ART. VII.—*On certain new and powerful means of rendering visible the Latent Photographic Image ;* by M. CAREY LEA.

THE development of the latent or invisible photographic image produced by the action of light is beyond all question the most remarkable and the most interesting fact with which photo-chemistry has made us acquainted. Our knowledge, however, of the substances capable of exhibiting this power, has increased with singular slowness. It commenced with the discovery, by the late Rev. Mr. J. B. Reade, in the year 1836, of the existence of this power in *gallic acid*, and not long after *pyrogallol* was found to possess the same property in a more energetic degree. Mr. Robert Hunt discovered that *ferrous sulphate* acted somewhat more powerfully than pyrogallol, provided that a soluble salt of silver was present. This was more than twenty years ago. Since then, no useful addition has been made to this list of so-called “developers,” though several of simply scientific interest. I was enabled to add to it *hæmatoxyline* about ten years since. *Morphia* has been found to have limited developing powers. When pyrogallol or gallic acid was employed in the absence of a soluble salt of silver, it was found that the activity of these bodies could be greatly increased by the presence of an alkali (alkaline development), for which purpose ammonium carbonate has been generally employed. It has been recently affirmed that in the ammonia-pyrogallol process, pyrogallol could be replaced (though with less energetic action, and therefore not advantageously) by a decoction of coffee berries, probably by reason of the quinic and caffetannic acids contained; and possibly by one or two other substances. This I believe represents the information acquired up to the present time.

In the following investigation I propose to show :

1. That the number of bodies endowed with the power of developing the latent image, so far from being very limited, as hitherto supposed, is, on the contrary, very large.

2. That contrary to what has been generally held, *potash* acts more powerfully in aiding development than ammonia; that there exist substances which develop with more or less energy in the presence of potash (e. g., mannite), but which have no such power in the presence of ammonia,* or alone.

3. It has been generally thought that the most energetic form of development, when no soluble salt of silver is present, is that which depends on the use of free alkali. I propose to show that there exists a form of development which under

* Unless possibly after greatly prolonged exposure.

appropriate conditions is more powerful than any yet known, in which there is *no free alkali present*.

4. It has been held that ferrous salts act only in the presence of a soluble salt of silver, and scarcely attack the silver haloid in the film, to produce an image in the absence of silver nitrate or other soluble silver salt. This also I think can be disproved.

As the development of the latent image depends (in the class of cases which I shall here consider,) upon a reduction of the portions of the sensitive substance which have been acted upon by light, it is evident that it is amongst reducing agents that we must look for bodies possessing this power. But here we are at once met by the fact that it is not the reducing power alone that is involved. We find that many substances which reduce silver salts energetically, have no power to evoke the latent image, and also that the developing power, where it exists, stands in no sort of relation to the energy of the reducing power. It is an *elective* power that is required, a tendency to reduce, not the whole surface, but only those parts that have been acted upon by light, and to spare the others. For example, it is easy to prepare alkaline solutions of ferrous salts, by having present a sufficient quantity of neutral potassium tartrate. But such solutions, applied to a sensitive surface that has received sufficient exposure under a negative, or in the camera, for ordinary development, seem to attack equally those parts that have been acted upon by light and those that have not. So that the sensitive surface darkens uniformly without showing the vestige of an image. Other similar cases will appear farther on.

In the following series of investigations a pure photographic paper was selected as the material for containing the sensitive substances. In the selection of the sensitive material itself, the object was to obtain the most highly sensitive possible. Silver iodide and bromide together are more sensitive to light than either separately, but also are more subject to irregular reduction. The best means of removing this difficulty without impairing the sensitiveness, I found to be the addition of silver chloride, which previous investigations had shown me to possess this power in a very remarkable way. Accordingly the present investigation was conducted upon surfaces containing these three substances together. The proportions used were those resulting from a solution containing eight grains potassium bromide, two of potassium iodide, and one and a third ammonium chloride, to the ounce. This proportion was that which gave the best results and was maintained in the experiments throughout. Facility of development is always increased by the presence in the sensitive film of some suitable organic substance. In these investigations a decoction of *cocculus indicus* was employed: this was applied together with the haloids,

first; after drying, the silver solution. Finally the sheets were very thoroughly washed out, to remove every trace of excess of silver nitrate and of all other soluble matter. To this careful washing much importance attaches. If any cocculus were left in the paper, it might, by dissolving out in the developing solution, confuse the result, inasmuch as cocculus with potash exhibits some developing powers. Every trace of it was therefore removed by the most careful washing, and as an additional precaution, the most important results were repeated on paper prepared with haloids only, in order to control the conclusions with exactness.

RESULTS.—A. *Sugars.*

Several sugars when heated with dilute aqueous solution of potash exhibit power of development. *Glucose* and *cane sugar* very slightly. *Milk sugar* produces a light metallic looking image on a dark ground. *Glycocine* was without effect. *Manna* acts very powerfully, producing an image perhaps as bold and strong as any substance hitherto known. The contrast between this strong action of mannite and the very weak action or entire inactivity of the other sugars named seemed very singular. It was thought that it might possibly arise from the fact of mannite not being a carbohydrate like the others mentioned but containing more hydrogen than sufficient to convert the oxygen into water. Therefore another sugar of the same class, *quercite*, was tried, but was found to possess no developing power whatever. The remarkably energetic action of mannite remains therefore without explanation. This substance and milk sugar, offer a good illustration of what has just been said of developing power being not necessarily proportional to reducing power. Milk sugar in conjunction with potash energetically reduces the silver haloids, but shows little developing power, while the converse is the case with mannite.

The image produced by mannite is of a redder shade than that resulting from any other developing agent.

B. *Glucosides.*

Daphnin gave a moderately strong image; its derivative, *Daphnetin*, a bolder and fuller. *Phloridzin* and *glycyrrhizin* gave no images. So-called *flavin* gave no image when simply heated with potash, but when boiled with potash and zinc turnings gave a moderately strong one, doubtless by the conversion of quercetin into *quercitrin*. Accordingly an infusion of *white oak bark* was found to give a good image. *Solanin* gave a moderately strong image, as also did *thuyine*. *Colocynthin* (decoction of colocynth was used) gave little or no result. *Æsculin*, a fair image. In all cases the substance was heated with dilute aqueous potash before use.

C. *Acids.*

Of a number of organic acids tried with excess of potash, one only, *cevadie acid*, exhibited tolerable developing power. *Phenol*, and *glyceric*, and *gentianic* acids powerfully reduced the silver haloids, but with little or none of the elective power necessary to produce an image. One, *oleic*, produced an image lighter than the ground. *Santonie*, *sinapic*, *gummic*, *malic*, and *hippuric* acids produced either faint traces of an image or none at all. *Vanadous acid* (potassium vanadite with excess of potash) failed to exhibit any developing power.

D. *Resins.*

Resinous substances for the most part dissolve easily in dilute aqueous potash, and exhibit more or less developing power. Foremost among them is *guaiacum* which gives a very vigorous image, not far short of what may be obtained with pyrogallol. *Balsam of tolu* and ordinary *resin* both have moderate developing power. Resin scarcely attacks the parts that have not been acted upon by light, whereas tolu does so. Resin of *podophyllin* gives a strong image.

E. *Essential Oils.*

When *oil of cloves* is boiled for a few moments with dilute aqueous potash, and the mixture is then much diluted with water, it acts slowly on the image, but as the action is sustained and clear, there results at the end of about an hour, a vigorous and very clear image. *Oil of Roman chamomile* acts somewhat similarly, but more feebly. *Oil of peppermint* produces an image of a gold color, and at the same time darkens the parts not acted upon by light, thus producing an image on a darker ground. Something similar has been already mentioned in the case of oleic acid. In these cases, where the light acts, the developing agent seems to reduce metallic silver, elsewhere, a dark basic salt, perhaps with organic matter in combination, is formed.

F. *Bases.*

Daturin (atropin?) gives a weak image. *Codein*, none. As a general thing the organic bases exhibit little tendency to evoke the latent image.

G. *Pyrogallol.*

In the course of this investigation, some interesting and new observations were made in connection with this well known agent, that deserve mention here.

Pyrogallol is well known to have, when employed by itself, considerable developing power, which however, is greatly increased by the presence of caustic or carbonated alkalies. It appears that these alkalies can be replaced with sodium *metaphosphate*, with about equal results. With sodium *hypophosphite*,

the effect is fair but inferior. But with potassium *formate*, a more energetic result is obtained than by any other method of using pyrogallol: a stronger development than by any of the methods now in use.

H. Various.

Trials were made with a considerable number of substances of vegetable origin whose constitution or properties seemed to indicate that they might exhibit power of development. In all cases they were boiled a few moments with dilute aqueous potash, as it was found that in that way their characteristic actions were most fully brought out. *Aloes*, *uva ursi leaves*, *areca nuts*, the bark of the *berberin tree*, *morus tinctoria*, exhibited very considerable developing power. *Gratiola*, *ipecacuanha*, *pimento nuts*, well marked power, but less than the foregoing. A decoction of *Iceland moss* exhibited the properties already described in the case of oleic acid and essential oil of peppermint. Many other substances were examined, and showed either faint traces only or absence of power, e. g., *litmus*, *carthamus*, *rutin*, *bryony*, *stavesacre*, *colchicum*, *turmeric*, *nux vomica*, *caffein*, *berberin*, etc.

Acetone, in conjunction with aqueous potash, is a powerful developer and gives a bold and vigorous image.

Aldehyde, with potash, gives no image, a result that seems somewhat remarkable.

I. Cuprous oxide dissolved in Ammonia.

A colorless solution of cuprous oxide in ammonia develops a strong image, and is interesting as being one of the very few entirely inorganic developers discoverable. As might be expected, its action is heightened by the presence of many organic matters.

When to a solution of cuprous oxide in ammonia, *formic acid* is added in quantity not quite sufficient to neutralize the bases, and this solution is applied to the latent image, a powerful development is obtained, resulting in a pure black image. *Lactic acid* exhibits a similar reaction, but less perfectly, and no doubt a large number of other organic acids share the same properties.

Various substances that develop in presence of potash, especially *gum guaiacum*, *gallotannic acid* and *mannan*, heighten the action of the cupro-ammonia solution. Others do not, of which *picrotoxin* (*cocculus indicus*) is an example. Of all the substances named, *guaiacum* appeared to have the most power, and next to it, perhaps *formic acid*.

J. Ferrous Salts.

The salts of ferrous oxide have proved to be the most interesting and remarkable of all the bodies examined, in their

action on the image. When a salt of silver is present in solution, to suffer reduction and to furnish silver for building up the image to be developed, as in the case of the so-called "wet process," ferrous sulphate is the most powerful developing agent known, and is accordingly, always employed. But in the absence of silver in actual solution it is powerless. It is in connection with such sensitive surfaces (i. e., those from which silver nitrate or other soluble silver salt has been removed by washing), that the present investigation is made, and I have verified this fact, already established, very carefully. A surface of sensitive paper, from which all silver compounds have been removed, may, after receiving a latent image, be left long in contact with ferrous sulphate without an image being developed.

Desirous of finding a means of applying ferrous salts to these developments, my first efforts were directed to the formation of alkaline solutions containing ferrous oxide in solution, but they did not appear to possess any power of development. I then tried ferrous oxide in combination with organic acids, and here at once most interesting results followed. Several organic salts furnished beautiful developments, among which may be especially mentioned *ferrous succinate*, *lactate* and *salicylate*. The succinate is best used by forming a slightly acid solution of ammonium succinate, and adding to it a solution of ferrous sulphate in quantity not quite sufficient to form a precipitate. Many other ferrous salts, among which may be mentioned *citrate*, *formate* and *tartrate*, give images, but much inferior to those already mentioned. The succinate and lactate develop so well that they might pass into use, were they not, as well as all other developing agents, so much exceeded by the oxalate.

Ferrous oxalate, when applied to paper sensitized in the manner already described, exhibits developing powers of a very remarkable kind. A piece of sensitized paper exposed for a very brief period to diffuse light under a negative, and then cut into two pieces and tried, the one with this development, the other with the ordinary alkaline pyrogallol development, exhibits the following differences:

The same exposure which with the alkaline pyrogallol gives a weak and sunk-in image after a protracted development, gives with ferrous oxalate a bright, bold image, and this in a much less time. The development is particularly clear and clean. The unexposed parts are not attacked: the developer possesses a great deal of that elective power previously spoken of, which causes it to react strongly on those parts which have received the influence of light, and spare those which have not.

Ferrous oxalate is easily obtained by adding a strong warm solution of oxalic acid to one of ferrous sulphate. A bright

yellow precipitate falls, which continues to increase for some time, and which may easily be washed by decantation. The method of employing it is by dissolving it in an aqueous solution of neutral potassic oxalate. The latter substance is to be dissolved in about three times its weight of hot water, and the precipitated and washed ferrous oxalate is dissolved in it to saturation. A deep red solution is obtained, which for use needs only to be diluted with from five or six up to twenty or thirty times its bulk of water, according to the energy of effect desired.

An active solution of ferrous oxalate may be obtained by simply adding a solution of ferrous sulphate to one of neutral potassic oxalate, in quantity just sufficient to avoid forming a permanent precipitate. But the first described method gives the best results.

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