Andrew Fyfe, “On Daguerreotype,” March 1840
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The intense degree of interest excited, a few months ago, by the accounts of the different photographic processes, has now given way to that raised by the disclosure of Daguerreotype. Though by photography beautiful representations may be obtained, yet, I believe, it is now generally allowed, that it does not come up to our expectations in giving delineations by the camera, with that degree of clearness and delicacy that was anticipated. In this country, at least, I have never seen designs taken by the camera of any value. This remark does not, however, apply to Daguerreotype. High as our expectations were raised by the first accounts of it, now that the secret is divulged, and that we have had opportunity of inspecting specimens, I would say that the accounts given of it were far from exaggerated—nay, that the delineations possess a richness and delicacy beyond what the most sanguine had anticipated.

My object in making a few remarks on this interesting process, is chiefly with the view of illustrating its rationale. The subject is as yet in its infancy. No doubt numerous improvements will, ere long, be suggested; and nothing, I conceive, is more likely to conduce to this than an accurate knowledge of the rationale of every stage of the process. It is with this view that I have been induced to investigate it; and I trust that the results I have obtained are not devoid of interest, not only as tending to illustrate what I conceive to be the action that occurs, but also as leading to some important practical applications in the arts.

On the first announcement of the mode of conducting daguerreotype, M. Arago conjectured that the effect, ultimately brought out by the hyposulphite, might be owing to its washing off the iodine, and probably to the sulphur of the salt acting on the silver, so as to convert it into a black sulphuret which, contrasting with the white mercurial coating, gives the dark and light parts of the picture. It is evident, however, that this is not the true rationale, because it is stated by Arago himself, that a similar result is obtained by washing the plate with solution of sea-salt, and where no sulphuret can be produced. The action, in my opinion, is altogether different; it does not depend on the formation of compounds differing in their nature and appearance, by the agency of the hyposulphite, but on metallic surfaces being presented, by which the light is reflected differently.

The first part of the process—the polishing—must be considered as merely mechanical; and certainly the more highly resplendent the surface, the more likely we are to succeed in getting a distinct image on it. With regard to the use of the diluted acid, its action is not so easily accounted for. That it should act on the silver, and form a nitrate, as
some have supposed, is not likely, when we consider its great state of dilution, and the very minute quantity employed—two or three drops being sufficient for a large plate. According to some it may wash off any copper adhering to the surface of the silver. To ascertain whether or not it acted on the metals, I raised a wall of wax-luting around a polished plate, and kept on it diluted acid (1 to 16) for some time, rubbing the plate occasionally with cotton. On testing the fluid, I could not detect the slightest trace of silver in it. Another plate was acidified and heated as recommended by Daguerre. It was then washed with distilled water; and the washings were tested for silver, with the same result.

The fluid from the plate in the preceding experiment, when tested for copper, gave indications of its presence. It is evident, then, that the acid acts merely by washing off impurities, and thus allowing a purer surface to be afterwards exposed to the iodine.

Different opinions have been entertained with regard to the action of the iodine. Some suppose that the golden-coloured coating is merely a thin film of iodine, adhering to the surface of the silver; while others maintain that it is an iodid of silver. Were it the former, we should expect it to be easily rubbed off, and more particularly that it would be dissipated by heat; neither of which occurs. When heated—excluded from light—the plate still retains the golden-yellow colour. Potassa has no action on it, which it should have, were it a mere film of iodine. From these and other experiments of a similar nature, it is evident that the iodine does not merely adhere to the silver, but that it combines with it and forms an iodid; the colour of which depends on the time the plate has been exposed to its action.\(^{(2)}\)

When the iodinized plate is kept in the camera for the proper time, it does not appear to be affected in the slightest degree, and it is not till after it is exposed to the mercurial vapour that the image appears. It is evident, however, that the light must exert some peculiar action on the iodid. Either the affinity between the iodine and the silver must be overcome, and the iodine be set free from the silver, or the constitution of the iodid must be altered. When the plate is kept long in the camera, it may be so affected as to bring out an indistinct image, a circumstance which I have occasionally observed; but this result is more easily obtained by exposing the plate to the direct rays of the sun, or even to a dull light, with an object—say an engraving—placed on it, as in the common photographic process, with paper prepared with the chlorid or phosphate of silver, in which case a distinct representation of the object on the engraving is produced—those parts exposed to the light becoming dark, while those excluded from it retain their original golden hue. When the plate is long exposed, on the parts on which the light impinges, the yellow is changed to dark violet, and, by slight friction, a dark coloured powder is removed. When this is treated with water or alcohol, the fluids do not, on the addition of the usual tests, indicate the presence of uncombined iodine. The iodinized plate, after long exposure to light, so as to darken it, does not, when heated, give off vapour of iodine; nor is its surface at all changed, from which it is evident that the powder liberated from the plate, by the agency of the light on the iodid, is not free iodine. Most probably it is the iodid set free from the silver, but the quantity procured is so very minute that I have not been able to satisfy myself as to its chemical composition.

The most important question regarding this interesting subject refers to the last stages of the process—the mercurializing and washing with hyposulphite.

When the plate is removed from the camera, and without any image observed on it, and is then exposed to the vapour of mercury, the mercury evidently adheres to those parts only which have been acted on by the light. Of course, the greater the action of the
light, the more is the iodide acted on, and the thicker is the mercurial coating acquired, or the more readily does the mercury adhere to the silver; thus giving different degrees of density, or a difference of surface, while those parts on which the light has not impinged still retain their golden-yellow hue.

On washing with hyposulphite, the whole of the iodide is removed, and silver and mercurial surfaces are then exposed; and it is the contrast between them, and not any particular chemical action exerted on the silver, by the hyposulphite, that produces the effect. In fact, it is a mere difference in reflection of light from a highly resplendent silver plate, and from a dull mercurialized surface; the former presenting the dark, the latter the light parts of the picture; the variety of shades, from dark to light, being brought out by a difference in the density, or by inequality in the mercurialized parts, according to the action of the light; for we can easily conceive that, the less and less the action of light, the thinner and thinner, or more imperfect, may be the mercurial coating, and thus all the variety of shades may be given, keeping in view that the silver surface always appears dark when in contrast with the mercurial one.

That this is really the cause of the brilliant effects brought out, is, in my opinion, proved by a very simple experiment. If a plate, polished as for daguerreotype, with its highly resplendent surface, have an object placed on it—as a piece of paper cut to any form, and moistened to make it adhere, and be then exposed in the mercurializing box, the mercury being heated to the temperature recommended by Daguerre—those parts exposed become mercurialized, while those covered with the paper are not acted on. When the paper is removed, we have a representation of the object, having all the appearance of a daguerreotype, excepting that it is merely in profile; the silver surface, or that representing the object, being dark, the merculiarized surface being light. A similar result may be obtained on other surfaces, as tin, tinned iron, and copper, provided they be highly polished; even on glass the same effects may be produced, but in this last case it is necessary to mercurialize at a higher temperature than for daguerreotype, and the plate, after being mercurialized, must be held in a particular position, otherwise the object is not distinctly observed.

Daguerre has stated that, in Paris, the time that the plate should be kept in the camera, during favourable weather, should not exceed about three minutes; and points out the necessity of operating in the dark with the iodinized plate. Though it may appear to some that there is no absolute necessity for this precaution, I may mention, as corroborative of what Daguerre has stated, that if an iodinized plate, with an object placed on it, be exposed to direct sunshine, and instantly withdrawn, a distinct image will be found on it by mercurializing and washing with hyposulphite.

Daguerre has also remarked that, when inspecting the plate during the mercurializing process, the light, even from a candle, should not be allowed to flow long on it. However improbable this may appear, yet it is not less true. The light of a gas lamp affects it powerfully; and hence, by exposing a plate to a gas flame, brilliant impressions can be procured. I have in this way succeeded in getting impressions from engravings, having all the delicacy of the original. For this purpose it is necessary to have the engraving on thin paper, placed on the plate with the engraving exposed to view, so as not to have a reverse. They are kept together by putting them into a glass frame, and then exposed near the flame either of an argand or flat burner for about twenty minutes or so, according to the light and the thickness of the paper, after which the plate is to be mercurialized and washed with hyposulphite.
I have already mentioned that when a polished plate, with an object placed on it, is mercurialized, an image is presented similar to a daguerreotype, and which, like it, is easily obliterated. It is remarkable, however, that if, instead of mercurializing at the temperature of about 160° Fahr., we raise it to about 400° Fahr., not only does the mercury present a whiter surface, but it adheres so firmly to the plate that it requires the polishing powder to remove it. This affords an easy method of producing and multiplying to any extent profiles on silver. The profile on paper is cut out, and, after being moistened on both sides with the tongue, or with very weak mucilage, is placed on the polished plate, and pressed down so as to make it adhere to it at all points; after which it is put into the mercurializing box, and kept exposed to the vapour of the mercury till the temperature reaches to about 400° Fahr. The lamp is then removed, and the temperature allowed to sink before taking out the plate. In conducting this process, the only precaution necessary is to take care that the paper does not separate from the silver, which it is apt to do when the heat is raised too high, or the plate is long kept in the box, in which case the image is indistinct. To prevent this, the weak mucilage is used, which is easily washed off from the silver by keeping the plate in warm water, or rubbing it softly with a sponge. Should the profile not be sufficiently sharp, the process may be repeated on the same plate, by removing the mercury with the polishing powder.

*\(^{(1)}\) Delivered before the Society of Arts for Scotland on 15th January 1840.
*\(^{(2)}\) When the plate is long exposed to the vapour of iodine, it presents a rich display of prismatic colours, sometimes in concentric rings, sometimes passing from side to side.

**EDITOR’S NOTES:**

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