

ART. XLVII.—*Identity of the Photosalts of Silver with the Material of the Latent Photographic Image*; by M. CAREY LEA, Philadelphia.

IN the first part of this paper I described certain strongly colored forms of silver chloride, bromide and iodide, obtained independently of any action of light, for which I proposed the name of photosalts, by reason of their identity with the products of the action of light on the normal silver haloids; both with the substance of the latent image itself and also with the principal results of the continued action of light on these haloids. It remains to prove this identity.

First as to identity with the product of the continued action of light.

If we expose silver chloride precipitated with excess of HCl to light, we get a deep purple black substance which boiled with dilute nitric acid gives up a little silver, at the same time somewhat lightening in color and forming a dull purple material which closely resembles some of the forms of photochloride described in the first part of this paper, most those produced by the action of sodic hypochlorite or of ferric chloride on metallic silver: it shows the same reactions with ammonia that they do. The brighter colored photochlorides are not formed by the action of light on silver chloride.

But these brighter colored chlorides can also be shown to be formed through the action of light. Most salts of silver darken by exposure, and when these dark products are treated, first with HCl, and then after thorough washing, are boiled with dilute nitric acid, we can obtain results perhaps as varied as those which I described in the former part of this paper as arising from purely chemical action.

*Silver oxalate* exposed for two days to sunshine, covered with water and with frequent agitation, changed to a deep brownish

black which by treatment with HCl became a little lighter. When this product was washed and boiled with strong nitric acid, it acquired a fine deep copper red color, the acid taking up silver. This red substance dissolved in ammonia readily, leaving a small amount of black residue; the same with sodium hyposulphite.

(This examination, made a year ago, has recently been repeated with a view to obtaining a quantitative determination of the proportion of  $\text{Ag}_2\text{Cl}$  contained in the red product. The exposure was for about a day, the oxalate at the end of the exposure seemed absolutely black. After treatment with HCl it assumed a purple black shade. After thorough washing and boiling with dilute nitric acid, which removed a large quantity of silver, perhaps 12 or 15 per cent of the entire quantity, it had a fine lilac purple color. Analysis showed that it contained about one-half of one per cent of subchloride, or more exactly, 0.45 per cent  $\text{Ag}_2\text{Cl}$  was found).

The red chloride thus obtained from silver oxalate, not only closely resembles the red chloride obtained by means exclusively chemical, but shows the same behavior to reagents.

Treated with ammonia it dissolves leaving a black residue. The formation of this residue takes place precisely in the same manner with both substances. As fast as the material dissolves the liquid becomes clouded and an extremely fine black substance seems to form within it, which gradually falls to the bottom.

Treated with solutions of the alkaline haloids, the red chloride derived from exposed silver oxalate remains unchanged after 24 hours contact with potassic chloride and becomes paler and more lilac under potassic bromide; under potassic iodide becomes gray. These reactions correspond with those of the photochloride.

*Silver phosphate* belongs to the more sensitive silver salts and easily darkens in sunlight. In a few hours it becomes greenish all through, after which further exposure produces little visible effect. This product becomes with HCl quickly gray, and by treatment with nitric acid after washing, light pink.

*Silver tartrate* by exposure to sun became quite black. With HCl this changed to reddish gray or dull pink. This product well washed and let stand with cold nitric acid 1.36 became first lavender and then light pink.

*Silver carbonate* by prolonged exposure became greenish black, and with the above treatment yielded a dull pink photochloride.

*Silver pyrophosphate* even by several days' exposure to winter sun did not blacken, but assumed an ochreous or buff shade. With HCl this passed to a sort of salmon pink and by heating

a few minutes with dilute nitric acid, to a beautiful copper shade.

*Silver acetate* was singularly little affected by sunlight, it looked blackish, but on closer inspection was found to be very little altered. By the same treatment as above it yielded a pale pink photochloride.

So far as examined, all silver salts thus treated yielded pink or red photochloride.

These facts may serve to show the identity of the photochloride with the principal product of the continued action of light on silver chloride and on other salts of silver, subsequently converted into chloride. I should wish, however, to use this word identity in a somewhat limited sense. When the photochlorides are formed by different methods without the aid of light hardly any two forms can be considered absolutely identical: they differ in color and in proportion of subchloride, as already often mentioned, but they also differ in other respects, especially in resistance to reagents. Some forms are far more easily destroyed by nitric acid: those obtained by the action of sodium hypophosphite (as presently to be described) are amongst the most easily destroyed by nitric acid. There is variation, too, in the degree of their resistance to ammonia.

Very similar differences are found in the stability of the photochlorides obtained by the action of light: some are much more readily attacked by nitric acid than others. The product obtained by the action of light on silver chloride resists ammonia more strongly than that obtained by the action of  $\text{HCl}$  on exposed silver oxalate. This last is quickly attacked. Generally, I think the dark colored forms are the most stable.

At a future time it may perhaps be possible to distinguish more exactly between these varieties.

I next pass to the consideration of the identity existing between the photosalts 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 photosalts, 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. Wurtz. 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 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 per cent 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, whilst the nitric acid takes up small quantities of silver.

IDENTITY OF PHOTOSALTS 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.

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

3d. 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 subsalt, 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 an 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 a 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 oxidable 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 photosalts.

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 photosalts 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 photosalts.

### 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 two per cent solution; the first mentioned effect comes with a solution of 25 or 30 per cent. 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 potassio-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 photosalts with the material of the latent image 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 photosalts and by the material of the latent image.

The question of the identity of the photosalts 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.

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