ART. XXIX.—*On the Nature of the Action of Light upon Iodid of Silver*; by M. CAREY LEA, Philadelphia.

MUCH difference of opinion has long existed in respect to the explanation of certain phenomena of photographic action. In the vast majority of cases the action of light is a reducing one. Salts of iron, of uranium, and of other metals are reduced from a higher to a lower stage of oxydation, and the same is the case with the combinations of certain metallic acids, such as bichromates and tungstates. These phenomena present no difficulty. It is only when we come to the silver haloids that obscurity commences.

It is generally held, and there seems no reason to doubt it, that chlorid and bromid of silver undergo reduction when exposed to light. I shall therefore pass over these compounds, and discuss only the action of light upon the iodid.

In respect to this, two opposite opinions have divided those chemists who have seriously occupied themselves with the subject. Some believe the action of light on the iodid to be purely physical, others hold it to be connected with an absolute chemical change; some again holding this chemical change to be a reduction to a sub-iodid, others to metallic silver.

There can be no doubt that when iodid of silver is exposed to light in the presence of free nitrate of silver, it undergoes reduction. An examination of this reduced substance showed that it still contained iodine; when treated with nitric acid, a solution of nitrate of silver was obtained, with a product of yellow

¹ In the following series of investigations it has been the object of the writer to endeavor to fix, with greater exactness, the obscure chemical and physical phenomena which form the basis of the photography of the day. The details have been published in the journals especially devoted to photography. It has been suggested to him to make a brief abstract of these studies in their essentially chemical and physical relations.

iodid of silver. If the iodid of silver, after exposure to light in the presence of free nitrate, is carefully washed, the free nitrate is thereby removed. Digestion with hyposulphite of soda removes all neutral iodid present, and the residue consists wholly of that portion of the iodid that has been altered by the light. If this altered substance were metallic silver, it would of course dissolve wholly in nitric acid. But as just said, this it does not do, but leaves behind yellow iodid of silver perfectly soluble in hyposulphite of soda. It is clear, therefore, that iodid of silver is reduced by the action of light, when free nitrate of silver is present, to sub-iodid. This sub-iodid is converted by nitric acid into nitrate of silver and iodid of silver. And I have found the same to be the case when *tannic acid* is substituted for free nitrate of silver, though the action is greatly slower: as in the former case a sub-iodid is formed.

There is a question, however, far more difficult than these, to answer, and it is this: Does reduction of some sort invariably accompany the action of light upon iodid of silver? Is, or is not that action, in its essence a chemical action?

Before proceeding to investigate that question, another presents itself, demanding solution. It had been long held as an indisputable fact, which none had attempted to controvert, that perfectly pure iodid of silver was insensitive to light, and that sensitiveness only appeared when free nitrate of silver, tannic acid, or other "sensitizer" was present.

I soon satisfied myself that this asserted fact (for the explanation of which long discussions had taken place) had no existence whatever, and that pure iodid of silver was always sensitive to light. The long series of experiments, made with the most careful and multiplied precautions, and varied in many different ways, need scarcely be detailed here, except to say that I finally adopted, as most free from opening for cavil, the method of producing specular films of pure metallic silver on plates of glass: these were thoroughly iodized by very prolonged exposure to solutions of iodine, then thoroughly washed, and on these, invisible impressions made by light were developed without difficulty. The demonstration was so convincing that I have had the pleasure of seeing those who were the most earnest supporters of the old view, abandon it entirely.

I return then to the main question, which is: Does chemical decomposition necessarily accompany the production of an impression upon iodid of silver? In my opinion *it does not*. I hold that: 1. When perfectly pure iodid of silver, isolated, is exposed to light, it receives a physical impression only. 2. But that when certain other substances, for example, nitrate of silver, tannic acid, and perhaps many others, are present, then a chemical action, a reduction, does, or may, take place.

The second of these propositions is generally admitted; the first, on the contrary, is much contested. I shall therefore briefly state the results of the several series of investigations undertaken to arrive at a clearer view of the principles involved.

When pure iodid of silver, isolated, is exposed to light for a very brief period, an invisible, or latent image is produced, which by the action of a solution just ready to precipitate metallic silver, becomes evident.

If the action of light in producing an invisible image upon pure iodid of silver isolated be a chemical one, it is not possible that it should be destroyed except by chemical means.

A piece of glass supporting a film of pure iodid of silver isolated from all other substances was exposed for many hours to a strong sunlight. It was then placed in a dark closet for thirty-six hours, at the end of which time it was placed under a negative and exposed to light for two seconds. On pouring a developer over it, a clear bright picture instantly appeared. Thus the action of the sun for many hours had produced an impression which completely disappeared in thirty-six hours.

Now if the action of light is to reduce iodid to sub-iodid, how did this sub-iodid recover its lost proportion of iodine? The fact that the iodid was much more powerfully affected by a recent exposure of two seconds than by one which though thirty-six hours old, was many thousand times as long, and in light much more intense, seems fatal to the chemical theory. That theory holds that the production of a latent image is accompanied by a reduction. The plate in question then either should under the action of the developer have received a deposit all over, or else must have recovered its iodine. The latter case is not supposable, the other alternative did not take place, therefore the action of light could not have been chemical.*

In some cases, the action of light upon perfectly pure iodid of silver, isolated from all other bodies, may produce a visible

* The only objection to this argument that I have seen made is one by Dr. Vogel, who remarks that in one case when actual chemical decomposition undoubtedly does take place, sensitiveness is recovered by repose in the dark. This is in the case of Obernetter's paper; paper imbued with perchlorid of iron and protochlorid of copper. Light reduces the iron salt, which again converts the copper salt to dichlorid; on applying a sulphocyanid a precipitate is produced on the parts altered by light. It is alleged that this capacity to precipitate disappears in a day. It is a sufficient answer that iron and copper are highly oxydable metals, and that the action of the light upon the above salts, though undoubtedly chemical in its nature, is rapidly undone by the action of the air, which, as is well known, quickly converts protochlorid of iron into oxychlorid, and dichlorid of copper into a green mixture of oxychlorid and cupric chlorid. This explanation—evidently the correct one in the case of the iron and copper salts—cannot be applied to a metal like silver which has no tendency to oxydize by atmospheric action. Even if this answer were not in itself sufficient, it is further to be remarked that there is no analogy in the two developments—the silver development being accompanied by no decomposition of the image, as is the case with the iron and copper mixture.

image. This very remarkable fact, a description of which I published early in June last, and which has been since verified by other observers,^{*} might seem to be inimical to the physical theory. A careful study proved the contrary. Pure iodid of silver, still moist, in considerable quantity, freshly precipitated and washed, was placed in a porcelain basin and exposed to sunlight. It instantly showed the slight darkening above referred to, but even after the action of the light and direct sunlight was continued for several hours, no reduced silver could be detected. The iodid after exposure was treated with dilute nitric acid, which restored the iodid to its bright yellow color. Now had this been effected by the action of the acid upon any sub-iodid formed by the action of light, then some portion of silver should have dissolved in the nitric acid. None however could be detected in it. It appears therefore that the effect of light upon pure iodid of silver, isolated from all bodies that can modify its action, is not a chemical one, whether its effect be visible or invisible, and that even when the action of light is prolonged to many thousand times the period sufficient for the production of a developable image, still no chemical alteration can be detected in the exposed iodid.

In addition to the foregoing, which are direct arguments, is to be placed the following indirect.

Believing that the action of light upon isolated pure iodid of silver is purely physical or molecular, it occurred to me to try whether another form of physical action, viz. *simple mechanical pressure*, could not be made to afford a basis for development. These experiments resulted in the formation of those curious effects which may be called *pressure images*. If a sensitive plate, ready for the camera, be pressed upon in any way, without removal from the dark room, and then be exposed to the action of a developing solution, all the parts so pressed upon will receive a heavier deposit of silver than the rest. This fact gives rise to various curious experiments.

If, for example, a piece of wood with lettering or figures cut out of it in open work be pressed forcibly on the sensitive film for a few seconds, and the plate then be developed the image of the lettering or open work will come out distinctly.

So if an embossed card be used, the embossed work will appear upon the film as soon as the developer has produced a deposit. The experiment may be varied in many ways: the material, so long as it is one which does not act chemically upon silver solutions, is unimportant; all that is required is a difference of pressure.[†]

^{*} See paper by Major Russell in Sutton's Notes, vol. xi, No. 245.

[†] These experiments have been since repeated by Girard with substitution of glass and rock crystal, with like results.

Chemists are very familiar with the fact that in cases of slow precipitation, the precipitate tends to follow the path which the glass rod used to stir the solution, has travelled over. The analogy which this and the development of a latent image present cannot be missed, and they are brought closer still by the pressure images just described. In all cases a molecular alteration takes place, and the molecules thus altered seem to have their attraction for exterior objects increased, and for each other and the surrounding homologous particles diminished.

This has been beautifully illustrated by some experiments lately published. A steel burnisher being drawn firmly over a plate of glass, yet so as not to scratch it or abrade the surface, the glass on examination by polarized light showed its structure altered by a line of color where the burnisher passed. This molecular effect slowly diminishes, and in a few days the particles return to their wonted state.

The foregoing experiment beautifully illustrates the changes of molecular condition which bodies are capable of undergoing. I have just remarked, that by drawing a blunt glass rod over the inside of a glass vessel, the parts so treated attract to themselves the particles of falling precipitates in a very striking manner. Often if a glass beaker containing a solution has been much stirred before a precipitate takes place, that precipitate will search out and develop, so to speak, all the invisible lines which were the path of the glass rod. This development of these invisible lines has a very striking analogy with the development of a latent photographic image, and the experiment just cited, reveals by polarized light a change of structure in those paths over which the body has been drawn. In the course of hours or days, this molecular change gradually passes away, and the body recovers its original condition, just as I have shown that when as in the case of pure iodid of silver, isolated, no reduction takes place, the effect of light gradually passes off, leaving the iodid free to receive a new impression.

It seems almost superfluous to say that what is here stated of the development of pressure images is not given by way of explanation, but as illustration and confirmation of the general view expressed.

Before concluding, a few words seem required as to what explanation is to be given to the ordinary process of Negative Photography.

In the foregoing I have reasoned on the action of light upon pure iodid of silver isolated. In the camera, light is made to act upon iodid of silver in a very different condition. It is in contact with nitrate of silver and with organic matter, and here bromid of silver is present.

I think it is evident from what has been already said, that in this case *several* images are formed, superposed as it were, on each other,—First, a physical image upon the iodid of silver. Secondly, if the exposure be sufficient, an image formed of sub-iodid of silver produced by the action of light upon the iodid and nitrate. Thirdly, there may be an image formed by the action of light upon the silver or its iodid in connection with the organic matter of the film (collodion or albumen). And, fourthly, if bromid or chlorid be present in the film, these may undergo reduction.

The separate nature of these images, or some of them, which may exist in the same film, interpenetrating each other, may be shown by the following experiment.

If an ordinary bromo-iodized collodion plate be exposed in the camera for the ordinary time and then be thrown into a dilute solution of acid pernitate of mercury, the whole of the *iodid and bromid will be dissolved*, leaving a film just as clear and transparent as the glass on which it rests. Let now this be well washed, and then a developer of silver and reducing agent be applied in the ordinary way. An image will at once start out, which by care and redevelopment may be brought up to any strength desired. Now the acid nitrate of mercury has the property of quickly dissolving not only iodid and bromid of silver, but also sub-iodid and metallic silver. Consequently whatever basis was afforded by the first, second, and fourth sources as above enumerated, was completely removed. Nothing remained but the third, and it is not improbable that in some of the “dry processes” this third source is the principal basis of the picture, though evidently only a subsidiary one, in the ordinary “wet process.”

Another form of this experiment consists in developing the picture *before* immersing it in the solution of acid nitrate, and then in leaving it but a short time in that solution, so that only the visible picture shall be removed, and the film of iodid and bromid be left.

Here all basis for development depending upon reduction is removed, and the production of the picture must depend wholly upon the first and third of the foregoing causes to the exclusion of the second and fourth.

Without having extended my observations to the *Daguerreotype*, I may remark that this process must be ranked along with those in which there is a reducing substance present, and therefore reduction may take place. The metallic back of the daguerreotype plate stands in the same relation to the iodid that tannin and other so called sensitizers do. It seems probable therefore that in the case of the daguerreotype, there may be

sub-iodid of silver produced, and this seems to correspond with Hunt's results, and those of other experimenters since his time.

In fact I have succeeded in showing the analogy between these processes by a new experiment which seems to establish it in a very striking manner. I impressed a wet collodion plate in the camera and then treated it with a pyrogallic solution in which proto-nitrate of mercury was substituted for nitrate of silver. The reducing tendency of the pyrogallic acid predisposes the mercury to precipitate, just as it does the silver, and this precipitate is attracted to the modified iodid, precisely as the precipitation of silver. The result is the development of a picture on iodid of silver by mercury *in the wet way*: this is precisely the intermediate stage between the ordinary collodion process in which a plate is developed by silver in the wet way, and the daguerreotype in which it is developed by mercury in the dry way.

This experiment, though affording no direct proof that the ordinary impression of light is a physical one, still tends to confirm that view. For if the chemical theory be true, it is a reduced image that attracts the precipitate of silver, and such an image would not be likely to attract a foreign metal. But if we conceive the phenomenon to be altogether a physical one, the dissimilarity of the precipitate from the surface on which it falls, imposes no more difficulty than the dissimilarity of the nature of the glass from that of the precipitate which is attached to those parts of the glass which have been pressed by the rod in stirring.

In fact it may be truly said that whenever one body is pressed against another, the particles of the body pressed against tend to have their attraction for each other diminished, and their attraction for external bodies, whether homogeneous or heterogeneous, increased.

I have endeavored in this brief review of a subject replete with difficulties, to show that the action of light upon pure iodid of silver isolated cannot be a chemical reduction:

1st. Because that effect, even when carried many hundred thousand times further than in the ordinary photographic processes, perfectly disappears in a few hours, spontaneously, under circumstances which render it impossible to suppose that iodine could have been restored to replace that which (had reduction taken place) must have been disengaged.

2d. Because, even where the action of light is prolonged many hundred thousand fold the ordinary time, no reduced silver nor sub-iodid can be detected as present.

3d. I have shown that another metal, mercury, is capable of developing these images as well as silver.

4th. I have endeavored to show that a purely physical cause, to wit, mechanical pressure, is capable of producing a developable impression, thereby answering the objection of the inadequacy of a physical influence to create a basis of development.

And finally, I may remark that although the chemical theory is supported by some distinguished chemists of the present day, I am not aware that there is a single well verified experiment which can be brought forward in support of that view. Had there been, I should have submitted it to a most careful study, my object being to arrive at the truth, not to support a theory. In the absence of such, I have been necessarily obliged here to confine myself to the affirmative side of the question, in support of the existence of a physical image, distinct from chemical reduction, and though often accompanied by it, yet never necessarily.

I cannot conclude these remarks without expressing my thanks for the kind assistance given me by my friend Mr. Thomas P. Shepard of Providence, Rhode Island.

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