THE ELECTROCHEMISTRY OF LIGHT. VIII

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The Theory of Solarization. Part II

Liesegang¹ has coined the word "pseudo-solarization" to describe cases in which both a positive and a negative image occur on the plate, the positive being the more dense. Lüppo-Cramer² considers that there are numerous instances of pseudo-solarization and he describes the matter as follows:

"Eder³ first noticed that a reversal was obtained with a normally exposed plate when hyposulphite was added to the ferrous oxalate developer. Kogelmann⁴ observed the same phenomenon when a good deal of ammonia was added to a metol or an amidol developer.⁵ Liesegang offered an explanation to which we shall return later.

"Recently Adrien Guéhard has made a careful study of reversals on normally exposed plates in his interesting and illustrated papers: 'Inversion de l'image sous-posée par sur-développement lent,'⁶ 'Un mode nouveau d'inversion photographique'⁷ and 'Sur l'inversion photographique.'⁸ This investigator mentions often the appearance of the dichroic fog in connection with the phenomenon; but does not have in his solutions the conditions which other authors have believed to be absolutely essential. The reason for the solution of silver bromide in Guéhard's experiments or for the reduction of silver bromide to colloidal silver, to speak more generally, is evidently the great dilution of the developer.

¹ Phot. Correspondenz, 1895, 558.

² Photographische Probleme, 184 (1907).

³ Eder's Handbook der Photographie, 5th Ed., 3, I, 114 (1902).

⁴ Eder's Jahrbuch der Photographie, 13, 379 (1899).

⁵ Cf. also Reeb. Bull. Soc. Franç. (2), 21, 207 (1905).

⁶ Ibid., 20 (1904).

⁷ Sciences, Arts, Nature, 6, 148.

⁸ Revue des Sciences Photographiques, 1904, 257; 1905, 97. References are also given to the literature.

When I repeated Guébbard's experiments, using the pyro developer diluted to one-third, fifteen hours stand development of ordinary dry plates brought out reversed images similar in every respect to those obtained by Eder and by Liesegang as a result of adding substances which dissolve silver bromide to developers of normal concentration. If one takes a developer with only one-third the water in it that Guébbard recommends, a normal development is obtained with the same exposure. This is a further confirmation of what has been stated previously, that the reducing power of the solution must be decreased to cause the formation of a dichroic fog.

"When diluted sufficiently, any developer will fail to develop either the latent image or the chemical fog on an ordinary plate. Its only effect will be to reduce the whole of the silver bromide to colloidal silver. Thus a twenty- to thirty-hour treatment of normally exposed plates with a very dilute hydroquinone developer did not bring out a trace of an image, and the plates looked, after fixing, almost as though they consisted of unchanged silver bromide. This phenomenon was first described by Liesegang¹ who assumed that a thin film of metallic silver prevented the thiosulphate from fixing the plate. This hypothesis is incorrect because the apparently unfixed plates are made transparent by being bathed for a few minutes in a chromic acid solution. This proves that we were dealing with a very light modification of reduced silver and not with silver bromide at all. Under the microscope such films show only the uniform, round grain of the 'dichroic' fog and no trace of the ordinary fog-grain or even of unchanged silver bromide.

"With plates for transparencies, a fairly concentrated developer will cause the reversal of the image. Thus, with a *p*-amidophenol, soda developer, containing no sulphite, completely reversed images were obtained in two hours. In the same developer a highly-sensitive plate gave no sign

¹ Eder's *Jahrbuch der Photographie*, 15, 654 (1901).

of a reversal. The tendency to chemical development was so strong under these circumstances that even a long development brought out only a small amount of dichroic fog along with the normal image.

"Another case of pseudo-solarization, which has been known for a long time, depends on the use of thio-carbamides, and was described by Waterhouse¹ in 1891 in his paper entitled 'A New Method of Obtaining Direct Positives in the Camera.' A year later Waterhouse² attempted to give an explanation of the reversal caused by these substances and he described some electrochemical experiments in which these same compounds caused a reversal of the voltaic current. The action of the sulpho-ureas is however so similar to that of other substances which dissolve silver bromide that the same explanation must certainly apply throughout. In favor of this view are the later experiments of Waterhouse³ and of Emerson Reynolds⁴ in which it was shown that it is advisable to add ammonium bromide⁵ to the developer in addition to the thiocarbamide.

"My own experiments confirmed completely the view, which I had previously expressed,⁶ that the thiocarbamides act exactly like thiosulphate and other solvents⁷ of silver bromide. The action of thiosinamine (allyl sulpho-urea) and still more that of thiocarbamide is so rapid that only very small amounts can be taken if one is to get a satisfactory reversal. Starting with 5 percent solutions, I added 0.5 cc. of the thiosinamine solution or 0.1 cc. of the thiocarbamide solution to 100 cc. of a hydroquinone-soda solution. Waterhouse recommended⁸ especially the eikonogen developer

¹ Eder's Jahrbuch der Photographie, 5, 283 (1891).

² Ibid., 6, 170 (1892).

³ Ibid., 16, 482 (1902).

⁴ Ibid., 17, 460 (1903).

⁵ Cf. Lüppo-Cramer, Photographische Probleme, 176 (1907).

⁶ Phot. Correspondenz, 1905, 162. I afterwards found that R. E. Liesegang had expressed the same view before me (Phot. Archiv, 1985, 303).

⁷ The solubilities of the silver halides in the thiocarbamides were determined quantitatively by Valenta (Phot. Correspondenz, 1894, 283).

⁸ Eder's Jahrbuch der Photographie, 8, 405 (1894).

and later the metol developer; but the nature of the development is of no importance. As I have said so often, the result depends entirely on the rate of development by the developer. In other respects the same points are important for a successful reversal, as with the reversals studied by Eder, Kogelmann, and Guébbard. The exposure must be just the right length and the amount of the substance dissolving silver bromide must depend on the relation between its own reaction velocity and that of the developer; a great deal depends also on the degree of ripening of the plate, on the time of development, etc., etc. Waterhouse himself mentions in his first paper that the composition of the solution must vary with the nature of the plate and with the object to be photographed. In fact he says at the end that the whole process is so new, so sensitive and involves such complicated chemical reactions that it will probably be some time before the process finds its way into practical use.

“When describing the experiments on pseudo-solarization, Liesegang¹ stated that the images that he obtained became very much darker when dried, and lighter when moistened again. I observed the same thing with plates developed in presence of thiocarbamide and this hangs together with the behavior of every fine-grained silver precipitate as is well known, for instance, in the case of silver chloride emulsions.²

“It may also be mentioned that the development with the thiocarbamides apparently never gives the lighter, distinctly ‘dichroic’ silver precipitates which are obtained with some of the other ‘dichroic’ methods of development. The precipitate often had such a uniform chocolate shade that one might easily think that another reaction had taken place. It is well known that the sulfo-ureas are easily saponified to carbon dioxide, hydrogen sulphide and ammonia.

¹ Phot. Archiv, 1895, 300.

² Cf. Lüppo-Cramer (Phot. Correspondenz, 1906, 492); also the important paper by Schaum and Schloemann [Zeit. wiss. Phot., 5, 109 (1907)], which appeared while this book was in the press.

Valenta¹ has also proved that the solution of silver chloride in thiosinamine is decomposed by alkalies with formation of silver sulphide. Bogisch² confirmed this for thiocarbamide. The solutions of silver bromide also undergo the same change. Nevertheless the action of chromic acid on the precipitate obtained by development in presence of thiocarbamides is in keeping with the view that, in presence of reducing agents, the deposit is at any rate chiefly silver. A microscopic examination shows a complete identity between the form of the grain in this case and in those in which other 'dichroic' developers were used. Also, the reversal with thiocarbamide occurs when one is using the acid iron developer, and the silver sulphide reaction cannot then occur.

"Among the reversals caused by substances which dissolve silver bromide, we must also include the normal development of plates exposed to the solarization point. This was done by Kogelmann,³ using thiocarbamides, ammonium sulphocyanate, or thiosulphuric acid. The action is really not surprising, because at those points at which the greatest reduction would take place after a solarizing exposure, the reduction of the dissolved silver bromide would take place to the least extent. Since the silver reduced from the dissolved silver bromide has a much greater covering power than the other, the heaviest precipitates occur where there has been the greatest action due to light. I obtained only traces of the reversal of solarized images with thiocarbamide in the developer; but I got satisfactory reversals when I gave the plate a preliminary bath in a very dilute solution of thiocarbamide. Of course, with a reaction so complex and so dependent on a large number of variables, it is only occasionally that one gets a good picture. Since the Kogelmann solution of thiosulphuric acid is known to decompose very rapidly, it must be very much more difficult to get good results with it.

¹ Eder's Jahrbuch der Photographie, 8, 413 (1894).

² Ibid, 8, 413 (1894).

³ Phot. Mittheilungen, 31, 6 (1894).

In fact Kogelmann himself says that it is a difficult art to work successfully with thiosulphuric acid.

"Whether Kogelmann's development of solarized films with thiosulphuric acid corresponds to the similar experiments by Vidal¹ and to my explanation² of the latter depends chiefly on the exposure and on the time that the thiosulphate acts in Vidal's experiments. The brown color³ of the image indicates that the change of the solarized latent image to a normal one is due at least in part to pseudo-solarization as a result of dissolved silver bromide.

"The cases of pseudo-solarization which have been described are all special cases of the phenomenon that ordinary development and the reduction of dissolved silver bromide are mutually antagonistic. We owe the first careful study of color fog as well as of many other points to R. E. Liesegang, and he explains⁴ the tendency of the dichroic fog (red fog) to precipitate chiefly on the unexposed portions of the plate as follows:

'We shall see why the red modification of silver precipitates only on the unexposed portions and not on the exposed portions, if we recall that the red modification results from the reduction of a dissolved silver salt. On the exposed portions less silver bromide can dissolve in the small amount of thiosulphate because the silver bromide at those points has already been reduced to a certain extent to metallic (black) silver.'

"If we consider this explanation in connection with the obvious fact, also previously recognized by Liesegang,⁵ that the fine-grained silver of the red fog has a very much greater covering power than the ordinary silver grain of a negative, and if we also keep in mind what I have previously pointed out, namely that silver germs, resulting from ex-

¹ Bull. Soc. Franç., 1898, 582.

² Lüppo-Cramer, Phot. Correspondenz, 1904, 123.

³ Cf. Eder's Jahrbuch der Photographie, 16, 79 (1902).

⁴ Phot. Archiv., 1895, 302.

⁵ Ibid., 1895, 290.

posure to light, decrease the solubility of silver bromide, the phenomenon of pseudo-solarization becomes fairly intelligible.

"When comparing the fine-grained plates for transparencies with highly-sensitive plates, we must keep in mind the greater tendency of the latter to develop chemical fog and the readier solubility of the fine grains of the former. This difference comes out noticeably in those cases where colored fog is formed when there is no substance present which has a special tendency to dissolve silver bromide, with developers requiring no sulphite, such as *p*-amidophenol or pyrocatechuic acid. If one adds substances which dissolve silver bromide very rapidly, such as sulphocyanates, ammonia, etc., there is nothing like so marked a difference in the colored fog on the ordinary and the fine-grained plates.

"From the special case of stand development as it occurs in Guébbard's experiments, we deduce the important fact that when a developer of definite composition is diluted more and more, the power to produce chemical development decreases very much more rapidly than the power to reduce silver bromide to colloidal silver."

Lüppo-Cramer's idea is that the silver bromide dissolves and that metallic silver is then precipitated from the solution. This precipitation would naturally be heaviest at the points where there was the most silver bromide and could therefore cause a reversal. Lüppo-Cramer¹ has also shown that, with a metol-silver intensifier, silver is deposited very rapidly on fine-grained silver and much less rapidly on a silver with coarser grain.

Although recognizing the accuracy and ingenuity of Lüppo-Cramer's experiments, the work that we have done at Cornell leads us to suggest a somewhat different explanation, one that is really based on Lüppo-Cramer's own experiments.

In the previous paper,² it was suggested that the Waterhouse reversal, with thio-urea in the developer, might be the

¹ Eder's *Jahrbuch der Photographie*, **19**, 411 (1905).

² Bancroft, *Jour. Phys. Chem.*, **13**, 459 (1909).

result of a displacement of the curve for composition and rate of development. On this hypothesis, the case would be precisely similar to the one which we meet when we change from a weak developer to a stronger one. Experiment has since shown that this hypothesis does not represent the facts. While the hypothesis does account for the production of a positive with a shorter exposure than is usually necessary, it postulates the possibility of developing a negative if the exposure is made shorter still. We have found that this negative cannot be realized and it is therefore necessary to account for the phenomenon in another way.

When a plate is immersed in a developer containing thio-urea, a negative first appears and afterwards a positive. After the plate has been fixed, it is usually possible to detect the two images on the plate by means of reflected light. The negative image is on the air side of the film while the more dense positive image is underneath it, and can be seen on the glass side of the film. It was found possible to duplicate these results by developing a weak negative in an ordinary developer and then immersing the plate in the developer containing the thio-urea. This proved that the negative image was the normal silver image usually obtained by development. To show that the presence of this silver image is not essential to the reversal, it was dissolved in a bath of acidified permanganate before the plate was placed in the developer containing thio-urea. The positive image, which was thus obtained, was of course somewhat better than that obtained under ordinary conditions because it was not blurred by the presence of a superposed silver negative. It was supposed that the positive image was silver sulphide; but analysis showed that it was almost entirely silver, so nearly so that the traces of silver sulphide could be attributed to side-reactions which had nothing to do with the theory of the phenomenon.

Since the positive image was essentially silver, it was clear that the sulphur in the thio-urea was of no importance as such and that some other property of the thio-urea was

the important one. Since there is a minimum exposure below which a given developer will not produce any image on a given plate in a given time, it was believed that the negative image might be suppressed entirely if the exposure were made sufficiently short, and that only the positive image would appear. Experiment confirmed this prediction completely. If the light had produced no change in the plate, no developer could have brought out an image, either positive or negative. Consequently we see that a so-called minimum exposure does change the plate although this change cannot be detected by means of the developer which contains no thio-urea. Since the developer containing thio-urea develops a positive image, it must develop the unexposed silver bromide more rapidly than that which has been exposed. A necessary corollary is that a developer which contains thio-urea will fog a plate which has not been exposed to the light. This was also confirmed experimentally. After we had reached this point, the rest was plain sailing. We know that ammonia dissolves silver bromide which has not been exposed to light more rapidly than silver bromide which has been exposed.¹ Thio-urea dissolves silver bromide.² Substances which dissolve silver bromide coarsen the grain and make the emulsion more sensitive.³ The action of the thio-urea is therefore to make the unexposed silver bromide relatively more sensitive than the exposed bromide. If the exposure has been so short that neither the unexposed nor the exposed silver bromide will blacken in the developer containing no thio-urea and if the effect of the thio-urea is to carry the unexposed silver bromide over into a state where the developer can blacken it we shall get a positive as we actually do. If this explanation is the correct one, it ought to be possible to divide the process into two stages. If we bathe an exposed plate in a solution

¹ Englisch: Eder's Jahrbuch der Photographie, **19**, 363 (1905). Lüppo-Cramer: *Ibid.*, **22**, 306 (1908).

² Reynolds: Jour. Chem. Soc., **53**, 861 (1888). Valenta: Monatsheft, **15**, 249 (1895).

³ Lüppo-Cramer: Eder's Jahrbuch der Photographie, **21**, 367 (1907).

containing thio-urea alone, this should ripen the emulsion and we should then be able to develop the plate as a positive by washing it and then immersing it in an ordinary developer. This has actually been done. The Waterhouse thio-urea developer is therefore one having two entirely distinct functions. The thio-urea ripens the emulsion and the developer develops it. Unless the times of the two processes are adjusted very carefully, the result is bad, just as it is in a bath in which one tries to combine developing and fixing.¹ The more rational way under most circumstances is to use two baths and to have the process completely under control.

According to this point of view, sulpho-urea causes an increase in sensitiveness which is followed by chemical development, while Lüppo-Cramer believes that sulpho-urea dissolves silver bromide which is then changed to silver by so-called physical development. When the process proceeds in two stages, there is no sulpho-urea present when the developer is added. Consequently there can be no physical development unless we are going to call everything physical development, in which case we should have made no progress at all. I am quite prepared to admit that dichroic fog results to a large extent, perhaps entirely, from reduction of dissolved silver bromide to silver; but I do not admit that the formation of a dichroic fog is a necessary accompaniment of a reversal. Lüppo-Cramer himself admits that there is little or no dichroic fog when the reversal is brought about by means of thio-carbamide and our experiments confirm this. Lüppo-Cramer's explanation applies therefore to what is merely a fortuitous though frequent accompaniment of the reversal.

In the case of the Guébhard reversal the sensitizing agent is undoubtedly the sulphite.² It being an ineffective one, the developer has to be very dilute and the time of development has to be long. Kogelmann³ found that a metol de-

¹ Baker: *Phot. Jour.*, **28**, 1 (1904).

² Cf. Liesegang: *Arch. wiss. Phot.*, **2**, 263 (1901).

³ Eder's *Handbuch der Photographie*, 5th Ed., **3**, I, 114 (1902).

veloper containing a good deal of ammonia gave reversals. Here the ammonia is the sensitizing agent.

In the previous paper,³ it was pointed out that for a certain range of exposures, a strong developer will bring out a positive image and a weaker developer a negative. There are one or two interesting cases of this to which I wish to draw attention. Einsle² made a specialty of photographing the interiors of churches. Although the exposures varied from ten minutes to two hours and a half, he did not get a single poor negative. He attributed this result to his having used a slow developer, hydroquinone with very little alkali. The composition of the developer was: 40 grams sodium sulphate, 10 grams hydroquinone, 2 grams potash, 400 cc. water. Development lasted from fifteen minutes to an hour. While these plates were probably none of them over-exposed to the point of solarization, some of them had undoubtedly reached or were approaching the first zero state for the ordinary developer. By using a special developer, the exposure corresponded to the ascending part of the curve and good negatives resulted.

Eder³ states that adding potassium bromide to a ferrous oxalate developer checks solarization with over-exposed plates while the addition of sodium thiosulphate increases solarization. The action of the bromide is exactly what one would expect because it slows up the developer. The action of the hyposulphite is not quite so simple. We are accustomed to look upon a hyposulphite solution merely as a solvent for silver bromide. As a matter of fact it is a reducing agent which may reduce silver bromide to metallic silver under favorable conditions. It may also act as a sensitizer to silver bromide and it can act on silver bromide which has been partially decomposed by light and can convert it into silver or a silver-rich substance by dissolving silver bromide out of it. This last property it shares with potassium cyanide,

¹ Bancroft: *Jour. Phys. Chem.*, **13**, 457 (1909).

² Eder's *Jahrbuch der Photographie*, **6**, 111 (1892).

³ Eder's *Handbuch der Photographie*, 5th Ed., **3**, I, 114 (1902).

ammonia, etc, etc. Eder¹ says that "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;" and also that "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 sub-bromide 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 and fairly well.

"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."

Whether a hypo solution is to act chiefly as a solvent, as a reducing agent, as a sensitizer, or as a precipitant of silver, depends on the nature of the plate, the degree of exposure, the other things in the solution, the concentration of the hyposulphite and the time that the solution is allowed to act. As I hope to discuss this more in detail at some other time in another series of papers, I will content myself with having pointed out the intricacy of the problem. Since Eder did not have all the possibilities clearly in mind, it is not surprising that he should have written as follows:²

"At the point where solarization is just beginning, thiosulphate changes the latent image so that it then develops

¹ Cf. *Jour. Phys. Chem.*, **13**, 63 (1909).

² *Ibid.*, **13**, 62 (1909).

as clearly solarized, even at those places where otherwise a normal negative would have been obtained, or at most 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."

In the particular case under consideration, the hyposulphite probably acts as a reducing agent, since we know that it accelerates the ferrous oxalate developer if added in the proper proportions.¹

There is now nothing obscure in Eder's remarks on the forcing back of the solarization limit by retarded development.²

"If one uses a very slow-acting developer, to which restrainers, especially potassium bromide, may be added if 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 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 1 percent solid acetone sulphite³ 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."

¹ Cf. Eder's *Handbuch der Photographie*, 5th Ed., 3, II, 465, 473 (1903).

² Cf. *Jour. Phys. Chem.*, 13, 80 (1909).

³ *Phot. Correspondenz*, 1902, 570.

The forcing back of the solarization limit by treatment with chromic acid or nitric acid before development is a simple matter theoretically. These acids dissolve silver readily, the silver-rich bromides less readily and the rate of action decreases as the silver content approaches that of the orthodox silver bromide. Consequently, nitric or chromic acid first eliminates the silver image of the second negative as has been previously pointed out.¹ It then dissolves silver to a certain extent from the silver-rich bromides, changing them into the form in which they develop as negatives. This method is applicable to almost any degree of over-exposure whereas it has been shown² that the method of retarded development gives positives when the over-exposure has been sufficiently great. This is exactly in line with the following statement by Eder³ in regard to the matter.

"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."

Englisch⁴ found that an over-exposed plate gave a positive on short development and a uniform blackening when developed for a longer time. If the plate is partially fixed before development, by soaking for five minutes in a 1:10 sodium thiosulphate solution, enough of the unexposed silver bromide dissolves to give a negative on long development. This change is a perfectly intelligible one. If silver

¹ Bancroft: *Jour. Phys. Chem.*, **13**, 461 (1909).

² Bancroft: *Ibid.*, **13**, 460 (1909).

³ *Jour. Phys. Chem.*, **13**, 83 (1909).

⁴ Eder's *Jahrbuch der Photographie*, **15**, 608 (1901).

bromide is dissolved more rapidly where the change by the light has been the least, there will be more left where the effect of light has been the greatest. When the remaining silver bromide has eventually been blackened by the developer, the greatest blackening will be where there is the greatest residual amount of silver bromide, and we consequently get a negative.

Vidal's experiments¹ are apparently of the same type because he soaks his plate before development in a two percent solution of hyposulphite for two minutes. Though he does not say so, it is quite impossible that his plate should have been completely fixed under these conditions. Englisch used a 10 percent solution and soaked his plates for five minutes; but he speaks of his plates specifically as being only partially fixed.

At first sight, Kogelmann's experiments² with thio-sulphuric acid and with sulpho-urea seem to come under this same head; but this is certainly not true as far as the experiments with sulpho-urea are concerned because the concentrations are so small that the amount of silver bromide actually dissolved by the sulpho-urea is negligible. The effect of the sulpho-urea must be the same as in the Waterhouse experiments and it must therefore increase the sensitiveness of the unexposed or partially decomposed silver bromide to the developer. In that case we should expect the greatest blackening where the action of light had been least, in other words, in the shadows. That would give a very dense plate consisting of two superposed positives, the blacker one coming from the sensitized silver bromide and the paler one from the latent image. Our experiments show that this is the normal result, though this seems not to have been recognized either by Kogelmann or by Lüppo-Cramer. It is probable that these gentlemen classed such plates among the "70 percent of failures." We have been rather more successful and we can

¹ Bull. Soc. Franç., 1898, 582.

² Phot. Mittheilungen, 31, 6 (1894).

duplicate our experiments indefinitely, getting positives or negatives as we please by varying the conditions of development.

As Lüppo-Cramer has pointed out, one has more control over the conditions if the process is carried out in the two stages of a preliminary bath in a sulpho-urea solution followed by development in a solution containing no sulpho-urea. If an old developer is used or a dilute one, there first develops an excellent positive which is the same positive that one would get if one were to omit all sulpho-urea. On further development the plate clouds and then a negative appears. This is the negative obtained by Kogelmann and by Lüppo-Cramer. It is rather a blurred negative because it is superposed with a positive. If the film is treated with a chromic acid solution, the negative image is destroyed before the positive image and we get back to a good positive if the attack is stopped at the right moment.

If the development of the plate is not stopped at the moment when the blurred negative is complete, the plate clouds again and we finally get a positive. If the developer is fresh and not too dilute, the intermediate stage of the negative is not detected. Kogelmann's negative image is therefore merely the result of retarded and incomplete development and does not represent anything more than a transitory stage. It seems probable that the appearance of the negative is primarily the result of a diffusion phenomenon, the sulpho-urea sensitizing the plate more rapidly at one point than at another. Why it should do this is of course an interesting problem but it does not come within the scope of this paper.

From the photographic point of view the Kogelmann negatives seem to be quite valueless because they are blurred. From the theoretical point of view, their value is not very great now that we know that they occur only as an intermediate step during development with exhausted or dilute developers. On the other hand, it would be of great interest if such an intermediate step could be brought to light in the Waterhouse process because that might give us extraordinarily

rapid plates. We are now making experiments along this line and we shall be able to report either positive or negative results in the next paper.

We can now take up Homolka's experiments.¹ Homolka² says:

"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." There is nothing surprising about this. When the silver bromide is reduced, the developer must be oxidized and the oxidation of the developer will be greatest at those points where the reduction of the silver bromide is greatest. In most cases the oxidation products of the developer are soluble. In the special case considered by Homolka, one of the oxidation products is blue (or red) and insoluble. Consequently we get a blue indigo image or a red thio-indigo image in contact with a silver image.

Homolka says further that "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 indigo picture dissolves as 'indigo-white' while the black silver image remains." There is nothing mysterious about this. The silver is removed by potassium cyanide which does not attack indigo, while sodium hydrosulphite reduces indigo without acting upon the silver. It would be easy enough to find other pairs of chemicals which would give similar results.

Instead of seeing that this result is the only one that could be expected under the circumstances, Homolka evolves a most ingenious theory. "From these facts we draw the

¹ Eder's *Jahrbuch der Photographie*, 21, 58 (1907).

² *Jour. Phys. Chem.*, 13, 86 (1909).

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 cause the indigo image. The other constituent is very probably a silver sub-bromide 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."

Homolka overlooked the fact that if a sub-bromide of silver is reduced to metallic silver by the action of indoxyl, the indoxyl must be oxidized and consequently there is no reason to assume the existence of a perbromide in order to get the indoxyl oxidized.

Although the assumption of a perbromide is apparently unwarranted, Homolka describes two very interesting experiments which at first sight seem to confirm his view. "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 sub-bromide image which develops in the indoxyl bath to a black silver image."

It does not seem probable that this is a full statement of the facts. In the first place there is nothing to show what would have happened if there had been no silver bromide in the gelatine. If we assume, pending further investigation, that bromine compounds of gelatine play no part in the results, then treatment with a suitable stannous chloride solution must produce the same result as light and we must get both a silver image and an indigo image when we develop in an indoxyl bath. If the stannous chloride solution were a trifle too concentrated, it would reduce the silver bromide to a substance relatively low in bromine and there would then be

less indoxyl reduced relatively to the amount of silver produced. The blue image might then have been overlooked by one who was not especially on the watch for it. The experiment with bromine water becomes intelligible when we remember that bromine and many other substances increase the sensitiveness of silver bromide to the developer to such an extent that an unexposed plate fogs readily in the developer. Since the silver bromide is not reduced by the bromine water or the other substances as it is by light, there will be more indigo image formed relatively to the silver image than under normal conditions and we then face the possibility of the silver image having been overlooked.

As to the fogging effect of bromine water and other substances, I quote from Lüppo-Cramer.¹

"Among the chemical reactions which point to a fundamental difference between chemical fog and latent image, the action of bromine water is of importance. In suitable concentration² it attacks the latent image on dry plates but leaves the chemical fog intact. With collodion plates neutral potassium bromide solution acts just as bromine water does on gelatine films, which is due to the greater 'protecting action' of gelatine previously mentioned. The action of bromine water is duplicated by that of a number of other substances,³ such as potassium ferricyanide, permanganate, ferric chloride, and cupric chloride. All these substances act upon the latent image rather than on the chemical fog. In fact, in certain concentrations they add a not inconsiderable plus to the fog already present in ripened emulsions. Bromine water is able to produce fog when acting in concentrations which vary a good deal with the nature of the plate. Nitric acid, sulphuric acid, hydrochloric acid, and persulphate all fog highly sensitive dry plates completely while the latent image suffers very little by such treatment. Hydrogen peroxide

¹ Photographische Probleme, 131 (1907).

² The details of these experiments are given in *Phot. Correspondenz*, 1902, 634.

³ Cf. *Phot. Correspondenz*, 1903, 224.

leaves a latent image completely intact even when it has produced the maximum amount of its well-known fogging action.

.....

"It is important to note that hydrogen peroxide, nitric acid, etc., only fog those plates which have a chemical fog¹ which accounts for the different way in which they act on different plates, as was pointed out also by Graetz in the case of hydrogen peroxide.² Since the peroxide also destroys the latent image and decreases the sensitiveness, we might assume that the action of radiation only takes place with highly sensitive plates, while with less ripened plates the chemical or oxidizing action predominates to such an extent that the radiation produces no perceptible effect.

"What however makes the action of these chemical reagents seem fundamentally different from that of light even though we should have to consider a radiation, is the fact that the light unquestionably causes a direct reduction which is quite out of the question with one class of fogging substances and is very improbable, to say the least, with another class, of which hydrogen peroxide in neutral solution is an especially good instance. At present we have practically no definite point of view as to the way in which fogging is caused by oxidizing agents, acids, salts of the metals, etc."

If the indoxyl developer has the power to reduce bromine compounds of gelatine in Homolka's experiments, it would not be necessary to assume that one of the images had been overlooked. This assumption would also be unnecessary in case Homolka did not wash out the bromine or the stannous chloride thoroughly. So far I have not been able to obtain copies of Homolka's original papers in *Photographische Cor-*

¹ Phot. Correspondenz, 1903, 227.

² The most remarkable instance is that of bromine water, the fogging effect of which has already been mentioned. Many kinds of plates are badly fogged by a brief immersion in very dilute bromine solution (5 cc. saturated bromine water to one liter of water). Many remain unchanged and some even lose some of their chemical fog. Similar irregularities were observed when sensitizing optically with some isocyanines. These are all cases which the orthodox chemistry of to-day fails utterly to handle.

respondenz and consequently I do not know definitely what precautions he did or did not take. It is quite certain, however, that there is an error somewhere in his results and we plan to repeat his experiments just as soon as we learn more details in regard to them.

Homolka's experiments in regard to solarization are also not conclusive.¹ "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 the silver sub-bromide one, were also not solarized. The amounts of the two effective constituents of the latent image—perbromide and sub-bromide—therefore increase 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 sub-bromide 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 sub-bromide (equal to one atom of silver nucleus) to one molecule of silver perbromide. If one exposes beyond this stage, there is an increase in the amount of silver perbromide and of silver sub-bromide (silver nucleus) while the amount of silver bromide decreases. If the plate is developed at this point, the silver

¹ Jour. Phys. Chem., 13, 87 (1909).

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."

Homolka has assumed that the latent image was a normal one because he was able to develop a negative under special conditions, preliminary fixing followed by physical development. This is the more inexcusable because the change from positive to negative with changes in the developer or as a result of a preliminary treatment with reagents is perfectly familiar. In this particular case, the thiosulphate sets free more silver¹ from the parts which have received the most exposure and consequently more silver precipitates at those parts during physical development thus producing a negative. As Homolka does not state in his paper how he obtained his indigo negative on a solarized plate, we shall have to leave this point until the experiments have been repeated. There is no ground however for the assumption that Homolka's reasoning is better in the case where temporarily we cannot check him than it is in the cases where we can check him.

The explanation of the solarization as due to the decrease in the amount of unchanged silver bromide is pretty unsatisfactory from any point of view and it involves the explicit assumption that the unchanged silver bromide "of course furnishes the material from which the silver image is developed." This assumption may be true, though I doubt it; but there is no of course about it and it should not be used as a starting-point in an argument until it has been justified to some extent. This is the more necessary because Englisch² states explicitly that only the silver bromide which has been exposed can be developed.

Stenger³ has noticed that thin films reverse more quickly than thick ones. Other things being equal, this would of course be the case because the light would have more chance to act on the silver bromide.

¹ Bancroft: *Jour. Phys. Chem.*, **13**, 548 (1909).

² Eder's *Jahrbuch der Photographie*, **15**, 605 (1901).

³ *Ibid.*, **22**, 384 (1908).

Englisch¹ claimed that solarization was not a continuous process; but his arguments seemed to have been disposed of by Vojtech² who showed that Englisch's results were vitiated by the unsteadiness of the burning magnesium ribbon which he used as a source of light.

Blanc³ has published a paper on sensitive reversible plates for the production of reversed positives in the camera and I quote an abstract of it,⁴ with a few verbal changes.

"The author says he has lately obtained a gelatino-bromide emulsion which is of interest because its action is just the reverse of an ordinary emulsion. Plates coated with it blacken completely without exposure to light, and, if exposed, the action of the developer diminishes in proportion to the length or intensity of the exposure. He at once took advantage of this curious property to obtain some copies by contact in a pressure frame and some transparencies in the camera, which, although weak, were well defined. They could be intensified by ordinary methods. With short exposures of a second in the camera, these plates gave a very feeble negative, and the film blackened all over if the development were pushed.

"An interesting experiment was to cut a plate in two, then to expose one-half for about a minute near a window, keeping the other in the dark. On developing them side by side in the same developer, the exposed plate began to darken slightly while the other remained white, but as the development went on, the latter darkened and became quite black, while the former did not change further, so that after fixing, the two portions of the plate showed a striking contrast when laid upon white paper, the one being black and the other a grayish white.

"The author's explanation is that the production of an emulsion of definite character is never homogeneous, it always

¹ Zeit. wiss. Photographie, 1, 364 (1904).

² Eder's Jahrbuch der Photographie, 19, 386 (1905).

³ Bull. Soc. Franç. (2), 17, 256 (1901).

⁴ Phot. Jour., 25, 319 (1901).

contains more or less of others in different states. He considers that, in his reversing plates, there is a minimum quantity of normal emulsion which, under the action of light, produced the graying of the piece exposed, and to this small quantity of normal emulsion may be attributed the weak negative image obtained in the camera with short exposure. And if, by under-exposure and prolonged development of normal plates, fog is produced, this is probably due to a small quantity of reversing emulsion formed at the same time as the normal emulsion.

"The author's reversing emulsion was obtained by carrying on the ripening of the normal emulsion until it showed a colorless image of the sun instead of a blue one. It would seem therefore that a certain degree of ripening may produce effects due to a prolonged action of light on ordinary sensitive plates. In the latter the formation of the latent image is attributed to a partial dissociation of silver bromide, the entire film containing this salt in the natural state; in the reversing plates, on the contrary, the entire coating would have undergone a commencement of dissociation and the latent image would be constituted by the renewal, by the light, of the silver bromide in its natural state."

What Blanc has done is to ripen his emulsion to such an extent that the silver bromide has been reduced either by the gelatine or by other substances in the emulsion to the stage corresponding to the zero state. Exactly the same effect could have been obtained by fogging with light or in a number of other ways. By retarded development it would probably have been possible to have developed a negative instead of a positive, though this cannot be proved now.

This case is fundamentally different from and must not be confused with one cited by Sterry which I shall now discuss. Sterry¹ published a short note on the reversal of the photographic image by means of under-exposure which seems to me of fundamental importance though I have not been able to find any further reference to the matter.

¹ Phot. Jour., 27, 290 (1903).

"Some forms of chemical fog in an emulsion are discharged by weak light, the greatest protective result being found with an exposure about equal to that which first causes reduction by development in the usual way. It is therefore possible to obtain a direct positive with an exposure about thirty to forty times less than that required to obtain a negative. A plate (preferably chloride) must be chosen which cannot be used in the ordinary way without a restrainer in the developer. It is then found only necessary to develop a short exposure without bromide to obtain a positive and a longer exposure with bromide (to obtain) a negative.¹ As the two images overlap, it has not been found possible so far to obtain the high lights without any fog. Similar results were obtained by General Waterhouse² by the addition of thio-carbamide to the developer, and by the writer³ by means of auxiliary exposure, but in the present case the result is obtained solely by development without bromide."

In the discussion that followed, "Mr. Sterry added that he had brought an example for those present to see. The upper plate, which had a variety of exposures, was cut in halves; the one part was developed in a solution containing bromide and made an ordinary negative, and the other without bromide, which showed as an ordinary negative at one end and as a positive at the other. Below that, he had made a positive from an autotype set up of test negatives from which a direct positive from the positive was obtained with a very short exposure. At present there had been no application of this, but General Waterhouse had said that, if done effectually, direct positives might be useful in astronomical work. In this case, however, he found that only special plates acted satisfactorily. Perhaps a study of emulsions might reveal something regarding the separation of the two images, and they might eventually obtain enormous rapidity."

¹ The examples shown were made upon a 'Gaslight' lantern plate with a paramidophenol developer, using a double quantity of potassium carbonate.

² Jour. Phot. Soc. India, 3, 160 (1890); 4, 21 (1891).

³ Brit. Jour Phot., 1893, 686.

We have succeeded in duplicating these experiments of Sterry's using ordinary bromide plates. Of course, if we have a plate which fogs in the developer and if light prevents the formation of fog, we shall necessarily get a positive on development, which is just what happens. A statement of what seem to be the experimental facts is not an explanation, though it may be the first step towards one. At present we do not know at all why light should check the formation of chemical fog under any conditions and it is possible that we may have to take up the whole question of chemical fog in detail before we can find an answer to the problem. For the moment we are busying ourselves with questions of manipulative detail. Later, we hope to discuss the theory of the process.

Carey Lea¹ has discussed some interesting analogies between the action of light and the action of sodium hypophosphite. Since the results appear to involve a reversal by sodium hypophosphite, I quote at length :

"I next pass to the consideration of the identity existing between the photo-salts and the material of the latent image. Before entering, however, on that matter, it is necessary to describe a reaction leading to the formation of these photo-salts, somewhat differing from the reactions already mentioned, and which has important bearing on the subject.

"The remarkable action which an alkaline hypophosphite exerts on salts of copper was described many years ago by M. Würtz. Its action on silver salts, though there is no parallelism between the two, has enabled me to find a key to some of the great difficulties of the latent image.

"A dilute solution of sodium hypophosphite, if poured over a mass of chloride, bromide or iodide of silver formed in the absence of light, produces no visible effect, but has the property of bringing those substances into the condition in which they exist in the latent image. Applied in strong solution and with the aid of heat, it produces brown-purple

¹ Am. Jour. Sci. [3], 33, 482 (1887).

photochloride, bromide and iodide of silver. I will here briefly describe the first of these compounds in order to continue the series of photochlorides, and then pass to the consideration of the latent image.

Photochloride of Silver by Sodium Hypophosphite

"Silver chloride, freshly precipitated with excess of HCl and well washed, placed in a flask with a strong solution of sodium hypophosphite and heat applied begins to darken before the boiling point is reached. Actual boiling for ten or fifteen minutes gives a deep chocolate color. This product well washed and freed from traces of metallic silver by cautious boiling with very dilute nitric acid has a pink, red or brown color varying in intensity according to the length of the action. Sometimes a lavender shade is produced, and this is more apt to be the case when the silver chloride has been precipitated with excess of silver nitrate instead of excess of HCl.

"Silver determinations of two specimens of the purified product were made, indicating the presence in one specimen of 1.77 percent of subchloride, in the other of 3.53.

"By the continued action of heat for many hours a complete reduction to metallic silver takes place.

"Photochloride obtained in this way has generally a brown or dull purple color. Boiled with nitric acid it is apt to break up in as many minutes as some other forms would require hours for decomposition, yielding white chloride, while the nitric acid takes up small quantities of silver.

Identity of Photo-salts with the Material of the Latent Image

"It is proposed here to show:

"1st. That in the entire absence of light, sodium hypophosphite is able to affect a sensitive film of silver haloid exactly in the same way as does light, producing a result equivalent to a latent image formed by light and capable of development in the same way as an actual impression of light.

"2nd. That these two effects, the impression produced by hypophosphites and that by light, comport themselves to reagents exactly the same way and seem every way identical.

"3rd. That the image produced by hypophosphite on silver chloride always gives rise to a positive development, but on silver bromide may give rise either to a direct or to a reverse image, both of these effects corresponding exactly with those of light. More than this, sodium hypophosphite may be made to reverse the image produced by light on silver bromide and conversely light may be made to reverse the action of hypophosphite. So exact a correspondence in these remarkable properties can scarcely be fortuitous.

I

"A silver haloid formed in the absence of light and subjected to the action of sodium hypophosphite gives rise to the gradual formation of sub-salt, which combines with the normal salt in the manner described in the previous part of this paper. This action of the hypophosphite closely corresponds with that of light. In its initial stages it is invisible, but can be brought out in both cases by development.

"If we form a film of chloride, bromide or iodide of silver and with a glass rod dipped in solution of hypophosphite make marks upon it, these marks can with the utmost ease be developed in precisely the same way as an image produced by exposure to light.

"A very simple mode of operating consists in imbibing photographic paper with a solution of alkaline haloid, drying, applying a silver solution and then thoroughly washing, all of course with careful exclusion of active light. If the silver solution is acidulated with nitric acid, a drop to the ounce, the result is brighter, but this is not important. In any case the washing must be thorough.

"Marks made on this paper can be developed with the oxalate developer with the utmost facility. If a strong solution of hypophosphite is applied cold, it may be washed off at the end of a minute, but a stronger impression is obtained

by allowing it to wait half an hour before developing. Or the action may be accelerated and increased in strength by laying the freshly marked paper on a hot surface, or better, by steaming it, before applying the developer. A convenient mode of steaming is to lay two pieces of glass on a small water bath kept boiling, with a space between them. Over this space the paper is rested for two or three minutes. Paper prepared with a solution of KCl, KBr, or KI, dried and floated on acidulated solution of silver nitrate and well washed, if marked with strong solution of hypophosphite and steamed for two or three minutes, will develop the marks as black as ink on a white ground. The use of heat simply gives a blacker development, but a very vigorous image may be got without.

“(A similar result may be obtained by substituting for the hypophosphite a dilute solution of potash and an oxidizable organic substance. With milk sugar the action is very energetic and heat is quite superfluous.)

“Both these are the initial steps of reactions which, when prolonged, result in the visible formation of the colored photo-salts. It is a matter of interest that sodium hypophosphite, which produces the above-described effects, has no developing power whatever.

II

“The two impressions, that formed by light and that by hypophosphite, are similarly affected by reagents.

“As an example of this identity of effect produced on the two impressions, I first take the action of nitric acid.

“Chloride, bromide and iodide papers were exposed to moderate diffuse light under a screen with openings, for a proper time to form a latent image, the chloride and bromide for four or five seconds, the iodide for twenty or twenty-five. They were then cut into halves and one-half of each was soaked in strong nitric acid for five minutes. These halves were then washed for some hours and were developed along with the halves not so treated. Result was, latent image on silver chloride almost if not quite uninjured; on silver

bromide, somewhat affected but still strong; on silver iodide entirely destroyed.

“Similar portions of the same papers were then marked with hypophosphite and were cut into halves and one-half was subjected to the action of nitric acid in exactly the same way as the previous. The result was exactly as before. The hypophosphite marks on the half of the chloride paper that had been treated with acid came out in development as vigorously as on the half that had not been treated. The bromide paper showed the marks weakened by the acid but still strong; on the iodide not a trace appeared. In all respects the result was the same: what the one resisted the other resisted, what destroyed the one destroyed the other.

“Another confirmation is presented by the action of the alkaline haloids upon the latent image.

“The latent images produced by light on chloride, bromide and iodide of silver were all treated with cold and moderately strong solutions of potassic chloride, bromide and iodide for half an hour, and were then subjected to development. It was found that all three silver salts bore the action of potassic chloride and bromide fairly well, the images were somewhat weakened but strong developments were obtained without difficulty. But when potassic iodide was applied the latent image was totally destroyed.

“The visible effect of the alkaline haloids on the photo-salts exactly corresponds with their action on the latent image. Potassic chloride and bromide, applied in moderately strong solution and cold have little effect, but potassic iodide quickly destroys them.

“Therefore the action as well of nitric acid as of KCl, KBr and KI is exactly the same on the latent image impressed by light on AgCl, AgBr and AgI as it is on the corresponding photo-salts.

III

“The impressions produced by alkaline hypophosphite upon silver chloride always give rise to direct images, darker

than the ground on which they are formed. The same substance produces an impression on silver bromide which may by development produce either a direct or a reverse image. So that there is a perfect parallelism with the action of light.

"The reverse action of light, sometimes called solarization, shows itself as follows. A film of bromide being exposed to light, part covered by an opaque screen, the exposed portion receives an impression capable of development, and this impression grows in strength to a certain point, then recedes and reaches a condition in which it is less susceptible of development than before exposure. All bromide films, even unexposed to light, will darken in a developing solution in time. The portion that under the action of light has reached the reverse stage resists the reducing action of the developer better than that which was not exposed at all, and consequently appears after development as light on a dark ground and is therefore a reverse image. As to the cause of this action we are as yet wholly in the dark. If the continued effect of light was simply to restore the affected part to its original state we might attempt an explanation by affirming that the continued action of light undid its own work. But the fact of the resistance to reduction being greater than before exposure shows that some as yet unknown action of light is in play. The reverse action cannot be due to oxidation as has been suggested, because hypophosphite reverses and certainly cannot oxidize.

"The reversing action of light on silver bromide finds its counterpart in the action of sodium hypophosphite.

"If we take bromide paper (it is immaterial whether in making it the bromide or the silver solution be applied first, but for these experiments on the reversal of the image it is essential that a pure neutral silver solution be employed and that after the second solution has been applied the paper should be thoroughly washed, all the operations being of course performed by inactive light :) If we take such paper and make marks on it with a strong solution of hypophosphite, and then throw the paper into potassio-ferrous oxalate,

we shall get a direct development; the marks will be stronger than the ground. If now we continually weaken the hypophosphite solution, we shall presently reach a point at which these marks are in development almost wholly indistinguishable from the ground on which they were made. But continuing the dilution still further we presently reach a point at which the marks reappear, but this time reversely, as lighter marks on a darker ground. This result is obtained with about a 2 percent solution; the first-mentioned effect comes with a solution of 25 or 30 percent. So that according as we use the hypophosphite solution stronger or weaker we obtain exactly opposite effects. Here the parallelism is striking but not perfect, at least it remains to be explained why the action in the two cases proceeds in a reverse order. All the other reactions show a perfect identity.

"Time will also sometimes produce the same effect as dilution. Paper marked and put away for 24 or 48 hours, giving at first a direct image, may after that time give a reverse one. This effect is extremely uncertain and I think, exceptional. I have kept very many pieces for periods from a few hours to several weeks, which first and last gave direct images only; a few became reversed. But the experiment itself, the opposite effect of strong and weak solutions, is liable to no such uncertainty.

"Again, we may make light and hypophosphite interact and each reverse the other's action.

"To make hypophosphite reverse the action of light, I take a piece of silver bromide paper, expose it to the action of diffuse daylight for a few seconds, then taking it to the dark room, make marks upon it with a glass rod dipped in solution of hypophosphite. On developing with potassium ferrous oxalate the marks appear lighter than the ground. Or what is perhaps more striking, we take two pieces of such paper, retain one in the dark room and expose the other from 5 to 20 seconds to diffuse light, then make marks on both with a glass rod dipped in strong solution of hypophosphite, and then, after allowing a few minutes for the hypophosphite

to act, place them both in a solution of potassio-ferrous oxalate. The marks will develop, in the one case, as dark on a light ground, in the other (that exposed to daylight) as light on a dark ground.

“ We have here made the hypophosphite imitate the action of light: it has reversed the image in the same way as would result from a prolonged exposure to light. It will next be shown that light may be made to imitate the action of hypophosphite and reverse the effect already produced by that or other reducing agent.

“ If we take the red or purple silver bromide, preparing it with exclusion of light and the same precaution as in the case of a dry plate and extend it over paper (it is best, though not essential, to mix it with a little gelatine to enable it to retain its hold on the paper in the subsequent treatment), dry it and expose it to light under a screen such as a piece of opaque stiff pasteboard with openings cut in it, then apply potassio-ferrous oxalate, we shall obtain a very remarkable effect: all the parts exposed to light take a reversed development and appear as lighter spaces on a dark ground. And this goes so far that we may expose till we get a visible and quite strong image, darker than the ground and yet in development this darker portion will come out lighter than the ground. Indeed I have one specimen which shows almost white figures on an intensely black ground. Before development these light figures were brown, by exposure to light, on a rose-purple ground. I have seen few more curious results than this.

“ From the foregoing it follows that red bromide, notwithstanding its intense coloration, is in the same condition respecting light as normal silver bromide that has received an impression of light so strong that any further influence of light would cause reverse action, only that a vastly larger proportion of its molecules are affected. In the case of the latent image formed by light on normal bromide it would seem that the particles affected, although numerous enough to serve as a basis of development, are still too few and too scattered to be visible or affect the color. The photobromide on the

contrary has its mass made up of them. Then if exposed to light, the light carries them a stage farther—brings them to the reverse or 'solarized' condition and the parts affected by light develop less strongly than those not exposed.

"So light can act the part of hypophosphite and hypophosphite that of light, interchangeably; each can produce a direct action, each a reverse and each can reverse the other.

"It then appears that in all the numerous ways in which it is possible to compare the photo-salts with the material of the latent images they are found to be identical. The proofs based on development generally, and especially on the reversal of the latent image seem very strong and these receive additional support from the exact identity of reactions shown by the photo-salts and by the material of the latent image.

"The question of the identity of the photo-salts with the products of light on the silver haloids might perhaps be left with some confidence to the cumulative proofs here offered. But I hope to be prepared to give in the next number of this Journal additional evidence from a new direction."

The extraordinary thing about Carey Lea's results is that he gets a dark image on a light ground with his concentrated sodium hypophosphite solution and a light image on a dark ground with the dilute solution. If we are to consider the sodium hypophosphite solution as equivalent to light, we are getting a negative with an intense light (concentrated solution) and a positive with a weak light (dilute solution), which is just the reverse of what we should expect. At first I thought that the negative with the concentrated solution corresponded to the second negative, in which case there should be another negative with a more dilute solution than any Carey Lea had used. This proved not to be the case. It was then found that one could get either a negative or a positive depending on the length of time that a concentrated sodium hypophosphite solution is allowed to act. The reason for this is that sodium hypophosphite can act both as a reducing agent and as a solvent for silver bromide. If a plate is long enough in a concentrated solution there is practically

nothing left to develop. If it is only immersed for a relatively short time, the reducing action of the hypophosphite is the more important and the treated portion develops dark. At the time that we made these experiments, we had not worked out the sensitizing action of sulpho-urea and consequently no experiments were made to determine to what extent, if any, sodium hypophosphite would sensitize unexposed silver bromide apart from a straight reduction.

In the next paper on solarization, I expect to discuss the methods of obtaining positives with relatively short exposures. The principles involved have now been brought out clearly, but there are some points in regard to the application of them which seem to me to be of interest.

The general results of this paper may be summed up as follows:

1. The Waterhouse reversal is due to a sensitizing of the emulsion by thio-urea. Better control is obtained by giving a preliminary bath in a thio-urea solution and then developing with an ordinary developer.

2. The Guébbard reversal is similar in principle to the Waterhouse reversal. The difference between the two processes is due to the relative inefficiency of sodium sulphite as a sensitizer.

3. Some special cases of retarded development have been discussed in detail.

4. Englisch's and Vidal's development of an over-exposed plate as a negative by means of a preliminary partial fixing has been shown to be a necessary consequence of the selective solvent action of sodium thiosulphate.

5. Kogelmann's work on developing negatives from over-exposed plates after treatment with thio-urea has been repeated and it has been shown that negatives are obtained only when the developer is old or dilute and even then only when development is not carried too far.

6. Homolka's experiments with indoxyl have been discussed in detail and the fallacies in his reasoning have been pointed out.

7. Blanc's reversing emulsions are emulsions which have been fogged to the zero state.

8. Sterry's experiments on the effect of light in discharging fog from chloride plates have been duplicated with bromide plates. The phenomenon is to be studied more in detail.

9. Carey Lea's apparent reversals with dilute sodium hypophosphite and not with concentrated sodium hypophosphite have been shown to be due to the fact that sodium hypophosphite may act both as a reducing agent and as a solvent for silver bromide.

10. It has been shown that thin films should reverse more rapidly than films provided all other conditions are alike; but it is not claimed that this is necessarily, or even usually, the case.

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