development, and be then immersed in water, it will be found that when the image appears the gelatine refuses to swell to the same extent that it does when the light has not acted. Taking these two experiments together, it is evident that the gelatine has played some part with the silver bromide. It may therefore be presumed that the three last phenomena are due,

¹ [Hydrogen peroxide.]

² Mr. C. Bennett described these phenomena in the *British Journal of Photography* in 1878.

the 1st to the oxidation of the surface-particles of the bromide and a consequent change in color, the 2nd to the change in color of these particles permitting the colored rays to which it is sensitive to strike a deeper layer, and the 3rd to the oxidation of this layer at the expense of the gelatine. The 3rd and 4th phenomena are so unimportant that they are scarcely worth investigating. The presence of organic matter is evidently necessary for their appearance; at least I have never been able to obtain them with collodion films not containing a preservative.

"As before, the experiment of saturating one of these gelatine films with bichromate of potash shows that the reversing action is very much increased by the presence of the oxidizing agent. Mr. Bolas¹ has recently described a plan of producing reversed negatives by allowing the bichromate to dry in the film, which is a practical application of this reversing action of light in the presence of an oxidizing agent.

"A convenient method of showing these phenomena on the same plate is to use a screen containing squares of graduated opacity, as suggested by the editor of the *Photographic News* or such as the sensitometer prepared by Mr. Warnerke, and procurable at most photographic warehouses.

"Having treated of these reversals of the image in a general way, it now remains to show which radiations are effective in producing them. For testing this, spectro-photography was resorted to, a special dark slide having been constructed capable of holding a cell which would contain the plate, and be immersed in a liquid of any gas or vapor whose action it might be desired to test. Three flint-glass prisms were used, and a lens to the camera of about 2 feet equivalent focus, the collimating lens being a duplicate of it. The time of exposure was, as a rule, three minutes to the sunlight or to that of the electric arc, care being taken in the latter case that an image of the positive pole fell on the slit so as to give a continuous spectrum. The action of potassium iodide on silver bromide will first be described.

¹ Photographic Journal, May (1886)

"A plate was exposed after being sensitized, and after washing was immersed in a cell containing a 1 percent solution of potassium iodide and exposed to the spectrum. The result is shown in Plate V,¹ Fig. 1; the same rays which cause an image to be formed in the usual manner likewise caused a reversal (dotted curve, Fig. 1).

"A plate similarly prepared was exposed in a 1 percent solution of potassium bromide for the same length of time, with the result that a reversal was obtained in the blue and likewise in the red, but much less marked in the latter. These two experiments tend to prove that, in reality, it is the bromide that is acted upon to some extent, and the effect is not entirely due to the silver salt. This was particularly manifest in the case of the iodide and bromide slightly acidified with a mineral acid, and was much less marked when the solution was alkaline—in the latter case, the reversal taking place in the blue, and not in the red, regions of the spectrum.

"To see if the silver salt had any marked effect on the rapidity of oxidation, a silver iodide plate was washed, given the same preliminary exposure, and then placed in the spectro-photographic apparatus without any surrounding fluid. A reversal was obtained in the blue, but not to anything like such an extent as when placed in soluble iodides or bromides. The reversal, therefore, when the plate is exposed in the latter, is partially due to the action of radiation on the bromide, and partly to that exerted on the silver salt itself.

"A silver iodide plate, treated as before, was next exposed in a weak solution of potassium bichromate, when there was a strong reversal in the red, and no action whatever in the blue. Permanganate of potash was next substituted for the bichromate, and the same reversing action was found, with the addition of a negative image in the blue.

"With hydroxyl the same phenomena were observed as with the permanganate, the reversal taking place a little further into the green. Studying the absorption due to these

¹ [The figures referred to in the text are not reproduced in this paper.]

three oxidizing agents it would appear that the reversing action is due to the action of light on the salt of silver, which is changed by the preliminary exposure to light, and not to the action of light on the medium in which the plates are placed.

"With mineral acids a reversal was always obtained in the red and in the blue, a portion of the spectrum in the green and yellow remaining unreversed. Now the action of these acids is not a strictly oxidizing action, but is probably a removal of the loose atoms of the silver which goes to form the subiodide, and leaving silver iodide behind as the result of the action. The result of the action of acids do not, therefore, vitiate the above deduction. A plate exposed in benzene or in nitrite of potash showed no reversal even with a very prolonged exposure. It should be remarked that the action of permanganate and bichromate of potash when very feeble is sometimes to give feeble negative images in the red and blue in lieu of positive images; also positive images in the blue, and feeble negative images in the red. But this is to be accounted for by the fact that the dilution of these oxidizing agents is so extreme that the reducing action on the unaltered sensitive salt is far greater than the rapidity of the oxidation.¹

"Ordinary bromide of silver in collodion or gelatine may be taken as giving almost identical results under the influence of a soluble bromide.² Now ordinary bromide is sensitive as far as B (see dotted curve, Pl. VI, Fig. 7), and it might be presumed that this sensitiveness to the rays of lower refrangibility would cause a modification in the action of the soluble bromide. A reference to Figures 7 and 8 will show that this is the case, but at the same time the features which are so marked with the action of bromide on silver

¹ There is one singular fact to be noted in this, and which I propose to treat of in another contribution, *viz.*, that the iodide of silver, when given a preliminary exposure, is sensitive in a region of the spectrum lying between a point near D and one near A. This phenomenon has been described before and not explained, though experiments show that the explanation is easy.

² As before explained, it is useless to expose such plates in a solution of soluble iodine, since silver iodide is immediately formed.

iodide are present. Fig. 7 is the curves due to silver bromide in collodion which has received a preliminary exposure and was then exposed in a 5 percent solution of acid potassium bromide. It will be seen that the curves in Figs. 7 and 2 are similar, showing that the principal action is due to light acting on the soluble bromide in the presence of an acid. Fig. 8 is a similar plate exposed in an alkaline solution of KBr, in which there is a modification of the curve. The last loop is probably due to the silver subbromide itself, since the oxidation of this salt by oxidizing agents occupies approximately the same position (see Fig. 10).

"Fig. 9 shows the effect of permanganate of potash; and when it is compared with Fig. 10, which is the curve due to oxidation by bichromate of potash, it will be manifest that the chief oxidizing action lies in the red and ultra red of the spectrum.

"Fig. 11 also shows the effect of bichromate of potash on silver bromide given a preliminary exposure, the plate in this case being a gelatine plate. It will be seen that the bichromate totally arrests all action in the blue, while it rapidly causes a reversal in the red.

"Fig. 12 shows the effect of mineral acids on silver bromide, by which it will be seen that a maximum of reversal takes place in the red and in the blue. As before stated in regard to the iodide, the action of these acids can scarcely be regarded as an action of oxidation.

"Fig. 13 shows the phenomena due to over-exposure of silver bromide, by which it will be seen that reversal takes place in the blue and not in the red. Comparing this with Figs. 7, 11, and 12, the effect of extraneous matter in causing a reversal is very marked.

"Collodion plates exposed in benzene, or in aqueous solutions of pyrogallie acid, potassium nitrite, and sodium sulphite gave no reversal whatever.

"Gelatine plates exposed in benzene gave the phenomena shown in Fig. 13, while with the other media no reversal at all was obtained.

"The explanation of the apparent contradiction shown by the behavior of a gelatine plate exposed in benzene has already been given.

"The action of many other liquids and gases¹ have likewise been tried, but it was thought that the examples given sufficed, since they all pointed to the same conclusions, which may be summarized as follows:

"1st. The reversal of an image is due, in the majority of cases, to the oxidation of the subsalt of silver which is formed by the first impact of light on the exposed salt of silver.

"2nd. The oxidation is due to the action of light, the rays of lower refrangibility being the most powerful accelerators of oxidation.

"3rd. Reversal of an image may be due to the presence of any haloid of an alkali, the reversal in this case being partly due to the tendency to oxidation of the subsalt of silver.

"4th. The presence of a mineral acid tends powerfully to cause a reversal."

More or less in line with this are the experiments of Schloemann,² who found that "the nitrous fumes from the action of nitric acid on copper turnings produce a solarizing action on ordinary dry plates in a relatively short time. If the gases are prepared by igniting lead nitrate, the reaction is less violent; with short exposures one gets a *normal* image, with longer exposures a solarized one." Since it is not quite clear whether the effective agent is nitric oxide or nitrogen peroxide or both, it is hardly safe to base any conclusions on Schloemann's experiments.

From Eder's Handbuch I quote the following passages:³

"If a silver bromide gelatine plate is exposed to light by increasing stages, it acquires to a greater and greater extent the property of blackening in the developer. If the ex-

¹ Ozone was most marked in its oxidizing properties, and gave a curve very similar to Fig. 12, both with the iodide and bromide of silver.

² Zeit. wiss. Photographie, 5, 187 (1907).

³ Eder. Handbuch der Photographie, 5th Ed., 3, I, 111 (1902).

posure is continued longer, the silver bromide plate gets into a state in which there is no increased blackening when developed. With a still longer exposure the photographic plate gradually loses the power of developing, the degree of blackening on development being less than with other silver bromide plates which have been exposed for a lesser length of time. This phenomenon is called solarization. It occurs when very long exposures in the camera are made in an intense light. The brightest portions then develop less black than the dark ones and we get a more or less complete positive direct instead of a negative.

"With an ordinary camera and a lens with a small stop, it is easy to show the phenomenon of solarization by photographing the sun's image direct on a silver bromide gelatine plate, giving an exposure of several seconds, and developing in the usual way. The sun's image on the plate is much more transparent than the sky and the halo¹ round the sun; in other words, we have a positive. When making contact copies on silver bromide gelatine in a printing frame either by daylight or lamplight it is easy to obtain solarized prints if the exposure is sufficiently long.

"When taking interiors against the light, the windows often show solarization effects, coming out less black on development than the adjacent portions (not counting the halo which is often much darker). If such plates are developed with a strong developer, the solarization is very evident. The solarization and also the blurring halos can be reduced to a minimum by under-developing, rinsing off the developer thoroughly, painting the high lights with a potassium bromide solution (1:10), letting it dry on a bit, and then developing the plate completely.

"If an emulsion plate has first been exposed to a weak diffused light, a much shorter exposure is then sufficient to solarize it than would have been the case if the plate had not been light-struck. Under some conditions a previously

¹ Due to irradiation.

lighted plate will show distinct signs of solarization with only ten seconds' exposure' to lamplight.

"Solarization phenomena also occur if a normally exposed plate is developed in the light. Silver bromide gelatine plates which have been stained with cyanine (made sensitive for orange), showed marked solarization effects if, during the development and before the picture is entirely out, the plate is exposed for several minutes to a powerful red or yellow light. This inversion of the image is more marked if eight drops of potassium iodide solution are added to the emulsion just before it is poured.¹

"Waterhouse² found that silver bromide gelatine plates which are colored with blue dyes, are in general less liable to solarization than undyed plates or plates dyed yellow.³

"The solarization process is to be considered as an oxidation phenomenon, and we assume that with short exposures some of the normal silver bromide is changed into a sub-bromide, Ag_mBr_n (where n is smaller than m), this sub-bromide being more readily reduced by the developer than is the normal salt. On further illumination, especially in presence of oxidizing agents, the subbromide takes up oxygen and forms an oxybromide of the general type $\text{Ag}_m\text{Br}_n\text{O}_x$, in which the silver molecule is saturated again and therefore less readily reducible. The consequence of this is that an over-illuminated silver bromide is less readily blackened than one that has received a moderate exposure. This theory was put forward by Abney and further extended by Luggin.⁴

"According to R. E. Liesegang⁵ solarized dry plates show a whitish fog on the glass side of the over-exposed portions and he explains this by assuming that the places,

¹ Schumann: Eder's Jahrbuch der Photographie, **12**, 391 (1898).

² Eder's Jahrbuch der Photographie, **13**, 489 (1899).

³ This cannot be true in general and must depend primarily on whether the dye acts as a sensitizer or as a color screen, and on how concentrated it is.—
EDER.

⁴ Eder's Jahrbuch der Photographie, **12**, 155 (1898).

⁵ Ibid., **11**, 384 (1897).

where the action of light has been most intense, have become less permeable to the solutions. For this reason he believes that the developer reaches these portions less completely and that they therefore come out thinner.

"As has previously been mentioned,¹ we assume that the silver bromide grain in a ripened emulsion consists of a complex of innumerable silver bromide molecules and we assume that the light acts first only on the surface of the grain. In the case of solarization the "solarized" silver bromide is therefore formed first at the surface of the grains and the production of it in the interior takes place but slowly. A careful examination of a solarized, developed and fixed silver bromide diapositive shows that the transparent portions are not clear glass. Although very transparent, they are nevertheless thickly covered with reduced particles of silver.

"Abney's microscopical measurements showed that the diameter of the solarized particles is smaller than that of normally developed silver grains.² One also finds on the surface of the film more of the fine particles than in the deeper portions. This is in favor of the view that solarization occurs chiefly at the surface of the silver bromide where the action of the light is the most intense (in consequence of the oxidizing action).

"With short exposures there is no solarization. In general, the less sensitive the plate, the longer one must expose it before solarization occurs. In round numbers one must expose several thousand times.³

"As a rule gelatine plates solarize much more rapidly than collodion dry plates containing preservatives, the difference probably being due to the much greater light-sensitiveness of the gelatine plates. Gelatine plates containing

¹ Eder's *Handbuch der Photographie*, 5th Ed., 3 I, 101 (1902).

² Eder's *Jahrbuch der Photographie*, 12, 393 (1898).

³ Eighteen thousand times according to Kogelmann, Eder's *Jahrbuch der Photographie*, 8, 379 (1894), (10,000 times on an average), as long as is necessary to produce a negative if one is to get a fairly complete solarization. This figure, however, is not constant for all kinds of plates.

both silver bromide and silver iodide solarize somewhat less readily than pure silver bromide gelatine plates.

"The development is not without effect on the phenomenon of solarization. The stronger the developer and the longer one develops, the more readily the plate solarizes. In many cases it is a question of the developer whether the plate solarizes or not. With very dilute developers solarization phenomena are much less frequent than with the 'rapid' developers. An oxalate developer containing a good deal of potassium bromide eliminates the solarization phenomena to a greater extent than the same developer without restrainer. On the other hand, addition of sodium hyposulphite to the ferrous oxalate developer increases the solarization effect with over-exposed silver bromide gelatine plates; the solarized, very transparent, portions of such plates have a different color (reddish) from the non-solarized (blackish) portions. [Eder].

"Metol with an excess of ammonia, or amidol with ammonia, are apt to give inversions analogous to solarization with silver bromide gelatine.¹ A similar effect is obtained with a dilute metol developer containing a good deal of alkali and some thiocarbamide² or with an eikonogen developer containing thiocarbamide, allyl thiocarbamide, or especially still better phenyl thiocarbamide. In fact, Waterhouse made this a method of preparing positives directly.

"Starting with an over-exposed silver bromide gelatine plate, which would show marked solarization phenomena when developed in the ordinary way, a normal development can be obtained by treating the plate for fifteen minutes with a solution of 100 cc. water, 3 cc. sodium hyposulphite solution (1:20) and 3 cc dilute sulphuric acid (3:100), washing, and then developing.³ The solarized silver bromide is presumably converted into the orthodox developable silver bromide. The result is very uncertain.

¹ Kogelmann: Eder's *Jahrbuch der Photographie*, 13, 379 (1899).

² Waterhouse: *Ibid.*, 9, 405 (1895).

³ Kogelmann: *Ibid.*, 9, 419 (1895).

"Solarization phenomena occur also when the silver bromide image is developed physically, in fact even when developed after being fixed as Sterry¹ has shown."

Sterry considers that there are two latent images, one organic and the other inorganic; and that these behave very differently under certain circumstances.²

"Soon after the introduction of the collodion process it was noticed that two distinct latent images were impressed upon a sensitive film at the same time by the action of light, but that which is found to remain after fixing the plate has received comparatively little attention.

"The late Mr. R. Carey Lea, Captain Abney and Dr. R. E. Liesegang have dealt with the subject; still, probably owing to physical development being so largely superseded by the introduction of the gelatine plate, it now seems to be almost forgotten.

"The late Professor Hardwich³ says: 'The formation of the invisible image is universally allowed to be a molecular and not a chemical change,' and in endeavoring to meet some objection brought against this theory, thus describes development after fixing (p. 42).'

"Mr. Young, of Manchester, was the first to show that if an exposed plate be immersed in a solution of hyposulphite of soda, until the yellow iodide is dissolved, a picture will still appear on applying the usual developing mixture." In explaining this phenomenon he says: "Pure iodide of silver is molecularly modified by the camera image, but its properties as regards the action of hyposulphite of soda are unaffected thereby; upon a plate so constituted no image could be developed after fixing. The sensitive surface of the collodion photograph is never, however, an absolutely pure iodide of silver, and sometimes very far from being so. It contains traces of an organic compound of silver in the wet collodion process and more appreciable quantities of the

¹ Eder's *Jahrbuch der Photographie*, **13**, 289 (1899).

² Sterry: *Phot. Jour.*, **22**, 264 (1898).

³ *Phot. Chem.*, 6 ed., p. 36.

same in the dry processes. Now with a compound film of this kind it may be supposed that while the iodide of silver undergoes its peculiar change in the camera, the organic combination of silver likewise changes, but in a different manner. Without altering in appearance it gradually loses its solubility in fixing agents, so that when the hyposulphite of soda is applied, its removal is not effected.

“Professor Hardwich further concluded that there was a catalytic action exerted upon the organic salt of silver by the actinically excited iodide of silver. This, however, does not at all seem to be necessary, because when gelatine is sensitized with nitrate of silver, development will take place after fixing, with suitable but much longer exposures.

“The molecular theory has recently been enforced by Messrs. Hurter and Driffield,¹ and though the experiments to be described are apparently opposed to that theory, because they indicate that there is some breaking up of the haloid salts of silver at a very early stage of the light action, they nevertheless really uphold it, by showing that the liberation of the halogen is antagonistic to development, not only by its detrimental action upon the remaining haloid salt, but also by its separation and partial loss before development.

“While searching for evidence of liberated bromine by the action of light alone upon gelatino-bromide films, various means were taken to intensify as much as possible the visible coloration by sunlight, which had been supposed to be entirely reduced from the bromide, and consequently evidence of bromine given off. Had the intensification been readily accomplished, it was expected to be able to prove that the action began even with the small light values used for ordinary exposures, because it had previously been found, that if part of a plate was given an exposure sufficient to secure about the highest possible density upon development, and was then exposed to diffused light with the other half,

¹ Phot. Jour., 22, 145 (1898).

that which had received the small initial exposure was the first to darken visibly, thus showing that the reduction had commenced though too small in amount to be visible. Upon attempting to intensify with mercury and ammonia the only result was to change the blue-gray color to brown, and upon using a physical developer as intensifier, no better result was obtained, because at the same time it acted as a developer, giving density to the latent image remaining after fixing, and did not follow the usual rule found for the correct period of either fast or slow plates, during which intensification is proportional to the silver visually found in the developed film.

"From this it was evident that the visible color was not an indication of liberated bromine solely, but probably included and was perhaps mainly composed of an organic silver stain.

"That the coloration is due to silver may be shown by making it into bromide, when the whole is readily dissolved in sodium thiosulphate leaving perfectly clear gelatine.

The latent image remaining after fixing

"Every gelatine plate so far tried—pure bromide or chloride, bromo-chloride, or bromo-iodide—has with suitable exposures given a latent image which, after fixing in sodium thiosulphate, washing and drying, is permanent in daylight, and yet may be developed at any time by means of a physical developer. One that does not necessitate very careful washing is of course desirable, and the intensifier described by Mr. J. B. B. Wellington¹ having proved the most satisfactory has been adopted for all the requirements. Hydroquinone used with acid, as recommended by Dr. R. A. Liesegang, was found to be very slow in action and failed to give sufficient density readily.

"The deposit of silver has far more the character of wet collodion than a gelatine film, with a tendency to a pur-

¹ Brit. Jour. Alm., 1889, 575.

ple-brown tint by transmitted light, especially when chloride is present, thus differing from the simple sensitization of gelatine by the addition of silver nitrate, in which case the deposit is of the transparent ruby color obtained by the direct action of light. If, however, an unexposed bromide plate is fixed, and carefully washed and then sensitized with silver nitrate, the deposit is not nearly so transparent.

"It has been suggested by Dr. Liesegang that the image remaining after fixing is due to the silver reduced by the light, but as it will be shown that this latent image is capable of reversal before the reduction by light alone has reached a maximum, it hardly can be the sole cause. Seeing that chloride of silver is readily soluble in 'gelatino-nitrate' of silver, and bromide also to some extent, it would seem more probable that it is partly due to the silver haloid being either dissolved in or perhaps even chemically combined with the gelatine; therefore following Prof. Hardwich's explanation, it will be called the organic latent image in contradistinction to that impressed upon the visible haloid particles, and which will be described as the inorganic image.

"By giving a plate a series of exposures and comparing portions developed before and after fixing, it is found that usually no agreement beyond a single tone can be obtained (Table I).

TABLE I

Exposure	Density		
	A Inorganic latent image. Development before fixing	B Organic latent image. Development after fixing	A-B Difference
1	1.53	0.7	+0.83
4	1.71	1.0	+0.71
16	1.82	1.35	+0.47
64	1.87	1.7	+0.17
256	1.57	1.75	-0.18
1024	1.37	1.64	-0.27

"If the ordinary development is made to agree with either a high or low tone of the organic image, the scale in either case rapidly separates.

"If a number of plates are exposed, fixed and developed together, the organic image upon each is found to have points of agreement not found in developed inorganic images, while at the same time some relationship is maintained between the two latent images, organic and inorganic.

"The most striking results found are:

"1. That the highest density is with an occasional exception obtained with the slowest plate.

"2. The highest density is so very different with slow and rapid plates that it is necessary to divide them into at least two classes, say above and below H and D,¹ speed 10.

"3. That reversal usually takes place at or near the same exposure, not differing more than one exposure, and this in favor of an earlier reversal with the most rapid plate.

"4. Reversal is always reached earliest by the inorganic image and re-reversal by the organic.

"5. Giving much smaller exposures so as to obtain commencement of visible reduction it is found that there is very little difference in the plates (in either class taken separately), the higher speeds showing about one exposure before the slow, from which it would seem that whatever means are used to produce rapidity in gelatine emulsions, the sensitive organic compound, in this respect, remains far more nearly constant than the inorganic.

"6. The organic image is developed throughout the film, often leaving the surface as bright as the glass, while the developed inorganic image is evidently largely upon the surface.

"7. The inorganic latent image is not completely insoluble in sodium thiosulphate as supposed by Prof. Hardwich, but it is, however, far less soluble than the inorganic, thus giving the opportunity of isolating and developing it. Pro-

¹ [Hurter and Driffield.]

longed immersion appears to remove it entirely, though very slowly, after the first half hour. The reduction is found to follow the usual rule, entirely altering the gradation and giving an appearance of under-exposure.

"After fixing, the length of time required for washing is at least fifteen minutes, otherwise with some plates there will be a tendency to deep red fog. The more completely the washing is performed the quicker and better will be the development.

"It will be well to note at once, where accuracy of comparison is desired, this partial removal of the latent image and alteration of the scale of gradation during fixing, necessitates each experiment being made complete in itself. After various trials the time of fixing was settled at eight minutes, with thirty minutes' washing in running water.

"While it is evident that after fixing it is the organic image alone that is dealt with, it is not so clear that the reduction of silver by ordinary development is due to the action of light upon the haloid salt alone. That the organic image is in some way connected with the inorganic seems highly probable, seeing that there is an apparent inverse relationship between the density obtainable from the organic image and the speed of the plate to ordinary development, and also because the form of the original bromide particles is reproduced with the physical development of the organic image.

"After development of the inorganic, no trace of the organic image can be found. The physical developer does not then add the densities due to the organic image, but, as previously stated, a proportional increase of the developed densities, and largely upon the surface. This is no proof whatever that the organic image is either used or destroyed in the development of the inorganic, because it is possible greatly to retard the development of the inorganic image while leaving the other practically uninjured. It would seem, however, that little or no building up of the organic image can take place in the presence of the silver ordinarily

reduced by development. If the development is stopped with the merest trace of image, and is followed by the intensifier, the organic image may be sometimes traced.

Speed relationship

"The following table gives the comparative speed relationship of a few different plates (Table II):

TABLE II
Comparative Speed of Organic and Inorganic Images, Hurter and Driffeld Speed Nos.

Inorganic	Organic	Development factor	Inorganic	Organic	Development factor
1.6	0.7	1.2	34	6.0	0.65
4	1.0	1.3	41	8.0	0.50
4	1.6	0.9	75	11.0	0.45
5.5	2.0	1.25	87	11.0	0.43
17	2.0	1.00	115	28.0	0.30

"While the H and D speed numbers of these plates vary from 1.6 to 115, a ratio of 1 to 72, the speed numbers of the organic image taken in the same manner range from 0.7 to 28, a ratio of 1 to 40, still it must not be considered that the speed varies so much in reality, because, as Messrs. Hurter and Driffeld have pointed out, the actual speed of the plate is indicated by the point of double flexure in the characteristic curve, and the flatness of the curves obtained with the high-speed plates is really misleading, precisely as they have shown is the case when a plate is too thinly coated.

"The point of double flexure is difficult to ascertain accurately, but the greatest apparent difference is not more than 1 to 8, or one-sixth of the variation in speed of the inorganic latent image.

"In a very large number of cases the relative speed of plates to development may be correctly estimated from the simple comparison of the densities obtained from the physical development of the organic image in equal times, and so far the method has been found to fail only when the color of

the original plate differs greatly, so that the proportions of chloride, bromide and iodide apparently affect the results obtained, the chloride having by far the greatest influence. Indeed, were it not for the complication due to the mixed haloids, the speed of plates could probably be fairly well estimated from standard plates, by simple comparison of the reflections of a gas flame from the surfaces. Many successful trials have been made in this way, only failing as in the previous case when the color differed greatly.

"A sa general rule when two plates are compared together by means of the physically developed organic image, the slowest will give the greatest density at three points: 1. Between correct exposure and reversal. 2. Between reversal and re-reversal. 3. Density of re-reversal. Table III:

TABLE III

Exposure	Density			Exposure	Density		
	A	B	C		A	B	C
	Speed 17	41	87		Speed 17	41	87
1	1.24	0.73	0.63	158	1.51	0.71	0.58
3.55	1.46	0.79	0.68	562	1.56	0.75	0.63
12.6	1.60	0.77	0.59	1970	1.72	0.88	0.72
44.7	1.55	0.70	0.57	—	—	—	—

"The exposures were made at one time in diffused daylight under a negative constructed with layers of celluloid of equal density, giving approximately the exposures shown.

"With the organic latent image the period of reversal is very short indeed, and a rapid, and compared with the inorganic, intense re-reversal sets in quickly, 30 seconds to diffused daylight being sufficient to show the commencement, whereas using the most rapid plate, eight days has been the shortest time so far found for the re-reversal of the inorganic image, and a slow plate had not nearly completed reversal at the end of two months' exposure.

"With plates below 30 H and D, exposures may be obtained in the camera and lantern slides made, and under some circumstances might prove useful, owing to the almost complete absence of halation. Above this speed, the density obtained is so small that the plates are not readily available practically.

"Before development the films are perfectly transparent and colorless, while all needed density can usually be obtained in from 5 to 10 minutes.

"As to the practical value of the organic image probably not much can be said. The advantage of working in white light is not sufficient to counterbalance the disadvantages of the longer exposures required, and the tendency of the strong developer to bring out the slightest deterioration in the film. There is, however, one point worth notice. The great density readily obtained without halation when chloride is present in quantity and the exceedingly abrupt commencement of the curve, especially when reduced in the fixing bath, permits of great contrasts being obtained and may possibly prove of service in process work.

"In a former paper¹ the results were given of a number of experiments specially arranged to ascertain the effects of moisture and free bromine, as likely to be disturbing causes in the estimation of the speed of plates and to throw light upon the differences mentioned. The following conclusions were given (p. 127):

"A. Moisture increases the reduction of silver by development in a given time during the correct, over-exposure and reversal periods.

"B. Concurrent with the formation of the developable condition by the action of light, a constantly increasing counter-action is set up by the halogen liberated.

A. Moisture. Effect upon Organic and Inorganic Images

"A plate is invariably in its most rapid condition when thoroughly dried, the speed rapidly decreasing when moistened.

¹ Phot. Jour., 19, 118.

"At the same time moisture increases the amount of silver reduced in a given time as indicated by the increased development factor, and thus is in accord with the usual rule, the slower the plate the quicker the development.

"It is when the greatest density and reversal period is studied that the effects of moisture become more evident. The intimate relationship between the light and the amount of silver reduced which is found during the correct exposure period, no longer exists. Dealing still with the inorganic image, the slightly increased reduction found throughout the scale during the correct period rapidly increases, delaying reversal, and causing the fall during that period to be far less rapid.

"It is also noticeable that the greatest density attained is far higher in the moist than in the dry plate.

"Turning now to the organic latent image, it is found that moisture has a similar but far less marked effect.

"With some plates little or no difference is found until reversal is approached, but, as before, this seems to be invariably delayed by the moisture (Table V).

TABLE V

Exposure	Density Organic latent image		
	Dry plate	Plate moistened before exposure	Difference
1	0.40	0.45	0.05
8	0.66	0.72	0.06
64	1.12	1.22	0.10
512	1.03	1.46	0.43

"The effect of moisture thus appears to be a very general one, for it has already been shown to apply to the visible reduction by light alone.¹

¹ Phot. Ann., 1894, 293.

B. Bromine. Effect upon Organic and Inorganic Images

“The second conclusion was that concurrent with the formation of the developable condition of the action of light, a constantly increasing counter-action is set up by the halogen liberated.

“This counter-action was supposed to be directly caused by the action of the released halogen upon the latent image, and though it could not be actually detected, appeared to be the main cause of the anomalous results obtained under different conditions of exposure.

“If a pure chloride or chloro-bromide plate is taken, there is not any difficulty in showing visible reduction of silver by light alone with exposures far short of reversal with the organic image and a little short with the inorganic, and as it is these slow plates which have always been found to exhibit the most striking differences under varied conditions of exposure, support is given to the view that such variations even with bromide plates are in some way connected with the release of the halogen.

“Further investigation, using the organic as well as the inorganic latent images, throws more light upon the subject, the reversal period being especially helpful.

“The bromine known to be liberated with high exposures cannot be considered simply as the direct cause of reversal, nor does it really destroy the latent image, though for practical purposes that appears to be the case, but its real action is to retard development, which will take place if sufficient time is given.

“It was before shown that the application of a solution of bromine to a plate before and after exposure produced similar results, development being retarded in proportion to the strength and time of application. The effect is also found to be much greater than after exposure, and always (except when the quantity is very small) giving the appearance of under-exposure.

“With the organic image similar results are found, but there appears to be much more difference in the behavior

of fast and slow plates; all bear far stronger solutions, especially the rapid, ten times the strength for the same length of time being sometimes required to obtain an equal reduction. When this is the case there is not any difficulty in practically discharging the inorganic image by means of the bromine and yet leave the organic image capable of development. Generally therefore it would seem that the organic image is far more stable than the inorganic. In *Brit. Journ.*, December 22, 1865, the late Mr. R. Carey Lea noticed its extraordinary persistency.

"There is, however, one marked peculiarity: the organic latent image of all plates tried has been seen to have a short and sharp reversal period followed by re-reversal, and the effect of bromine when applied of suitable strength is to remove the reversal altogether, making one unbroken curve up to what was before the re-reversal period.

"It is then found that the curves of the organic and inorganic images, with some plates, cross one another, giving a positive and negative from the same exposures (Table VI).

TABLE VI

Exposure	A Inorganic latent image	B Organic latent image	C Organic latent image Bromine before development
1	2.15	0.75	0.28
3.55	2.14	0.83	0.35
12.6	2.05	0.96	0.45
44.47	1.51	1.03	0.64
158	1.05	0.97	0.80
562	0.76	0.94	0.98
1970	0.49	0.97	1.04

"The organic gives the negative, and the inorganic the positive, by means of ordinary reversal.

"Whether applied before or after exposure the effect of bromine upon the organic image is always to delay reversal, and this rule is found to include the inorganic image also. Being the most important, proof only of this result when applied after exposure will be given.

"The first effect found when the time and quantity is small is delay in development, but if sufficient time is given to obtain the same development factor the plate is apparently increased in speed and that instead of a falling off in the density of the highest exposures, there is a decided increase. If a longer time is given this latter peculiarity is still more strongly marked, while at the same time the lower tones fall off and there is a decrease in the speed of the plate indicated.

"The action of bromine is thus seen to be exactly opposite under different conditions (Table VII).

TABLE VII

Exposures	A Ordinary develop- ment	B Bromine, 2 min- utes before development	C Bromine, 8 min- utes before development
1	0.10	0.14	0.05
4	0.32	0.40	0.33
16	0.66	0.87	0.97
64	1.13	1.32	1.66
256	1.57	1.77	2.36
1024	1.97	2.28	3.36

"From these results it is clear that if the time of application of the bromine is adjusted half-way between the curves *A* and *B* there should be a considerable prolongation of the correct period of the plate (Table VIII shows that this is the case).

TABLE VIII

Exposures	A Front of plate	B Back of plate	C Front of plate Bromine before development	D Back of plate Bromine before development
1	1.46	1.05	0.44	0.42
8	1.96	1.74	0.92	0.88
64	2.41	2.44	1.50	1.41
512	2.46	2.77	1.87	1.78
4096	2.04	2.50	2.29	2.26

"The curves *A* and *B* are the same exposures and development, the only difference being that *A* was made upon the face of the plate and *B* upon the back. *A* gives the plate as more rapid for the correct period and therefore requiring less exposure for ordinary work, but the density reached is less than *B*, reversal also is earlier and more rapid.

"Other portions of the same plate (*C* and *D*) were also exposed at the same time back and front, and were placed in one percent of saturated solution of bromine for eight minutes and then washed.

"Development was greatly retarded, but the exposures are now shown to be practically identical for both back and front of plate, and the correct period has been greatly extended, giving almost a true representation of light intensities from 1 to 4,000.

"It was shown in the previous paper that the difference found with exposures given for a short time with strong light and longer time with a weak light, were not due to any differences in the lights themselves, for when the duration of exposure was made the same and the lights placed at proportionate distances the results were identical. That this is accounted for by the action of bromine is further proved by the last experiment, in which the bromine has been made to play a double part, preventing the surface from being developed (a coating of bromide covering the whole plate before fixing), thus giving time for the low tones to be developed at the back of the plate, and at the same time bringing the reversed portions again into a developable condition. The whole is of course an artificial arrangement but based upon what appears to be the reversal of the ordinary conditions of action within the film.

"It has long been known that bromine absorbents delay reversal, but it does not appear to have been suggested that they do so by returning the bromine.

"The action of the moistened plate would seem to be due to its great power of temporarily holding the bromine, for it has been noticed that the visible reduction is much

greater than with the dry plate, and consequently much more bromine must be given off.

Summarizing briefly the results obtained it would seem

"1. The organic image may be due to three different causes:

"A. An organic silver compound (Hardwich). B. Silver haloid dissolved in, or combined with the gelatine. C. Intensification of the silver reduced by the light alone (Dr. Liesegang).

"2. The perfectly developable condition of the inorganic image is probably a molecular change only.

"3. With different plates, as also under varied conditions of exposure, more or less molecules of silver haloid are broken up and the halogen liberated, causing a reduction in the development.

"4. Reversal is mainly due to two causes: 1. Directly, by loss of the halogen. 2. Indirectly, by the injurious effect of the halogen upon the development of the remaining haloid salt.

"5. When the conditions permit of part of the halogen being returned either directly or from the gelatine, development is greater, and the tendency to reversal is delayed."

In an article on the nature of the latent image, Eder¹ comments as follows on the assumptions of Hardwich and of Sterry in regard to the existence of an "organic" image.

"Hardwich based this theory on some badly carried out experiments of his own. He held the erroneous belief that pure silver iodide collodion films lose the latent image when fixed and that an image, which can be developed, remains after fixing, only in films which contain organic substances such as albumen, etc. He therefore considered the organic substances as important constituents of the latent image. As a matter of fact, however, even after fixing there remains on a *pure silver iodide collodion film* a latent image which

¹ Zeit. wiss. Photographie, **3**, 331 (1905).

can be developed, so the bottom falls out of Hardwich's proof.

"Sterry made no attempt at a proof and merely assumed that the component of the latent image on silver bromide gelatine, which remained after an initial fixing, must be a decomposition product of silver bromide with gelatine,¹ apparently because he could think of no other explanation for the unexpected behavior of the latent image after fixing. When one reflects that exactly the same phenomenon is shown not only by silver bromide gelatine but by silver bromide collodion even in presence of a concentrated nitric acid or silver nitrate solution, the existence of this hypothetical compound of silver subhalide and organic substance seems very doubtful, and the doubt increases if one studies more closely the behavior of the latent image in silver bromide collodion towards chemicals."

Lüppo-Cramer² records the following observation with a silver iodide plate:

"I noticed one surprising occurrence in a solarization experiment with silver iodide gelatine. Under a negative the plates gave a properly exposed image when exposed three seconds in diffused daylight. A plate exposed for six hours under the same negative was developed in the same dish with the plate which had been exposed for three seconds, using amidol-potash. At first the plate seemed not to reduce at all, even when all the details had appeared on the plate with the short exposure. After some time a picture was noticed on the over-exposed plate. It was to be seen, however, only in the *deeper layers* and was a normal diapositive, *i. e.*, not yet solarized. Only after a longer development could anything be seen on the surface. When the plate was fixed, it was clear that there was no image in the *upper layers*. When only a few minutes in the fixing-

¹ Silver nitrate, mixed with gelatine, also gives an image which can be fixed and then developed physically. Sterry: Eder's Jahrbuch der Photographie, **14**, 290 (1899).

² Eder's Jahrbuch der Photographie, **17**, 46 (1903).

bath, the image appeared more powerful by reflected light, evidently because the unreduced silver iodide of the upper layer was removed."

The same author considers that the gelatine is an essential factor in the solarization process, for he says:¹

"Chemically-pure, dry silver bromide, precipitated in a pulverulent form from aqueous solution and free from a bonding medium, shows no absolutely certain solarization phenomena. On the other hand, the solarization of silver bromide gelatine dry plates can be followed by quantitative analyses. When silver bromide gelatine is given a normal exposure and developed with ferrous oxalate, the reduction to metallic silver is five times as great as when a similar plate is given a moderate solarizing over-exposure (one minute of daylight, for instance). Only after a twenty-minute exposure to direct sunlight,² does a silver bromide collodion show solarization effects when developed. Treating with dilute bromine water or with strong nitric acid destroys the solarized image and gives rise to a normal negative on development. Stronger bromine water destroys also this last-mentioned negative image."

This view is disputed by Schaum who obtained quite different results.³

"The phenomenon of solarization is often attributed to an action of the binder (hardening). While this is possibly a not unimportant secondary factor with gelatine plates, the actual solarization process must, however, have its cause in some peculiar change in the silver bromide itself, for our films solarize quite distinctly, and a smaller phenomenon has been reported for Daguerreotype plates. Luther did not obtain such an effect with his films. Our solarized films behaved exactly like solarized dry plates. Bathing in ammonium persulphate solution (five percent and twenty-two hours' soaking) destroys solarization completely, so the strips,

¹ Lüppe-Cramer: *Ibid.*, 16, 481 (1902).

² It was proved that bromine was set free.

³ Schaum: *Eder's Jahrbuch der Photographie*, 18, 76 (1904).

which have been exposed the longest to light, become the blackest when developed.

"The action of Röntgen rays on silver bromide, containing no binder, is interesting in some respects. Whether precipitated on glass or on potassium foil, the silver bromide, free from binder, is changed by Röntgen rays into a state in which it can be developed. The Röntgen rays therefore themselves cause a change in the silver bromide quite apart from any fluorescence arising from the supporting plate or the binder, as has sometimes been assumed.¹

"After an exposure of eighty minutes to the Röntgen rays, we were able to detect a solarization of our silver bromide, free from binder, even though this was not observed by F. Hausmann² with dry plates."

In the paper referred to, Miss Hausmann³ "studied the relation between the amount of silver bromide gelatine when subjected to the action of light in the one case and to the action of Röntgen rays in the other. The silver was determined volumetrically after the plate had been developed, fixed and washed, and the gelatine film then removed and treated with nitric acid. Ferrous oxalate was used as developer and Lumière plates were selected because the unexposed emulsion was least attacked during development. The development lasted five minutes in each case. The illumination was made with a benzene candle at a distance of one meter. By comparison with an amyl acetate lamp the light was expressed in terms of meter-candles. The amount of silver precipitated increased up to an exposure of 180 seconds and decreased for longer exposures. The experimental increase with the time was compared with the change required by the formulas of Bunsen and Roscoe, of Hurter and Driffield, and of Abney. No one of the formulas holds very well. When a Welsbach light was used, the maximum effect was obtained in 10 seconds. As the exposure was in-

¹ Cf. Eder's *Handbuch der Photographie*, 5th Ed., 3, 69 (1902).

² *Beiblätter*, 27, 359 (1903).

³ *Ibid.*, 27, 359 (1903).

creased to an hour, there was a rapid decrease in the amount of silver precipitated. With still longer exposure (1-8 hours) the decrease was relatively slight. In daylight and in sunlight the maximum was reached in the first second. With Röntgen rays the effect at first increased rapidly with increasing length of exposure, then at an ever slower rate until a maximum was reached at about 10 minutes; there was, however, no definite decrease on still longer exposure. At the same distance, the action of the normal candle was 33.6 times as great as that of the Röntgen rays when the exposure was ten seconds. For ten minutes' exposure the figure was 22.3 instead of 33.6."

Schaum's experiments on the solarization of pure silver bromide have been confirmed by Weisz,¹ who, however, had difficulty in getting the phenomenon and who says:

"We are therefore only in the position to state the fact that solarization occurs with plates containing no binder. Although it is probable that the best way really to learn something about solarization is by experiments with plates containing no binder and although we have worked hard along this line, we have not yet succeeded in being able to repeat our experiments satisfactorily when using plates containing no binder."

Some very remarkable cases of reversal have been recorded by Goldstein:²

"The coloring of alkali salts, which was first obtained with cathode rays, can also be produced by ultra-violet light.³ Daylight causes the color to disappear. The change produced by ultra-violet light, or by cathode rays (whose action can also be referred back to ultra-violet light⁴) is thus reversed by light of a greater wave-length. The colors which silver salts acquire under the action of light or of cathode

¹ Zeit. phys. Chem., **54**, 351 (1906).

² Verh. deutschen phys. Ges., **3**, 182 (1901).

³ E. Goldstein: Tätigkeitsbericht der Physik. Techn. Reichsanstalt für 1895: Zeit. Instrumentenkunde, **16**, 211 (1896).

⁴ E. Goldstein: Sitzungsber. Akad. Wiss. Berlin, **1901**, 227.

rays resemble the colors developed in the alkali salts, and the question at once arises whether these changes may not also be reversed by light or other physical agents.¹ A reversal by action of light is of course only to be expected with such silver salts as are not affected by daylight and are blackened by ultra-violet light or cathode rays. For the sake of convenience we will denote by 'blackening' all darkening of the illuminated silver salts, regardless of whether the actual color is blackish-violet, dark greenish-gray or something else. By 'regeneration' is meant the return to the color characteristic of the unexposed salt.

"First to be described is a type of regeneration which apparently contradicts the previously established limitation of unchangeability in light because it refers to silver bromide and silver chloride, both of which salts blacken in daylight under ordinary circumstances.

"When silver chloride in a sealed tube has been blackened by the action of sunlight, it is well known that the salt takes up the freed chlorine gradually in the dark, becoming white. Previous experiments have shown that, with a continuous illumination in a closed vessel, a state of equilibrium is reached beyond which the blackening does not go. The state of equilibrium is reached when the concentration of the chlorine set free by the intensity of the light in question has reached the corresponding dissociation pressure.

"It appears not to have been observed that under these conditions a reversal of the blackening may take place, running even to complete regeneration. The action in question is particularly easy to obtain with silver bromide. Granular or pulverulent silver bromide is blackened by being allowed to slide many times through a sheaf of powerful cathode rays generated at a very low gas density. The blackened salt is then placed in a vertical half-filled glass tube about 16-18 mm in diameter and exposed to the direct sunlight.

¹ According to Abegg, *Wied. Ann.*, **62**, 433 (1897), silver bromide, which has been made gray by the action of rays, can be changed back into the yellow salt by heat.

At the end of about three-quarters of an hour only the free surface and the illuminated ("front") half of the cylindrical column of salt is black. The back, and especially the whole interior, of the mass is completely regenerated and cannot be distinguished by the eye from freshly prepared salt. If the tube is placed in a diffused light at a bright window instead of in direct sunlight, about two summer days are necessary to regenerate silver bromide while several months are needed for silver chloride. The experiments succeed also with silver bromide or silver chloride preparations which have been blackened by daylight in the open air and not by cathode rays.

"The regeneration in the closed space is due to the fact that the sun acts on the side towards it and gradually works in deeper, setting free bromine and tending to produce the dissociation pressure corresponding to the prevailing intensity of the light. On the less strongly illuminated portions, the back and the inside, the dissociation pressure, corresponding to the chemical equilibrium, is lower. Therefore bromine diffuses from the front to the less strongly illuminated blackened portions combining with them to form regenerated salt. This continues so long as the mean pressure of bromine in the tube exceeds the dissociation of the weakly illuminated portions. The explanation is the same for the case of the regeneration of the salt blackened by the cathode rays. A special case of the action in question is that in a closed tube lighted from above, it is impossible with continuous illumination to blacken both the upper and the under sides of silver bromide simultaneously. What is at the moment the surface is always blackened while the under side loses its color.

"With a continuous illumination in the open air, diffusion and air currents prevent the utilization of the free bromine and there is therefore an increasing blackening and decomposition without regeneration.

"This way of looking at the phenomena is in harmony with the facts that blackened silver bromide is made yellow

again when brought in contact intentionally with free bromine, and that the fresh yellow salt is not blackened at all by direct sunlight provided there is present a sufficient excess of free bromine.

"In a second type of regeneration the relations seem not to be quite so simple. It is interesting because blackened silver bromide, which is usually so stable, can be changed back in a few seconds into the yellow salt. It is best for this purpose to use a silver bromide prepared pretty closely according to the process described by Abegg.¹ Silver chloride is first precipitated from a silver nitrate solution by means of hydrochloric acid; it is dissolved in ammonia, and silver bromide is then precipitated from this solution by means of potassium bromide and nitric acid. The object aimed at by Abegg in this process is to prepare a salt which can be pulverized easily and which will not cake. For the effect which interests us the salt works best when it is not washed until completely pure, but when a trace of a definite impurity, presumably ammonium nitrate, is left in. The salt is then to an extraordinary degree less sensitive to daylight than the ordinary modification of silver bromide. Only after exposure of hours or even days is it darkened as much as the ordinary silver bromide after an exposure of a few seconds. When subjected to cathode rays, however, it rapidly becomes greenish-black. It therefore satisfies pretty completely the condition originally laid down for a regeneration produced by light. An extra advantage is that under the influence of the positive light of the discharge through air at very low pressure the salt also remains yellow even on long exposures.

"In consequence of the trace of the other salt adhering to it, this silver bromide, when heated in a vacuum, gives off a gas whose color and spectrum is that of nitrogen. The necessary heating is produced by the cathode rays which blacken the salt at the same time. If the discharge tube has the form of Fig. 1 for instance, the cathode rays from the aluminum

¹ Wied. Ann., 62, 425 (1897).

disc *K* meet the salt at *S* and blacken it. The blackened salt is moved, by tipping the tube, into the region of the stratified positive light, corresponding to the discharge through the gasified trace of the other salt; the blackening disappears in a fraction of a minute. Even without a displacement of the salt, the regenerating action of the positive light can be detected by the asymmetric distribution of the color if the salt is scattered all along the tube *R*. If the vessel is pumped out only to the point at which the cathode rays are still visible with their blue light, the purely optical effect of this light is to blacken the salt not only where the cathode rays strike it at the region *S* but also at the left end of the tube. To the right of the cathode rays however the salt remains yellow because the blackening due to the blue light is continually compensated by the regenerating action of the positive light.

Fig. 1

“If one wishes to make the conditions simpler, it is possible to dispense with the blackening by the cathode rays and to produce both the blackening and the regeneration with the positive light. To do this, the portion of the salt to be examined is brought into the field of the positive light and in the region of the cathode light there is only left a trace of salt from which the cathode rays generate gas, chiefly as a result of heat action. If the gas pressure during the discharge has reached a certain value, very small in itself, but at which the positive discharge no longer fills completely the tube *r* which is about 16 mm. in diameter, we get a light which is dull to the eye but which is apparently rich in ultra-violet rays and which blackens the salt very rapidly (inside of two seconds). Simply by pumping out to the earlier and

smaller gas pressure, the light becomes brighter and the blackened salt changes back again into the yellow salt. In this experiment if one puts in a stop-cock between the tube and a pumped-out vessel, the gas pressure in the tube will rise quickly when the stop-cock is closed and will fall again when connection with the pumped-out vessel is restored by opening the stop-cock. Under these conditions the salt can be repeatedly blackened and decolorized merely as a result of turning the stop-cock.

“Regeneration can also be brought about at constant gas pressure. By closing the stop-cock and allowing the pressure to rise, blackening is produced by the positive light. If the pressure is then kept constant and the salt heated from without by means of a Bunsen burner, the blackening disappears in a few seconds but re-appears again as the salt cools once more. A necessary condition for these changes is always the simultaneous action of the positive light. If one heats or cools without having a current passing at the same time, there is no change in the color. In this experiment the heating by means of the cathode rays can of course be omitted.

“Though the positive discharge passed over the salt in all these experiments, the regeneration is not due to a specific action of the positive discharge on the salt. This follows from the fact that regeneration also occurs when the salt has been blackened in the positive light and is then brought into a part of the tube through which no discharge passes, for instance into *R* while the discharge is made to take place between *a* and *b*.

“I will now record some observations on the behavior of silver iodide.

“When silver iodide is prepared from silver nitrate and an excess of potassium iodide, its yellow color is known to change but little in daylight. According to Stas there is no loss of iodine during this change. Under the influence of the cathode rays the salt becomes dark black and does lose a little iodine. This can be shown by bringing a few pieces

of bright copper foil close to the illuminated silver iodide. At first the copper does not light up in the cathode rays, but in a short time it phosphoresces with an intense fiery-red light. The iodine set free from the silver iodide reacts to form cuprous iodide which phosphoresces with this color.

"If silver iodide is blackened by cathode rays in a sealed tube containing no copper and if this tube is then placed in daylight, after a few days the salt will be found to have bleached to the same whitish-yellow color which fresh silver iodide acquires in daylight. The iodine, which had been previously set free, recombines under the influence of daylight.

"Regeneration takes place in a few seconds if silver iodide, blackened by cathode rays, is brought into the field where the discharge of positive light can pass through the iodine vapor. If the salt is to be regenerated, it must also be heated a little.

"If one starts with yellow silver iodide in the part of the tube through which the positive light passes and if, after the tube is exhausted very thoroughly, a little silver iodide is decomposed by the cathode rays, the silver iodide exposed to the positive light takes on an orange to red color. This is the color which also appears if iodine vaporizes in a closed space near yellow silver iodide. The coloring is due solely to a physical adsorption of the iodine. One special factor comes in, however, in the production of the color by means of the discharge, as can be seen if one spreads the yellow silver iodide over the whole length of a tube like that in Fig. 2. In the middle of the tube the cathode rays, starting from *K*, set free some iodine. In a short time the silver iodide becomes colored a deep orange over the stretch *KA* where it is exposed to the positive light. The salt in the left half of the tube remains unchanged in color and only after a long period of discharge does the left side assume a color which even then is much fainter than that of the right half and which corresponds to the ordinary adsorption.

"If now a part of the highly colored right-half is wrapped in black paper while the rest is exposed to daylight, the orange

color disappears in a short time from the illuminated portion while the shaded portion remains unchanged. It looks therefore as though very refrangible light increases the absorptive power of silver iodide for iodine, while light of greater wave-lengths decreases it. Experiments were made to see whether under similar conditions all substances acquired a strong absorptive power for iodine. This proved not to be the case for barium sulphate. On the other hand, amorphous silicic acid anhydride (from Kahlbaum) becomes active and is colored a beautiful pink when placed in a discharge tube in which silver iodide was placed under the cathode to act as a source of iodine. When brought in contact with iodine in a test-tube, barium sulphate was not colored while silicic acid anhydride became pink. The discharge light therefore seems only to strengthen a previously existing power of absorption, which is weakened by ordinary light."

Fig. 2

Coming back to the action of ordinary light, we find that the degree of solarization is not a function of the exposure alone, but depends on the chemical treatment which the plate receives before or during development. Thus Lüppo-Cramer¹ says that "on treating solarized plates with bromine and nitric acid, I obtained a change of the solarized image to a normal image on developing, though curiously enough the image, which was present before development, persisted."

Eder² found that washing the plates before development in a bath containing

- 2 g potassium bichromate,
- 2 cc nitric acid, sp. gr. 1.4,
- 100 cc water,

ensured the development of a normal negative even though

¹ Eder's *Jahrbuch der Photographie*, 16, 54 (1902).

² *Phot. Correspondenz*, 1902, 645, 703.

the exposure had been several million times too long. Weisz¹ found that the solarization was eliminated to the same extent regardless of whether the plate was transferred direct from the chromic acid bath to the developer or whether it was washed for fifteen hours in running water. Of course if the chromic acid solution is too concentrated, the normal latent image is also destroyed, as has been shown by Sheppard and Mees,² who say:

"It has frequently been maintained that halogenizing and oxidizing agents do not actually destroy the latent image, but only retard development. Sterry,³ for example, considered that their effect was to delay what he termed "secondary development," *i. e.*, an assumed intensification of a primarily formed image by silver from neighboring granules. Our experiments with chromic acid subsequent to exposure led to the following conclusions:

Plates were dipped by rotation in CrO_3 solution for a given time, then rinsed by rotation and developed.⁴ The plate-curve was distorted at the top, but $\log i$ and γ_∞ were unchanged.⁵ The velocity constant K of development was diminished, approximately in proportion to the *logarithm* of the strength of the preliminary CrO_3 bath. Prolonged washing never entirely annulled the effect, but it was diminished. The values of K (the velocity of development) decreased with the time of immersion in CrO_3 , ultimately reaching a minimum for each concentration, the function of the effect on K being independent of the concentration.

"From these facts we conclude that the CrO_3 is irreversibly absorbed in the film, probably both to the film and to

¹ Zeit. phys. Chem., **54**, 341 (1906).

² Proc. Roy. Soc., **78A**, 463 (1906).

³ J. Sterry: Phot. Jour., **54**, 50 (1904).

⁴ For the author's experimental methods, and for the meaning of the symbols $\log i$ and γ_∞ , etc., see the previous papers. Roy. Soc. Proc., **74**, 447 (1904); **76A**, 217 (1905).

⁵ [i is a characteristic constant of the plate, termed the inertia, and γ is a constant depending upon the development and called the development factor." See Proc. Roy. Soc., **74**, 466 (1904)].

the silver halide, forming with the latter something of the nature of a solid solution. Freshly precipitated AgBr is colored yellow by chromic acid, and the color is not removed by long washing. The retained oxidizer then shows development by oxidizing the developer in the film. This view was further confirmed as follows: Plates were treated, after 'chromating,' with a solution of sodium sulphite, which restored K to its normal value by reducing the chromic acid.

"This 'sulphite reaction' enabled us to decide without doubt that the prolonged action of CrO_3 destroyed the latent image, *i. e.*, both $\log i$ and γ_∞ were altered. After sulphiting, since K is now restored to its normal value, any change in γ is due to a lessening of the mass of the latent image. The following table exemplifies the results for N/50 CrO_3 , with a subsequent bath of N 10 Na_2SO_3 , all developed in M/20 quinol for five minutes:

t = time of immersion in CrO_3 in minutes.

	$t = 0.$	2.	20.	40.	120.
γ	1.65	1.65	0.77	0.48	0.34
$\log i$	1.25	1.25	1.30	1.50	1.80

"The rate of attack on the latent image was found to increase very rapidly with the concentration of the CrO_3 . The phenomena point to a re-oxidation (possibly involving the release of halogen from a combination with gelatin) of a reduction product, the latter being in solid solution in the normal halide."

In a paper on the nature of the latent image, Eder¹ records a number of important facts in regard to solarization. He finds that "with pure silver bromide collodion and chemical development, solarization begins at approximately the same time as the visible blackening of the silver bromide. Solarization occurs also with physical develop-

¹ Zeit. wiss. Photographie, 3, 338 (1905).

ment; but then it usually lags somewhat behind the direct blackening.

"At 15° to 16° , nitric acid of specific gravity 1.30-1.40, destroys the solarization image on silver bromide even when only allowed to act for five minutes. The silver bromide film then gives, when developed, a rather thin but normal negative. More dilute nitric acid (sp. gr. 1.20) acts in a similar way but more slowly.

"If one takes the minimum time necessary to produce a normal, latent image on silver bromide collodion as the unit, and considers the beginning of solarization with chemical development as 300, then nitric acid (sp. gr. 1.20) destroys the normal, latent image in five minutes for exposures up to 2 or 4. After three to five minutes' action the solarization image is only partially destroyed; but it is changed very much by an attack lasting fifteen minutes, much more than the normal image, so that the film afterwards develops almost entirely as a normal image whether developed chemically or physically. Concentrated nitric acid brings about this change more rapidly and more effectively."¹ . . .

"These experiments also furnish the proof that the visible blackening of the silver bromide stands in no causal relation with the formation of the substance composing the solarized image. In some cases, the two phenomena seem to run parallel; but, with silver bromide containing silver nitrate, visible blackening takes place long before any solarization image is formed. With pure silver bromide collodion

¹ If a pure silver bromide collodion be moistened with water and be given a five hundred to three thousand fold exposure, the solarized image is destroyed by concentrated nitric acid (sp. gr. 1.40) acting for only five to six minutes. With chemical development there is then a normal development. The normal image due to an exposure up to 20-100 times the unit value is destroyed by concentrated nitric acid. When a longer exposure is given the normal image resists the attack by nitric acid better. With physical development the relations are approximately, though not exactly, similar. Normal images due to an exposure of 15 can be detected by this method after the nitric acid treatment. By the same test it is shown that the solarized image is destroyed, though not always completely, for here and there are to be seen traces of mixed images (half negative and half positive).

under water, the solarization image can be easily destroyed by nitric acid, while the visible, blackened product withstands the action of this acid to a great extent.¹

"Nitric acid therefore acts in different ways on silver bromide collodion, depending on the degree of exposure which the latter has received, the difference being something as follows:

"1. The normal latent image, formed on silver bromide collodion as the result of a short exposure, is destroyed by nitric acid.

"2. The normal, negative, image due to a longer exposure is not destroyed but only weakened.

"3. The solarized, latent, positive image is somewhat attacked by dilute nitric acid and is destroyed by concentrated acid to such an extent that on development no solarized positive is formed; but, instead, a weak negative whose density depends on the length of exposure, the thickness of the sensitive film, and the nature of the development. Probably we are dealing with the super-position of two entirely different images.²

"With a silver bromide collodion containing silver nitrate (10 percent silver nitrate solution) solarization takes place very much less readily, a conclusion reached by Lüppo-Cramer³ and others, and one which I have confirmed by many experiments. Solarization is noticeable only when the exposure is 3000-5000 times the unit value and even then it is much less marked than in the case of pure silver bromide collodion. It is noteworthy that the presence of silver nitrate in the film increases the total light-sensitiveness two to four-fold, while it shoves back the solarization limit to such an extent that solarization becomes marked only when the

¹ The same thing was observed by Lüppo-Cramer: *Phot. Correspondenz*, 1902, 694.

² Engliš reached the same conclusion as the result of entirely different experiments.

³ *Phot. Correspondenz*, 1904, 65. (Potassium nitrite acts like silver nitrate.)

exposure is 3000-5000 times the unit exposure, thus much longer than is necessary with a pure silver bromide collodion exposed under water. The traces of silver nitrate, which cling to the silver bromide even after long washing with water, cause a very quick and dense blackening of the plate, so that the solarization is quite masked by it. A short treatment of such a plate with nitric acid (sp. gr. 1.20) after the exposure and before the development changes the plate to such an extent that solarization can readily be detected when the exposure is 1000 times the induction value. The solarization image, however, will not stand up long against nitric acid (especially a strong acid); but it is gradually destroyed so that finally a quite clear, pure negative is obtained either by physical or by chemical development."¹

"If one exposes a silver bromide collodion plate under a scale photometer for different lengths of time from the limiting minimum way up into the region of solarization and of visible blackening, up to 3000 to 10000 times the normal exposure; and if the plate is then fixed with thiosulphate and afterwards developed physically, we find:

"1. On the portions which have received but little light, scarcely more than the induction limit, there appears a normal negative (*negative of the first order*). The substance forming the latent image withstands to a certain extent treatment with nitric acid before the development or a fixing with thiosulphate and a subsequent treatment with nitric acid.

"2. With strong over-exposure we get the *solarization image*, a positive. The limiting illumination at which this appears is undoubtedly displaced by the preliminary fixing and subsequent physical development, but the approximate point is easy to recognize, and the silver bromide is also

¹ I assume that it is well known that the solarization limit for exposed silver bromide plates can be forced back very far by the so-called retarded development (alkaline pyrogallol with a great deal of potassium bromide, for instance, develops with very little alkali, etc.). Cf. Eder's *Handbuch der Photographie*, 5th Ed., 3; Eder's *Jahrbuch der Photographie*, 17, 20 (1903).

blackened visibly at this point.¹ If applied after the fixing and before the development, moderately dilute nitric acid attacks the solarization image slowly, though more rapidly than it acts upon the negative of the first order.

"3. If the over-exposure is enormous, proceeding way beyond the first appearance of solarization, there is quite a distinct blackening of the silver bromide, which can easily be seen after the fixing and which gives rise to a negative (*negative of the second order*) when developed physically, the enormous over-exposure to the contrary notwithstanding.

"When there is a marked blackening of the silver bromide due to an enormous over-exposure, the solarized image is either above or alongside of the strongly blackened product, which last probably contains metallic silver in addition to sub-bromide. If the plate is first fixed with thiosulphate and then developed physically, the very strongly over-exposed parts develop with a blue-gray color as a negative (*negative to the second order*). At the same time the moderately over-exposed portions develop as a solarized positive, while the portions, which have received only a little light, develop as a negative (*negative of the first order*).

"If, however, one takes a silver bromide collodion plate which has been enormously over-exposed (3000-20000 times the induction limit), fixes it, and then treats it for several minutes with dilute nitric acid (sp. gr. 1.20), the nitric acid dissolves the substance forming the latent image of the negative of the second order (metallic silver?) and leaves behind a fairly well-defined though partially destroyed solarization image which with physical development comes out as a clear brown positive on those portions where otherwise there would have developed the blue-gray negative of the second order.

¹ The silver precipitates which form on the visibly blackened silver bromide ($\text{AgBr} - \text{AgNO}_3$) are of a bluer, more transparent color than those which form on the latent AgBr image where there is no visible blackening. Probably on the visibly blackened portions of silver bromide, the fixing sets free metallic silver which acts as nuclei for the precipitation of metallic silver during physical development over and above the nuclei due to the normal subhalide and to the solarized silver bromide image.

"The silver bromide collodion image resulting from enormous over-exposures consists therefore of three kinds of images which can be separated by fixing and subsequent treatment with nitric acid (1.20). After fixing with thio-sulphate, the image due to the *visibly* blackened silver bromide, which gives a negative of the second order when developed physically, can be destroyed by nitric acid. There is then left the substance corresponding to the solarization image though somewhat attacked. On the portions which received less light the substance corresponding to the negative of the first order is left by this treatment in a state in which it can be developed.

"The behavior, therefore, of the latent, solarized and normal silver bromide images towards thiosulphate and towards physical development depends to a great extent on the degree of exposure to light, which rather inclines one to believe that probably different kinds of silver sub-bromide of different chemical compositions are present in the latent image or possibly that we are dealing with solid solutions having continuously varying chemical and photographic properties.

"Further, at the point where solarization is just beginning, thiosulphate changes the latent image so that it then develops as clearly solarized, even at those places where otherwise a normal negative would have been obtained, or at most only traces of solarization. When used for fixing the image before development, thiosulphate makes it possible to develop a solarized image as a normal picture or the normal latent image as a solarized picture. I was not successful, however, in determining any regularities, since the phenomena seemed to occur in a haphazard manner.

"The latent solarized image, if fixed before development, resists the action of dilute nitric acid to some extent and can still be developed. There is, however, a gradual destruction of the solarized image by the nitric acid so that the solarization limit is gradually forced back as the acid acts longer, and consequently the normal image becomes more in evidence.

Behavior of the latent image towards potassium cyanide, ammonia and ammonium bromide with preliminary fixing and subsequent physical development

"A preliminary fixing with a five percent *potassium cyanide solution* destroys most of the latent image on silver bromide collodion, so that only slight traces of it can afterwards be developed physically. A solution of potassium cyanide, to which a lot of sodium sulphite¹ has been added, is somewhat less destructive; but the slight residue of the substance forming the image which survives is easily destroyed by nitric acid and then physical development yields no result. Probably cyanide of potash is more effective than thiosulphate in splitting the sub-bromide into the soluble silver bromide and metal, so that nitric acid dissolves what is left of the image.

"*Ammonia as a fixing agent* acts like thiosulphate. It is easy to see that ammonia dissolves the illuminated silver bromide more slowly than it does that which has been exposed to light. I have myself confirmed this fact first recorded by Englisch.² The color of the silver bromide, which has been exposed to light for only a short time and which contains the substance forming the latent image, is identical with that of silver bromide which has not been exposed, and consequently the latent image cannot be detected by the eye. What remains of the image after the preliminary fixing with ammonia can be developed physically very well so that ammonia is not as effective as thiosulphate in decomposing the silver subbromide or, to put it in a better way, the substance forming the latent image. Instead it probably leaves a large part of the hypothetical subbromide intact and consequently this residual latent image withstands the action of concentrated nitric acid fairly well.

¹ Recommended by Lüppe-Cramer because the mixture of sulphite and cyanide attacks metallic silver much less readily in presence of air than does a pure solution of potassium cyanide. Eder's *Jahrbuch der Photographie*, **17**, 43 (1903).

² *Zeit. wiss. Photographie*, **2**, 516 (1904); Eder's *Jahrbuch der Photographie*, **19**, 363 (1905).

"If we start with washed silver bromide collodion and expose the silver bromide to a strong light until it is blackened visibly, we shall find that ammonia, like thiosulphate, precipitates so much metallic silver during the fixing process, that this silver interferes with the phenomenon of development—physical development—and that only after this metallic silver has been removed by nitric acid (sp. gr. 1.20) does one see clearly the solarization effects always present in a silver bromide collodion plate which has been over-exposed so enormously.

"A saturated *solution of ammonium bromide* can also be used as a fixing bath for silver bromide. Silver bromide collodion plates come out clear from this bath and after this preliminary fixing there remains a slight residual image which can be brought out by physical development. This was first noticed by Lüppo-Cramer¹ and my experiments confirm his statement except that I found that the destruction of the latent image by ammonium bromide was more nearly complete than when thiosulphate was used. The portions of the silver bromide receiving but little light were especially strongly attacked, which is not surprising since Lüppo-Cramer² found that solutions of bromides in general weaken considerably and partially destroy the latent image on silver bromide collodion (reverse formation of normal silver bromide from subbromide). For this reason the latent image after the preliminary fixing may be only a very small fraction of the original latent image. If the silver bromide collodion plates are very much over-exposed, to the point of marked solarization, traces of the solarization image can be brought out by physical development after the plate has been fixed."

"Even when there is a preliminary fixing with ammonium bromide and a subsequent physical development, it is possible, by taking pains, to establish the existence of a negative of the first order, of a solarization image, and of a negative

¹ Phot. Correspondenz, 1901, 418.

² Ibid., 1902, 635.

of the second order. These residual traces of images react with nitric acid in much the same way as do the latent images which have had a preliminary fixing with thiosulphate.

"In consequence of this proof that the residual traces of the latent silver bromide image, which result from a preliminary fixing, do not vary in any definite way with the sulphur content of the fixing medium, we are justified in rejecting, as the most insufficient of all such theories, the one put forward by Precht,¹ without any decent foundation, to the effect that silver sulphide (*silver sulphide theory*) is the substance forming the latent image after a preliminary fixing.

Proof by spectrum analysis that the substance forming the latent image is independent of the wave-length of the light

"If one lets the solar spectrum (quartz spectrograph) act on a silver bromide collodion which has been made sensitive for greenish-yellow, red or green by means of eosine, ethyl violet or some similar color sensitizer, it is well known that one can develop the normal image equally well chemically (for instance with an alkaline hydroquinone solution) or physically (iron vitriol and silver nitrate).

"If one treats the latent image of the spectrum with a sodium thiosulphate solution and if one then develops the film physically, it is possible to develop such a latent image, after fixing, over the whole spectrum for which the sensitized plate would have been sensitive under normal development.

"When the plate has been very much over-exposed, the preliminary fixing leaves just as easily developable traces of the latent image in the portions where the maximum of sensitiveness occurs, in the yellow-green or the red, as it does in the violet or the ultra-violet. When treated with nitric acid in a way similar to that of the previous experiments, the substance of the latent image showed no effect

¹ Cf. Eder: Phot. Correspondenz, 1900, 667; Lüppo-Cramer: Ibid., 1901, 358, 418; Schaum: Phys. Zeit., 1901, 536, 542; Eder: Chemiker Zeitung, 1904, 1005.

due to the wave-length of the reacting light in so far as any qualitative behavior towards chemical agents was concerned.

"From this it follows with great probability that silver bromide plates treated with eosine or other sensitizing dye undergo the same photochemical reaction in the region of the induced light-sensitiveness (yellow-green for instance) as in blue, violet or white light, at any rate as far as the formation of the *normal latent image* is concerned. It is doubtful whether this is also true for the *solarization phenomena*¹ in the red end of the spectrum; but I have not yet been able to settle this question conclusively.

The latent image on silver iodide

"*Silver iodide*² in the form of the 'wet collodion plate,' as used in making reproductions, acts very like silver bromide. If silver iodide collodion is first dipped in a silver nitrate solution and then exposed to light, a ferrous sulphate solution will bring out a latent image after an exposure to daylight equivalent to an optical intensity of about 6-10 second-meter-candles (induction limit). With the Welsbach light which contains less violet, an exposure of about 200 S. M. K.³ is necessary to reach the induction limit. The latent image on silver iodide is but little attacked by nitric acid (sp. gr. 1.40) in six to ten minutes, and still less by more dilute nitric acid (sp. gr. 1.20). After this treatment with acid, the latent image can still be readily developed physically by means of ferrous sulphate and silver nitrate solutions.

¹ When silver bromide collodion is sensitized for green by means of eosine silver, it is easy to obtain normal negatives of the spectrum. After standing for a few days, however, such an emulsion undergoes a spontaneous decomposition in the dark to such an extent that the silver bromide, even without exposure to light, is reduced by the developer and fogs just as though the film had been exposed. When these silver bromide emulsions, which have changed in the dark, are exposed to sunlight and then developed, they show distinct solarization phenomena, like previously exposed silver bromide plates and these phenomena are more marked in the blue and violet than in the green. These same solarization images occur even when the plates are first fixed with thiosulphate and then developed physically.

² Eder: *Rezepte und Tabellen*, 6th Ed., 1906, 26.

³ [Second-meter-candles.]

"If the latent silver iodide image is first fixed with thio-sulphate solution and then developed physically, it turns out to be partially destroyed, up to about 3-5 times the minimum exposure.¹ If the latent image on the silver iodide is first fixed with thiosulphate, then washed and afterwards treated with nitric acid for five or six minutes, the image is destroyed up to exposures of about 25-40 times the minimum. Portions, which have received more light, come out perceptibly with physical development, though the resulting image is considerably weakened." . . .

"The substance of the latent *solarized* image with silver iodide plus silver nitrate solution (wet collodion process), attracts less silver during physical development than does the image resulting from normal illumination; there is thus definite solarization. Aqueous chromic acid destroys both the solarized and the normal latent image to about the same extent² (different from silver bromide). Both forms (the normal as well as the solarized latent image) resist a thio-sulphate solution at least to the extent that they afterwards respond to physical development. In spite of this the thio-sulphate has actually caused an important chemical change in the nature of the latent image. Originally the normal latent image, resulting from a sufficient exposure, withstood the action of nitric acid very well. After the preliminary fixing with thiosulphate solution, the image is completely destroyed by nitric acid (sp. gr. 1.20) acting for only five minutes. On the other hand, the latent *solarization* image on silver iodide, after fixing with thiosulphate, resists nitric acid for a short time to such an extent that a solarized image may afterwards be developed physically. If the nitric acid acts for a longer time, however, there is such a change that a normal negative develops instead of the solarization image. These reactions make it probable that the latent, developable image on silver iodide collodion consists of silver subiodide

¹ The figures vary a good deal with the time that the thiosulphate acts and the nature of the developer subsequently used.

² *Ide Photr., Correspondenz*, 1902, 645.

which is decomposed by thiosulphate almost completely into silver iodide and metallic silver (different from the behavior of the hypothetical silver subbromide in the latent image).

Explanation of the recorded phenomena in terms of the subhalide theory

"The subhalide theory is able to explain without difficulty the complicated experimental behavior, toward chemical reagents, of the latent image in a silver bromide film.

"The substance of the normal latent image (negative of the first order) consists of silver bromide reduced in varying amounts to subbromide.

"We assume further for the case of progressive illumination that, in consequence of a photochemical setting free of bromine, at the beginning of the exposure to light there is found a silver bromide corresponding very closely in composition to normal silver bromide. This subbromide, however, as we see from the process for making photographic negatives is more rapidly reduced by reducing agents to metallic silver than is the pure unexposed silver bromide. This modification of subbromide is destroyed by thiosulphate as well as by nitric acid. By means of this assumption we explain all the phenomena recorded in regard to the latent silver bromide images which result from very short exposures.

"With a somewhat longer exposure there is formed a silver subbromide which constitutes the latent image of the normal negative. It is only slightly attacked by nitric acid. With increasing exposure it yields on development a normal negative with the normal characteristic blackening curves corresponding to it. This silver bromide is less readily soluble than silver bromide in solutions of the fixing media, such as ammonia, ammonium bromide or thiosulphate. After the preliminary fixing of the latent image this subbromide therefore remains as a residual image which can be developed physically in spite of its having undergone certain changes. Depending on the chemical nature, the

concentration, or the temperature of the fixing bath, this silver subbromide is developed more or less completely into the soluble silver bromide and undissolved metallic silver so that the residual image consists of subbromide mixed with more or less of metallic silver. Potassium cyanide causes the greatest decomposition and with it the residue consists of metallic silver only.

"If one allows nitric acid to act on the latent image after it has been fixed, the substance forming the image is destroyed still more, the destruction being greater the more completely the image consists of metallic silver. Since the silver is dissolved, more or less of the image will be removed and there will remain behind some subbromide, the presence of which can be shown by physical development. But even this is broken down, by a continuous treatment with concentrated nitric acid, into silver which dissolves and silver bromide which does not respond in the dark to physical development, but which at once forms new nuclei for physical development if it is exposed to light and this converted again into a developable subbromide.

"With a very strong over-exposure of the silver bromide there is formed a *solarization image*, the substance of which is not identical with the directly blackened silver bromide which is apt to be formed at the same time. This substance has a different chemical composition and different chemical properties from the substance forming the negative image of the first order.

"With more intense over-exposure and subsequent development we get the negative of the second order. The latent image from which this was formed probably consisted of a mixture of at least three chemically different substances, namely of metallic silver, of the substance constituting the solarization image, and of the subbromide constituting the image which yields the negative of the first order. All these substances are shown to be present not only by their photographic behavior towards the photographic developer, but by their different chemical behavior towards thiosulphate,

ammonia, nitric acid, etc. The substance formed by the direct blackening of silver bromide in light shows a different photographic action from that of the latent or the solarized image. This can be explained less well on the assumption of a solid solution of variable amounts of Ag_2Br in silver bromide. It is more probable that different modifications of silver subbromide occur in the differently illuminated portions of the silver bromide film.

"The latent image on silver iodide with an excess of silver nitrate seems also to consist of silver subbromide, which, however, seems to be more easily decomposed into metallic silver and silver halide than is the case with silver subbromide.

"The substance forming the normal latent image on silver bromide does not vary in its qualitative behavior towards chemical reagents with the wave-lengths of the light that produced it. Color sensitizers (eosine, ethyl violet, etc.), which make silver bromide light-sensitive to light of longer wave-length, force the silver bromide to the same photochemical reaction of the silver subbromide formation in the production of the latent image which is characteristic of silver bromide by itself in the blue, violet and ultra-violet regions of the spectrum."

Abney believed that the forcing-back of the solarization, when potassium nitrite is added to the film before exposure, is due to the reducing action of the potassium nitrite. Lüppo-Cramer¹ maintains, however, that the only action which nitrites, sulphites and silver nitrate have in common is that of accelerating the splitting off of bromine from the silver bromide. Being "chemical" sensitizers they increase the light-sensitiveness of the plate, but Lüppo-Cramer feels that we do not know at all why they prevent solarization.

"Wilbert² made experiments with silver bromide plates which were exposed beyond the solarization limit. With an exposure of one minute to diffused daylight under a dense

¹ Phot. Correspondenz, 1904, 65.

² Eder's Jahrbuch der Photographie, 17, 461 (1903).

diapositive, there was partial solarization; with exposures of from four to eight minutes there was complete solarization with but slight differences due to the length of exposure. In the camera an exposure of one-half second gave a normal negative; with a larger stop and a longer exposure, eighty times the amount of light still gave a negative, though a flat one, when the plate was developed with the same metol-hydroquinone developer. With eight times as much light the plate was in the so-called zero state, being pretty thoroughly fogged, but showing signs of reversal. With ten thousand times the amount of light, a completely reversed, solarized image was obtained, the development taking place in the dark and lasting three minutes. A similarly over-exposed plate was developed in diffused daylight and a solarized image was also obtained, but the development took three times as long.

"Among the developers, the least suitable for bringing out solarized pictures were: pyrogallol, amidol, eikonogen, metol. These work too rapidly and consequently irregularly. Hydroquinone is much better, either with or without alkali; in the latter case the picture is reddish-brown.

"The reversal of under-exposed negatives has been studied by A. Guébbard,¹ who found that positives can be obtained from moderately sensitive, under-exposed plates provided these plates are developed slowly. As developer, he used a solution of the following composition: 3 g anhydrous sodium sulphite, 1 g pyrogallol, 3 g sodium carbonate in one liter of water. Guébbard worked at a temperature of 8° C and drew the following conclusions from his experiments:

"1. When under-exposed plates are developed slowly, the reversal begins at those points which received the least light.

"2. With two under-exposed plates, one of which had been exposed twice as long as the other, the reversal occurred much quicker on the plate which had had the shorter exposure.

¹ Eder's *Jahrbuch der Photographie*, 19, 388 (1905).

"3. In a normal developer a plate, which gave a good negative in two hours, was only half reversed in six hours and then with a formation of a thick fog.

"4. Provided an over-exposure does not reach the point of the ordinary reversal, it does not help this new reversal but rather retards it very much."

In 1890 Waterhouse found that the addition of small amounts of phenyl-sulpho-urea to the developing bath caused a reversal. In a paper¹ read before the Asiatic Society of Bengal in April, 1891, Waterhouse said:

"At the meeting of the Society in August last, I exhibited some specimens of a curious reversal of the photographic image produced by adding small quantities of thio-carbamides or sulpho-ureas to the ordinary eikonogen developer, and showed that although reversal of the image was by no means uncommon, it was usually caused by over-exposure or some other abnormal action of light, whereas to produce these new reversals even less than the ordinary exposure was sufficient, and they appeared to be entirely due to some peculiar action of the thiocarbamide added in very minute quantities to an alkaline eikonogen developer.

"At that time I was quite unable to offer any opinion as to the probable cause of these reversals, or as to how they were produced, beyond stating the probability that, although there were many points of difference, they would be found to be in accordance with the generally accepted theory worked out by Capt. Abney, and were due more or less to oxidation or rehalogenization of the exposed parts of the film, and that owing to the peculiar reducing action of the alkaline thiocarbamides the film during development was practically in the same state as if it were over-exposed. It seemed also probable that sulphur was the active agent in producing reversals.

"Further work with these curious salts and especially

¹ Major-General Waterhouse was good enough to send me reprints of several papers of his, on solarization, this one among others. These reprints have been of great assistance to me in preparing this paper.

with a compound salt of thiocarbamide and ammonium bromide, discovered by Prof. J. E. Reynolds in 1868 and called by him tetrathiocarbamid-ammonium bromide, which was found to be exceedingly active in producing perfect reversals of the image with very short exposures, led me to the belief that this complete change of deposit from the lights to the shadows of the photographic image must be more or less due to electro-chemical action. The subject of electro-chemistry is one of which I have little knowledge, but I have been able to make some simple experiments from which, though not conclusive, it seems probable that my surmise is correct, and so far as they go, they seem to establish that not only, as former observations by Lermontoff, Eder and Abney had shown to be probable, is the ordinary process of photographic development of sensitive surfaces containing silver haloids, accompanied by electrical action, but that the addition of these minute quantities of thio-carbamides to the developer, greatly increases the intensity of the electrical action and produces a reversal of the current which should also account for the reversal of deposit.

“With the aid of a very sensitive galvanometer, which has been kindly loaned me by the Rev. Fr. Lafont, S.J., who also assisted me in the experiment, it was found that when a pair of pure silver plates coated with finely precipitated silver bromide, one of which had been exposed to light and the other not, were connected to the galvanometer so as to form a galvanic couple and immersed in the ordinary eikonogen developer, the exposed plate formed the negative pole and the needle was deflected to the left, while in the developer containing a little thio-sinamine, the exposed plate formed the positive pole and the needle was deflected to the right.

“This experiment has been successfully repeated several times with several plates prepared in the same way and with other thio-carbamides, also with silver plates bromized by dipping them in bromine water; and so far the occurrence of the reversal is well established.

"I have also tried the same experiment with ordinary dry plates rendered conductive in various ways, the best of which appears to be gold leaf applied either on the face of the film or behind it. Gelatine offers very great resistance to the current, and though I have obtained distinct evidence of currents in both directions, they are not always observable, nor is it quite certain that they are caused by electrolytic action within the gelatine film, and further investigation as to this is necessary.

"I have also found that reversals of the reduction products, somewhat similar to those obtained by photographic methods, may be obtained entirely without the agency of light by passing a current from a single bichromate cell through a pair of silver plates coated with silver bromide and immersed in eikonogen developers prepared with or without thio-carbanides. In this case the plate attached to the carbon pole in the plain developer showed only a very little black deposit, while the plate attached to the zinc pole showed a very strong dark deposit all over. A pair of similar plates immersed in some of the same developer to which a few drops of a solution of thio-sinamine had been added showed quite different results, the plate attached to the carbon pole showing a strong black deposit, while the plate attached to the zinc pole was almost clear on the face and free from deposit, showing only a slight tarnish, caused by sulphur. I have some plates of this kind here, though the reversed effect is not quite so strong as it was on my first plates. I have found it difficult to obtain such marked reversals again though I quite believe they are obtainable and the best conditions for securing successful results have yet to be ascertained.

"Some similar effects were produced on Eastman's bromide paper and on ordinary dry plate films to the silver plates.

"Although results obtained with silver bromide on silver plates are not quite comparable with those obtained with ordinary gelatine plates, these experiments show that

under favorable circumstances the action of developing solutions on silver bromide is accompanied by distinct electric action, and that these thio-carbamide reversals may be produced by electrical methods and are attended by a reversal of current. How this reversal of current is brought about is not yet quite clear, but seems to be explained by some observations on metallic sulphides, by W. Skey, recorded in Vol. XXIII of the *Chemical News*. He found that sulphides which have the power of conducting can also generate electricity and that silver sulphide is positive to metallic silver. In a battery consisting of a sulphide and a metal in acidulated water, the gas liberated is sulphuretted hydrogen, the nascent hydrogen exerting a desulphurizing action upon the metallic sulphide, the ultimate effect of which is in some cases to completely reduce the mineral to the metallic state. He also shows that these sulphides are capable of performing the functions of the negative element of a galvanic couple.

"It seems probable, therefore, if electrolytic action does take place in gelatine films during the process of photographic development, that, according to the laws of electrolysis, with the ordinary developers the exposed parts of the plate form the negative pole and attract the metallic elements and hydrogen, while the bromine, or other halogen and acid radicals, with the hydroxyl go to the unexposed parts forming the positive pole.

"On the other hand, with the alkaline thio-carbamide developers, at the same time that silver is reduced on the exposed parts, silver sulphide is formed on the unexposed parts which then become the negative pole and attract the sulphur, the hydrogen and some of the silver from the exposed parts, while the halogen and hydroxyl pass to the positive pole and transform part of the remaining silver into silver haloid which is dissolved in the fixing bath.

"Although this theory, as stated in a rough way, seems to agree fairly well with the facts, and from the experiments I have made seems probably the correct explanation of the

reversals, I do not feel myself yet able to put it forward authoritatively, and a great deal of further investigation is required. The subject is a very difficult one beset with uncertainties, and requires more time and close attention than I have been able to give for working it out fully."

It is clear by this time that the effect due to an over-exposure may be modified profoundly by the treatment which the plate receives after exposure. In the following paper Precht¹ goes one step further and claims that solarization is a phenomenon of development only.

"From the law of mass action it follows necessarily that the splitting off of bromine from silver bromide under the influence of light must eventually lead to a state of equilibrium, and then the reaction will proceed no further. This is not changed at all, even if one assumes that a second reaction takes place between the bromine set free and the binding material of the film. The blackening curve of silver bromide gelatine must therefore end with the maximum possible density, with the so-called neutral zone. This is not the case, however, and one observes the phenomenon of reversal of solarization. Some work by Englisch on the lesser effect of intermittent illumination has rather led to the view that in the light there are two distinct kinds of change, one a normal and the other a solarizing change. Now films which have been much over-exposed and which are developed normally, show solarized and normal particles side by side. If such films are developed very slowly, they show normal pictures and no solarization. It has, however, been impossible so far to show a solarizing change due to light which has occurred quite independently of the normal change. On the other hand, Abney's experiments have proved conclusively that solarization can be checked by the presence during the exposure of certain reducing agents, such as potassium nitrite, and can be increased by the presence of oxidizing agents. It seems therefore quite possible to simplify

¹ Internat. Kongress angew. Chemie, Berlin, 4, 351 (1903).

our conceptions and to consider that solarization takes place entirely in the time *after the exposure*. When the action of the light has ceased, the bromine set free can convert the photobromide back into normal bromide which is more difficultly reducible and therefore causes the phenomenon of solarization. Of course such a conception has no other value than that of a working hypothesis.

"This conception has the special advantage of making the lesser effect of intermittent illumination intelligible. To test it more fully I have extended to silver bromide gelatine the experiments of Abney which referred especially to collodion emulsions. These experiments are closely allied to the earlier experiments on the use of acetone bisulphite in a retarded developer. Apart from the fact that the acetone bisulphite, like any acid sulphite, decreases the reduction velocity by neutralizing partially the alkali of the developer, there are other reactions which are probably the important ones. I have previously called attention to the fact that acetone bisulphite reacts with the oxidation products of the developer and therefore acts as a reducing agent. This is confirmed by a number of experiments in which plates were bathed in a 1-5 percent solution of acetone bisulphite, dried, and then exposed to intense light. When these plates are developed in a normal developing solution, it is seen that the amount of solarization is surprisingly small. Even the sun's image is only reversed with difficulty. At the same time another change becomes evident, the formation by tanning of large grains when the amount of acetone bisulphite is high. This tanning action is also one to which I have previously called attention. It decreases the diffusion in the film and I look upon this as the essential reason for the advantages due to this compound in the case of a retarded developer, though of course all three causes work together.

"A long time ago Abney¹ called attention to the fact that strongly illuminated portions of ordinary silver bromide

¹Treatise on Photography, 1893, 309.

swell less readily than the other portions. This is always very noticeable if one lays in water a plate which has received a long exposure to the sun.

"It appears to be important to establish that no solarization can occur if the developer is already present in the film at the time of exposure. To carry out the experiments the plates were saturated with a developer solution containing no alkali, and afterwards dried. They were then exposed to any bright source of light for a suitable time (long enough so that with ordinary plates and ordinary developer, solarization would be very marked, and were developed simply by being laid in a soda solution.¹ No solarization can take place so long as there is any unchanged reducing agent on the high lights. The following experiment, for instance, shows how far this holds: On an ordinary plate, lay one impregnated with developer, and on the film of the latter lay a piece of metal with holes cut in it. Expose to full sunlight for five minutes and then develop. The impregnated plate shows an ordinary negative while the normal plate is completely solarized even though the light falling on it has passed through the impregnated plate.² This result is entirely in accord with Abney's experiments and with the theoretical ideas I have outlined. There are, however, a number of necessary consequences which must still be tested."

Eder³ comments as follows on this theory of Precht's:

"It is well known that the blackening in the developer of a silver bromide gelatine plate, which has been exposed to the light, increases only up to a certain maximum exposure and decreases if exposed for a still longer time. This phenomenon is called "solarization." It is also well known that the appearance of solarization can be checked by a suitable development, by using weak developers or developers

¹ I have been informed that the technical use of such a process has been patented by the Farbenfabriken vorm. Friedr. Bayer and Co., Elberfeld.

² This experiment was first tried by Herr Süss.

³ Eder's *Jahrbuch der Photographie*, **17**, 20 (1903).

whose rate of reduction has been decreased by addition of restrainers (such as potassium bromide) or by a suitable change in the proportions of the developer. Under this we must also include the developers with a decreased alkali concentration such as the pyrogallol-sulphite developer without alkali or the edinol developer with acetone sulphite and very little alkali, as recommended by Precht. When the over-exposed plate is developed there first appears a normal negative which on further development changes into a solarized image (positive). *This is the usual phenomenon on developing partially solarized plates.*

"The theory of this phenomenon has hitherto been considered to be that in the solarized plate some other photochemical change in the silver bromide gelatine has taken place than that occurring in a normally exposed negative, that the two types of light images are superposed, and that one developer brings out the one image the more rapidly and another developer the other image, so that it is possible by a suitable choice of the developer to keep the solarization phenomenon (change of negative into positive) within any desired limits or to check it entirely.

"Precht¹ makes the assertion: Solarization is exclusively a phenomenon of development which has no necessary connection with the photochemical change of the silver bromide.

"This theory is however false and entirely unfounded, as I have shown,² for its experimental foundation is bad and it can only have arisen through ignorance of the literature of the subject.

"It is well known that a normal development can be obtained by a chemical treatment of silver bromide which has been over-exposed to the point of solarization. It is only necessary to treat the over-exposed silver bromide film with certain chemical reagents before developing and then to develop with an ordinary developer. Thus one can get a nor-

¹ Phys. Zeit., 1902, 426.

² Phot. Correspondenz, 1902, 570.

mal negative with the same developer which (without the previous treatment) gives a solarized picture.

"I will run over some characteristic experiments on the phenomenon of solarization which were recently described.¹ It is easy to prepare solarized plates if one places a dry plate in a Chapman-Jones scale photometer² and exposes it for ten to sixty minutes to a gas light at a distance of 40 to 50 cm.

"The silver bromide gelatine plates³ used by me behaved as follows with an ever-increasing exposure:

H. M. S.	Necessary quantity of light in candle-meter- seconds.
First appearance of latent normal image (induction limit)	0.1
Powerful half-tone of normal negative	1.3
Deep blackening in the lights	8-10
Beginning of the direct photographic blackening ⁴	3000-10000
Beginning of solarization at limit of neutral zone ⁵	27000-40000
Satisfactory reversal	300,000 and over.

"If one takes as unity" the amount of light necessary to produce a normal negative, my experiments show that, with a pyrogallol-soda developer and no potassium bromide, there is a marked appearance of solarization for an exposure of 3000, while a fairly thorough solarization calls for an exposure of 10,000 or even 30,000. These figures vary a good deal with the nature of the plate.

Forcing back of the solarization limit by retarded development

"If one uses a very slow-acting developer, to which restrainers, especially potassium bromide, may be added if

¹ Phot. Correspondenz, 1902, 645.

² Ibid., 1902, 430.

³ Commercial plates of medium sensitiveness.

⁴ Varies very much with the nature of the plate.

⁵ Varies with the time of development and the use of the ordinary metal developer or of pyrogallol.

⁶ About 10 candle-meter-seconds (H. M. S.) with my dry plates.

necessary, the limit of solarization can be forced back very much and the greatly over-exposed portions of the silver bromide plate may be developed as a normal negative even though they would solarize with the ordinary developers.

"If one develops such a plate with a pyrogallol-soda developer to which 1-10 percent of crystallized potassium bromide has been added, the solarization limit is forced back considerably. It is forced back still more by the mixture of edinol developer (1:25) with one percent solid acetone sulphite¹ as recommended by Precht, but the pyrogallol and potassium bromide gives a stronger negative with better gradations in the region of great over-exposures, well beyond the solarization limit. The same is true of many other developers."

"With respect to the rate of development of over-exposed plates, I mention merely that it is well known that many developers without alkali develop the latent image very slowly and that they act more energetically with increasing amounts of alkali.

"One should not be misled, however, into considering solarization exclusively as a development phenomenon."²

Forcing back the solarization limit on over-exposed dry plates by treatment with chromic acid before development

"Aqueous solutions of bromine change the solarized image into a silver bromide gelatine which develops as a normal negative. If the bromine acts for a longer time, both images are destroyed. Lüppo-Cramer³ made this observation for collodion emulsion and for gelatine plates, with which last, however, there is a disturbing tanning of the gelatine. Then Schaum and Braun⁴ found that ammonium persulphate not only destroys the latent image but also removes the solarization. Solarized silver bromide gelatine films develop

¹ Phot. Correspondenz, 1902, 570.

² Cf. Phot. Correspondenz, 1902, 569.

³ Wissenschaftliche Arbeiten auf dem Gebiete der Photographie, 106 (1902). Cf. also Phot. Correspondenz, 1901, 134.

⁴ Phot. Mittheilungen, 1902, 224.

normally with hydroquinone if they have been soaked for twenty-four hours in a 2-5 percent persulphate solution. I found that in aqueous solution chromic acid¹ (1 g potassium bichromate, 3 g sulphuric acid and 100 cc water) works in a similar way but more rapidly and in a very reliable manner. This solution destroys the weak normal latent image² and decreases the solarization enormously. The highly solarized silver bromide is changed after fifteen minutes' action into a state which permits the development of a normal negative,³ instead of a solarization diapositive.

"During this change the visible photographic blackening on the over-exposed plate is partially destroyed for the weaker ranges of the sensitometer. The remaining blackened portions can be developed after the treatment with chromic acid, but as a normal negative and not as a solarized image.

"With a mixture of concentrated chromate solution and nitric acid (for instance, 2 g potassium bichromate, 6 cc concentrated nitric acid and 100 cc water), exceptionally strong solarization effects may be overcome by letting the solution act for one-quarter to three-quarters of an hour. When such an over-exposed plate is washed and developed for instance with the ordinary metol-soda developer, fifteen to twenty minutes' developing will bring out a negative free from fog and with good gradations, running from No. 1 to 13 or even 20 numbers of the Jones sensitometer, depending on the length of time the acid is allowed to act. Without the chromate treatment, the same developer would have developed a similarly over-exposed plate so as to produce the strongest solarization phenomena and a good deal of fog.

¹ First used by me in 1881 to remove fog. *Phot. Archiv* (1881).

² This is true, for instance, for dry plates which on development give a blackening from 1-16 of the Scheiner sensitometer. Such latent images are completely destroyed by chromic acid.

³ For the destruction of the solarization image by partial fixing with sodium thiosulphate, see *Englisch: Eder's Jahrbuch der Photographie*, 16, 73 (1900).

"In Figs. 5 and 6¹ are the faesimiles of silver bromide plates exposed up to strong solarization and developed, one before and the other after a treatment with chromic acid. Fig. 5 shows the solarization image resulting from the ordinary development. Fig. 6 shows the partial forcing back of the solarization limit due to treating for fifteen minutes with bichromate and sulphuric acid, and then developing. In places there is a normal negative, and the general fog, due to irradiation and to halos, is partially destroyed. In Fig. 7¹ we have the complete reversal of the solarization image, after the treatment with bichromate and nitric acid, into some thing which develops as a normal negative. All the plates were developed with the same metol developer.

"This treatment of solarized plates with chromic acid is more effective as a means of removing solarization effects than the mere variation (retarding) of the developer. This proves anew what Lüppo-Cramer had already shown that it would be false to consider solarization exclusively as a development phenomenon. As a matter of fact, by treatment with chromic acid, solarization can be eliminated over very wide ranges without changing the composition of the ordinary developer in the slightest. Furthermore, all the other methods which I have recommended for eliminating solarization, work well and in a reliable manner."

In the lecture before the Camera Club to which reference was made in the beginning of this paper, Waterhouse calls attention to the fact "that Dr. Luther has quite recently enunciated the theory that solarization is caused by free bromine hardening the gelatine, and so rendering it impermeable to the developer in the most exposed parts; so that, in some cases, the silver bromide is reduced more quickly on the less exposed parts than on the most exposed, and the result is the production of a transparent positive. By retarding development in various ways, this tendency to reversal may be overcome. This theory, though possibly ap-

¹ [Not reproduced in this paper.]

plicable to gelatino-silver bromide dry plates could not be so to the cases of reversal with other forms of sensitive plates in which the same phenomenon is observed.

"Dr. R. Englisch has pointed this out.¹ He says that if we have to do with the hardening of the gelatine film, the diffusion of solutions will be affected. Assuming that by prolonged exposure the subbromide is actually formed, the amount of bromine set free will increase with the length of exposure, and will exercise a strong hardening effect on the gelatine. The fixing solution will therefore be able to dissolve less silver bromide from the hardened parts than from the unaltered parts, and if a plate treated in this way is then developed a reversal of the image must result. By adding sodium thiosulphate to the ferrous oxalate developer, Eder obtained reversed images upon over-exposed plates. What happens in that case is not quite known, but here it depends directly on the reversed and separate actions of the fixing medium and developer. Englisch then describes an experiment in which rapid dry plates were exposed to magnesium light in slips with normal and over-exposures sufficient to produce solarization and loss of density. After exposure the plates were divided in two. One set was developed, and the other placed in a 10 percent solution of hypo for measured periods from 1 to 5 minutes, and then developed with metol soda, until the maximum density was attained. With the plates that had been in the hypo for 5 minutes, the slips which showed the greatest density on the directly developed plates showed clear glass, while the slips which were solarized on the developed plates developed with full density on the partially fixed plates. The full density of these plates was quite destroyed, but the sequence of the densities was entirely reversed, so that the solarized parts were the densest, and the normally exposed were the thinnest."

In a paper before the Berlin Congress of Applied Chemistry, Englisch says:²

¹ Archiv. wissenschaftliche Photographie, 230.

² Internat. Kongress angew. Chemie, Berlin, 4, 423 (1903).

"The normal development of slightly solarized films by means of acid sulphites is looked upon as the result of the prevention of the diffusion of the developer where the gelatine has been made insoluble at the solarized portions. The blackening is due to the slow diffusion of the developer, to its decreased reducing power owing to the acidity, and to its retarded action. It is believed that in the retarded normal development only the normally changed silver bromide grains at the surface are reduced. In contrast to this the normally changed portions are first oxidized when bichromate is applied, and the solarized portions are all that remain available for the subsequent development. The same thing occurs in the partial fixation, previously suggested by the author, in which the normally changed portions are dissolved before the solarized portions.

"Just where solarization begins, intermittent illumination gave clearer, apparently more completely changed portions than a continuous illumination of the same period. That was explained on the assumption that the simultaneously occurring normal and solarizing changes must both take place to a lesser extent with intermittent illumination; but that the normal changes will vary markedly and the solarizing changes but little from those under continuous illumination. Since the lesser difference in the solarization causes a greater blackening and that of the normal change a greater blackening, the difference between the two will be what counts. If only the normally affected portions are developed by means of a retarded developer, the difference in blackness between the two effects of light will be greater, while they will be smaller if only the solarized portions are alone developed by means of oxidation.¹ This expectation was confirmed by experiments. It appears also that the lighter and darker stripes which appear with a retarded development are surface stripes, but that the variations in blackness which ap-

¹ [I don't know what this passage means and this may have affected my translation of it. The reader is therefore advised to refer back to the original—W. D. B.]

pear during the normal development of a solarized plate are determined by the relations between the surface and a certain thickness of the film; they represent the integral of the prevailing conditions varying periodically with the illumination."

In an admirable paper from Luther's laboratory, Weisz¹ shows that a hardening of the gelatine is not the cause of solarization and that the explanation of the phenomenon must be sought elsewhere, "presumably in an actual chemical change in the nucleus of the latent image." Weisz goes on to say that the results of his experiment, No. 16, show that the strong oxidizing agents convert the substance forming the solarized image into something which can form solid solutions with silver. He points out that, according to Schaum, treatment with persulphate causes a normal development of solarized films. He then adds that "the fact that solarized layers give normal pictures when developed physically after being fixed (experiment No. 17*b*) shows that the substance forming the latent solarized image decomposes in presence of sodium thiosulphate into silver and something which is soluble in thiosulphate."

That there is still a radical difference of opinion as to what causes solarization is shown by a recent paper by Homolka² in which an entirely different explanation is given.

"In several papers which have appeared in *Phot. Correspondenz* during the current year, I have shown that one can develop the latent image on silver bromide gelatine by means of indoxyl or thioindoxyl and that the negative picture thus obtained is not homogeneous, but consists of a silver image and an indigo image. The two images can be separated without difficulty. If the developed and fixed plate is treated with a potassium cyanide solution, the silver image dissolves while the blue indigo image (or the red thio-indigo one) remains. However, if one treats the developed and fixed plate with an alcoholic sodium hydrosulphite solution, the

¹ Zeit. phys. Chem., 54, 344-350 (1906).

² Eder's Jahrbuch der Photographie, 21, 58 (1907).

indigo picture dissolves as 'indigo-white' while the black silver image remains. From these facts we draw the conclusion that the substance of the latent image also is not homogeneous but must contain two constituents. One of these I consider a silver perbromide, perhaps AgBr_2 ; it can oxidize indoxyl to indigo and thus causes the 'indigo image.' The other constituent is very probably a silver subbromide or the corresponding mixture of $\text{Ag} + \text{AgBr}$; under the action of indoxyl it is reduced to metallic silver, which presumably acts as a silver nucleus and causes the formation of the 'silver image.' In the following way it proved possible to prepare the two constituents of the latent image separately by purely chemical methods without the intervention of light. If an unexposed dry plate is treated with very dilute bromine water, there is formed a latent perbromide image which develops in an indoxyl bath to a pure blue 'indigo image.' On the other hand, if one treats an unexposed plate with a very dilute stannous chloride solution, there is formed a 'latent subbromide image' which develops in the indoxyl bath to a black 'silver image.' As a result of these experiments I adopted the view that the latent image is formed according to the following equation:

The film of a silver bromide gelatine dry plate, after exposure to light, consists therefore of the following three substances:

- "1. Silver perbromide, AgBr_2 .
- "2. Silver subbromide, Ag_2Br or $\text{Ag} + \text{AgBr}$.
- "3. The original unchanged silver bromide, AgBr .

"On the basis of these results and supported by further experimental data, I attempted finally to give an explanation of the phenomenon of solarization. On a silver bromide gelatine dry plate which had been over-exposed to the point of solarization, I was able to show that the 'indigo image' developed by means of indoxyl is not solarized and that, if the plate is first fixed and then developed physically,

the resulting 'silver image' is also not solarized. In fact both come out as normally graded negatives. From this the conclusion follows directly that the two latent images the 'silver perbromide' one and 'silver subbromide' one were also not solarized. The amounts of the two effective constituents of the latent image perbromide and subbromide—therefore increases continuously with increasing illumination and no reversal takes place. At first sight it appears paradoxical that the two latent images, when developed together chemically, should give a solarized picture. It becomes intelligible, however, if one reflects that the increase of perbromide and subbromide is necessarily accompanied by a decrease in the amount of the unchanged silver bromide—which last of course furnishes the material from which the silver image is developed. *I look upon this decrease in the supply of silver bromide as the cause of solarization.* With a certain degree of illumination there will be reached a certain equilibrium and the plate will perhaps show the maximum blackening if developed at the stage where there is exactly one molecule of silver subbromide (equal to one atom of 'silver nucleus') to one molecule of silver bromide. If one exposes beyond this stage there is an increase in the amount of silver perbromide and of silver subbromide ('silver nucleus') while the amount of silver bromide decreases. If the plate is developed at this point, the silver nucleus finds less silver bromide to influence than it did at an earlier stage and in consequence the density of the negative must decrease; in other words, there is a reversal of the image.

"Further experiments in this field have shown that, by purely chemical means, solarized images can be obtained from properly exposed non-solarized silver bromide gelatine dry plates. The necessary plates (about 11° to 12° Scheiner) were exposed behind the Chapman-Jones scale photometer for 30 seconds to a paraffin candle at a distance of 305 mm. They were then developed in an indoxyl bath, fixed and washed. If one treats the green negative, thus obtained,

with a potassium cyanide solution, the silver image dissolves, as I have shown before, and there now remains only the pure blue negative indigo picture. This statement as I have since found is only partially accurate and requires the limitation that the plate shall be developed in the indoxyl bath only long enough to produce a negative with plenty of detail, in other words for about 6 to 10 minutes at about 20° C. If one leaves the plate in the indoxyl bath for perhaps half an hour to an hour, the picture gains continually in strength and finally becomes a dark greenish-black. If one then fixes the plate and puts it in the potassium cyanide bath, the indigo image remains behind as a beautiful *solarization negative*. The scale fields from 1 to 10 appear to be solarized, while the others, up to about 22, come out as a blue indigo negative with normal gradations.

"It was not difficult to find an explanation for this *apparent solarization*; it turned out that finely divided silver in a potassium cyanide solution was able to reduce indigo, *i. e.*, to dissolve it as indigo-white. If one places finely-divided indigo and molecular silver in a test-tube, adds a twenty percent potassium cyanide solution, and heats slightly, after a while a portion of the indigo goes into solution as indigo-white. If the solution is now filtered, a clear, light yellow solution is obtained from which air quickly precipitates clots of indigo again. The same process obviously takes place when one treats with potassium cyanide solution a negative which has been developed much too long in an indoxyl bath. The 'silver image' dissolves the 'indigo-image.' When the amount of silver is the greatest the action lasts the longest, *i. e.*, at the points where the illumination has been strongest.

"On the other hand, if one fixes and washes a plate which has been developed for an excessive length of time in an indoxyl bath, and then puts the plate into a potassium cyanide bath to which a little potassium ferri-cyanide has been added, this oxidizing agent contracts the reducing action of the silver. The "silver image" dissolves very rapidly

and there is left a non-solarized indigo negative with normal gradations. If this treatment is given to these plates which have been exposed for an equal length but which have been developed in the same indoxyl bath, one for ten minutes, another for thirty minutes, and the third for an hour, the result is three indigo negatives of exactly the same strength and gradation. From this it follows that the prolonged action of the indoxyl developer intensifies the silver image only and not the indigo image. This is perfectly intelligible in view of what has been said in regard to the nature of the latent image and the process of development."

In Part II, I intend to take up the work of Nipher, Wood and Lugzin. There is also an important paper by Lüppo-Cramer to be considered, to say nothing of the recent work of Trivelli. After that I hope to show the usefulness of the theory of Grotthuss.

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