XVI. *On the influence of Iodine in rendering several Argentine Compounds, spread on Paper, sensitive to Light, and on a new Method of producing, with greater distinctness, the Photographic Image. By Mr.* Robert Hunt. *Communicated by Sir* J. F. W. Herschel, *Bart., K.H. V.P.R.S. &c. &c.*

Received May 13,—Read June 18, 1840.

THE magical perfection of the designs delineated by light on the prepared tablets of M. Daguerre, and the extreme sensitiveness of his photographic material, render the discovery of inappreciable value to art and science. It appeared to me unfortunate, that a process which promised to improve our perceptions of the beautiful, and which placed in the hands of the scientific observer an instrument of wonderful delicacy, should have its utility circumscribed by its expense and inconvenience.

Had the art of engraving the Daguerreotype tablets, or any other mode of multiplying copies of the original designs been discovered, nothing further would have been desired; but as it was, it appeared to be of the greatest importance, that means should be sought for of using some lighter and less expensive material.

Even M. Arago, when speaking on the Report of the Commission on Daguerre's pension, remarks, "It had unquestionably been preferable, for the convenience of travellers, and also on the score of economy, could paper have been here employed."

It will, without doubt, occur to all, that the original photographic processes discovered by Mr. Fox Talbot, and published by that gentleman some time prior to the disclosure of Daguerre's secret, were on paper; and, though compelled to admit the superior beauty, the infinite minuteness of detail, and the charm of the aerial effect, in the pictures drawn on the polished tablets, yet, it must be allowed, the great end of the art being the multiplication of an indefinite number of fac-similes of original drawings, we can only expect to arrive at it by following in the steps of our talented countryman, whose recent productions, with the sight of some of which I have been favoured by the extreme kindness of Sir John Herschel, are of the richest promise. To Mr. Talbot, therefore, we must concede the high merit of being the discoverer of the photographic processes, which will, probably, ultimately turn out the most convenient and most extensively useful.

By a careful examination of the means employed to give the required sensitiveness to the silver surface, particularly the application of heat, and the subsequent rubbing with nitric acid, which performs a more important part than merely polishing, I was convinced of the possibility of covering paper with a preparation on which the iodine and mercury might operate as they are found to do upon the plate of metal.

This led to many experiments, and as I consider that the results arrived at are of considerable scientific importance, I shall, without apology, proceed to detail a series of experimental observations, which, it appears to me, promise to extend the principles of photography to purposes of high interest and of much utility.

1. M. DAGUERRE has stated, that a solid silver plate is less effective than one of copper plated with silver. All my experiments go to prove the correctness of this statement. This has been attributed, and I think correctly, to electric influence called into operation in the preparing processes by heat and with the acid. It will be found that an *unprepared plate* requires as long again to become properly coated with iodine as does a *prepared one*; and a *pure plate*, though carefully prepared, a third longer time than a *compound one*.

It is necessary, to produce iodidation readily, and to ensure the best effect from radiation, that a semi-oxidized surface be presented to the iodine. This fact will render obvious the superiority of the two metals; common observation will show, that plated goods lose their lustre much sooner than silver articles, the process of oxidation being much accelerated by the compound arrangement.

2. If an unprepared plate be iodidated and exposed to light, it darkens, and its superficial coat may be easily rubbed off, leaving a surface of exquisite lustre, somewhat darker than that which results from the nitric acid process, and more susceptible of iodidation. Whether a film of oxide or iodide of silver is here produced, I am uncertain: I suspect the former*. It is, however, evident that the silver has undergone some change.

3. If a leaf of very *pure untarnished* silver be carefully spread upon card, or a piece of glass, and at once exposed to the vapour of iodine, it will be found to remain unattacked for a considerable time.

4. If a silver leaf thus spread be well burnished, it will be seen that iodine acts upon it more readily than before.

5. If we burnish half of a leaf, and tarnish a portion of both the dull and bright parts, the iodine will then attack, first, the tarnished, then the bright, and last of all the unpolished portion.

6. Spreading a leaf of silver upon a piece of copper foil, and, to render the adhesion perfect, applying a gentle heat, a surface was formed which received the iodine readily. A sheet thus prepared was perfectly iodidated in five minutes, whereas a surface of the same extent on glass required twelve minutes.

These results established in my mind most satisfactorily, the possibility of giving to paper all the properties of the silver plates. It is clearly shown, that a degree of oxidation is required on the metallic surface. From this fact, the necessity is suggested of examining the peculiarities of action manifested by iodine, on the oxides of silver produced in different ways, and their relative states of sensibility to luminous influence induced by iodidation.

* See Philosophical Magazine, vol. xvi. p. 271.

To prevent circumlocution in describing the results of the inquiries into which I was led, I would explain, that when I speak of a paper being rendered sensitive, I always mean, that it becomes, after exposure to light, capable of receiving the mercurial vapour.

7. Muriated photographic papers, variously prepared, pass, more or less rapidly, through the stages of oxidation, to a perfect reduction of the metal, by the operations of light.

An examination of the effects of iodine, on all varieties of these papers, was instituted.

Any of the ordinary photographic papers allowed to darken to a full brown, become, by long exposure to iodine, of a steel-blue, or a violet colour. If exposed in this state to sunshine for a long period, their colours change from gray to a clear olive.

Now, exposure to sunshine for a minute, or to diffused daylight for from five to ten minutes, produces no *apparent* change, but mercurial vapour speedily attacks the uncovered parts, and a faithful picture is given of whatever may have been superposed, but there is a want of sufficient contrast between the lights and shadows.

8. By allowing the first darkening action to proceed until an olive coating is formed on the paper, I find, although it is not more speedily affected by the iodine, that it is more sensitive, and a better picture is formed than upon the brown paper.

The kind of preparation used, appears to have but little effect upon the results. A chloride, iodide, or bromide of silver allowed to darken, answers equally well.

There are, beside the faintness of the picture thus produced, defects which will, I fear, prevent our availing ourselves of this easy method of producing a moderately sensitive Daguerreotype paper. In the first place, the coat of oxide formed at the instant of exposure, protects the under layers of the salt, and the decomposing process proceeds irregularly; and even the longest exposure appears insufficient to remove the whole of the chlorine, which obstinately, in the form of the sub-chloride of silver, remains in the paper. This occasions the iodidation to be less complete in some parts than in others, and, consequently, a variation in the photographic effect. Again, it appears, that upon the surface, long exposure effects a revival of the silver in minute points, around which the mercurial vapour is deposited in greater quantity than over the other parts of the paper.

9. My next object was the production of a perfect oxide of silver, equally diffused over every portion of the paper. In this I have encountered many very great difficulties: irregularities, almost beyond detection by other means, became of serious consequence in the delicate process I was studying.

The most effectual method I have discovered, is, first to soak the sheet in a weak solution of pure potassa, and after partially drying it, which must be done quickly, pass it through a solution of the nitrate of silver, and allow it to dry slowly in the dark. The paper is now a light brown; but by heating it over a metallic plate, or

in front of a clear fire, to a point just below that at which it would be scorched, a perfect formation of the olive oxide of silver results.

The iodine vapour requires an equally long time to produce any visible effect upon this paper, as upon those before mentioned (8. 9.). But half an hour is sufficient to render this preparation so far iodidated as is necessary, or indeed as is possible, without impairing its sensibility.

This iodidated oxide requires a strong light to yield any decided effect, and a greater heat than is directed by DAGUERRE must be applied to the mercury to bring out the impression, which is but faint at last.

10. The protoxide of silver, and some of its salts, now engaged my attention. Taking advantage of the facts pointed out by WOHLER*, I exposed papers saturated with a solution of the nitrate of silver, and dried in a cylinder which was kept hot by boiling water, to a current of very pure heated hydrogen gas. By this means I obtained a paper of a brick-red colour. This appears to be a nitrate of the protoxide of silver; by soaking this paper in rain water for some time, the free acid was removed from it, and on drying it became darker than before.

This paper is not very readily attacked by the iodine, but it is, by the exposure of an hour to a full volume of its vapour, rendered slightly sensitive.

11. By immersing a paper prepared as above (10.) in a solution of pure potassa, the salt is decomposed, and the paper on drying becomes a full black, which on being passed through steel rollers, assumes a fine lustre, resembling that given by PLUMBAGO.

This paper is more readily attacked by the iodine than the former (10.), but it is not more sensitive. In bright sunshine I have produced a tolerable copy of a leaf with its delicate vernations, but in the camera I have never succeeded as I desired, or indeed as I expected.

12. The deutoxide of silver is reduced to the metallic state by hydrogen at high temperatures. By the same arrangement as above (10.) I was enabled to get a very perfect silver paper, which in all respects was similar to the paper which is mechanically silvered (3.).

13. Having proved that iodine has the power of rendering sensitive, not only the oxides of silver, but a salt of the protoxide, it became an interesting inquiry to ascertain whether it would produce any like effect upon other salts of silver. The only one, however, I have yet discovered which admits of the desired influence, is the yellow-brown phosphate of silver. The iodine in two hours does not produce the slightest change of colour, but exposure to light and the vapour of mercury shows that the iodine imparts some sensitiveness to this salt.

14. A careful examination of the silver surfaces produced by the action of the perphosphuretted hydrogen gas on various salts of that metal, now occupied my attention, and undividedly engaged it for a very considerable time.

* Journal de Pharm., Juillet, 1839.

My first attempts at producing, by this means, extensive surfaces, were failures; the paper generally presented a gray silver spot surrounded by a series of highly coloured rings, and an external one of a velvet black; these were of course phosphorus and silver in various proportions. Even in this state, sunshine appears to have some effect upon the papers; the inner most circles, the redand yellow, pass with tolerable quickness into different shades of olive.

By exposure to iodine the coloured rings are attacked, and changed in their characters, long before any influence is apparent on the pure silver spot, generally, but not always, assuming their complementary colours. The sensitiveness of these bands is as their position; the black exhibiting a decided action, which lessens in every ring, and is lost on the verge of the gray silver. If the silver is allowed to assume the required golden hue from the iodine, the order of sensitiveness is reversed.

15. To prevent explosions of this spontaneously inflammable gas, I have, amongst other methods, used the vapour of ether. When this has been the case, at the moment of reduction a portion of carbon appears to be separated from the ether, and, combining with the phosphorus, is deposited on the paper, forming a band of a yellow brown tint, which is sometimes found within and at others without the coloured circle, the place appearing to depend on temperature. I was at first inclined to consider this as a simple combination of phosphorus and carbon; but the sensitiveness of the band inclines me to the opinion of its being a carbo-phosphuret of silver. I should state that it stands next to black in the order of sensibility: I find the same effect is produced by dissolving the nitrate of silver, with which the paper is washed, in spirits of wine.

16. By very carefully spreading a strong solution of the nitrate of silver over a highly-calendered paper, and then exposing it to the perphosphuretted hydrogen slowly evolved from the phosphuret of lime, a very even metallic surface was formed, from the leaden colour of which it may be concluded some phosphorus had entered into combination with the silver. This paper was soon attacked by the iodine, was little less sensitive than the silvered copper, but it was scarcely possible to remove the iodine, so as to preserve the picture when complete, without portions of the surface breaking away, so slight was the adhesion between the paper and the metal.

17. By allowing the paper to absorb the silver solution, and to become nearly, but not quite dry before exposed to the gas, and the gas, which I usually form from phosphorus and solution of potassa, being liberated in large quantities, a black paper possessing in a very eminent degree all that is desired, is the result.

Unfortunately, however, although I have used every precaution, I find it impossible to prepare more than a dozen quarter-sheets without an explosion of the gas. In placing and removing the paper, atmospheric air necessarily enters the vessel, besides which, a quantity of oxygen sufficient to occasion spontaneous inflammation is set free from the nitrate of silver and the water absorbed by the papers. On one occasion I so placed and arranged some papers in a vessel as to do away with the pos-

sibility of any admission of atmospheric air; the formation of the black phosphuret of silver was going on beautifully, when the large glass vessel burst with such violence that the largest piece I could find was but the sixteenth of an inch over.

I do not at present see any way of preparing those papers with safety, and, much against my inclination, I have abandoned the use of this gas.

18. The exposure of muriated and simply nitrated photographic paper, darkened by light to the vapour of phosphorus, suggested itself. It has been noticed, that most vapours have a disposition to attack by the edges; thus it is with that of phosphorus. If the paper be suspended, the edges will present a band of silver, slightly coloured, long before the other parts exhibit any signs of having been at all acted on. The precaution, therefore, of fixing the paper in a frame and exposing its flat surface over a large quantity of phosphorus broken into small pieces, is of great importance in the preparation. When carefully prepared, this paper stands above the oxides of silver for sensibility, but infinitely below the phosphuret.

19. The vapour of sulphur was next tried, and to a great extent with success. If the paper was placed in the vapour while yet wet, the reduction was too rapid, and the continuity of the surface was broken. If allowed to dry, a more perfect surface was formed, but it was exceedingly apt to become iridescent, and every shade, after the iodine was applied, was differently sensitive. It, however, sometimes furnished a very perfect paper, capable of producing a fine photographic picture.

20. The action of sulphurous acid gas was studied with attention, but only when the paper was absolutely dry and maintained at a high temperature, could I succeed in getting any revival of the silver, which was rapidly attacked by the gas and converted into a sulphate.

21. Papers prepared with the nitrate of silver are, when plunged into a vessel containing sulphuretted hydrogen, speedily covered with sulphuret of silver. The first action of the gas is the revival of very white silver, over which a brown shade is quickly diffused, which passes into a lead colour if the paper is *moist*, or becomes variegated if it is *wet*. These papers are equal in most respects to those prepared with the phosphuretted combination.

22. If a current of sulphuretted hydrogen be *thrown upon* a paper still wet with solution of nitrate of silver, beautiful coloured rings are produced. When the gas is fully saturated with sulphur, these rings are very dark, and of the richest lustre. If in this state they are placed between the leaves of a printed volume, a perfect copy of the printing is made in twenty-four hours, the letters being white. By passing the paper through an alcoholic solution of iodine the letters become a full black. The singular nature of this fact will account for its introduction in this place*.

* On several occasions, when papers variously prepared (but not darkened) and marked and numbered *with pencil* at the back have been laid together, face to back, in the dark for some time, the pencil marks on some of them have been found exactly copied (in reverse) in a dark brown impression on their neighbours. This

23. By plunging a paper washed with the solution of the nitrate of silver into a very diluted volume of sulphuretted hydrogen, and transferring it from thence into pure gas, a tolerably perfect surface is generally obtained.

The continual plague of this process is, the want of perfect uniformity in the texture of the paper, which will often, in spite of every care, occasion an unequal absorption and thus mar the effect.

24. Having tried every variety of paper I could procure, and finding all more or less objectionable, I had recourse to sizes of almost every variety. The difficulty was not, however, overcome by any of them; the one which answered best was starch, which has the very singular property of altering the general appearance of that portion of the picture which is formed by the mercurial vapour when it is immersed in solutions of the muriate, or hyposulphite of soda, destroying the downy appearance, and giving it a sheeted silvery one.

25. The experience gained by preparing these sulphuretted papers on an extensive scale, enables me to point out a method by which most of the defects arising from the inequalities of the paper, and its different rates of imbibition, may be overcome.

The paper is to be first *soaked* in a weak solution of the muriate of ammonia, carefully wiped with cotton cloths, and dried slowly. It is then to be dipped in a very dilute solution of the nitrate of silver, and the small bubbles which form on its surface to be carefully removed with a camel's-hair pencil. When the paper is dried, which must be done in the dark, it is to be exposed in a closed vessel to sulphuretted hydrogen, slowly formed from the sulphuret of antimony and hydrochloric acid: in a few minutes it will darken to an iron brown. The paper must now be passed through water slightly impregnated with chlorine, or hydrochloric acid, and again dried. It must then be immersed in a solution of silver rather stronger than the first, and dried, whether in the light, or otherwise, appears of little consequence, care being taken that no shadow falls on the paper, as some difference exists between the shaded and exposed portions; but the sensitiveness changes in a singularly uncertain way from the one to the other. It is to be again subjected to sulphuration, and by careful management the process is now generally completed. If, however, the paper is not considered as sufficiently dark, it must be once more washed in the solution of silver, and again subjected to the action of sulphuretted hydrogen.

26. If the above muriated paper (25.) be allowed to remain in the sulphuretted hydrogen gas after the maximum blackness is produced, it is again whitened with some quickness. This may be accounted for in two ways; the gas may be mixed

---

effect is not produced by all pencils on the same paper, as a preparation of the paper, nitrate of silver over borax, seemed to succeed best.

Gold-leaf printing (the common ornamental printing on cards, &c.) may be copied on nitrated paper, by simple juxtaposition and gentle pressure for some time in the dark, which is probably owing to the copper used as alloy, as the other may be by sulphur in the pencil.—J. F. W. H.

with a portion of muriatic vapour, or a quantity of chlorine, sufficient to produce this effect, may be liberated from the preparation on the paper, to react on the sulphuret of silver.

The most elaborate directions would be quite insufficient to ensure the production of perfectly equal papers: repeated experiments alone will ensure a certainty in the result. To produce a glittering metallic surface is less difficult, but the perfection of the papers consists in having a deep black ground to contrast with the mercurial deposit. No silvering on paper can be brought to the lustre of the metallic plates, and consequently, although the revived silver may be rendered tolerably dark by using very pure sulphuretted hydrogen and a strong solution of silver, yet the contrasts are not sufficiently decided. With the black papers the picture is seen equally well in all directions, and the adhesion of the mercurial particles is closer than where a glittering surface has been presented to the action of its vapour.

27. If the paper is removed from the sulphuretted hydrogen at the moment the first white silver is revived, or still better, if the silver is revived by hydrogen gas, it may be used to produce effects like what Sir JOHN HERSCHEL designates the negative variety of photographic drawing.

After the drawing is produced in the usual method of the Daguerreotype, it is only necessary to immerse it in a warm saturated solution of common salt. The silvered portion gradually acquires a beautiful whiteness, while the parts covered by the mercury pass into a deep gray. All the fine effects producible by the original muriated photographic papers are given by this process, and the picture has the advantage of being absolutely permanent.

Method of using those Papers.

28. All the kinds of paper above-mentioned may be rendered sensitive by being exposed to the vapour of iodine, the best mode of applying which, is to spread over a thin board, the size of the sheet, a paste of iodine with spirits of wine. This board is placed in a box, and the papers being fixed in a frame about three inches above it, are iodidated in a few minutes. This plan is equally applicable to the plates.

For the sulphuretted paper I recommend another plan, which has many very great advantages. It consists simply in drawing the surface of the paper lightly over a solution thus formed: a saturated solution of any hydriodic salt is made to dissolve as much iodine as possible; and of this liquid two drachms are mingled with four ounces of water.

Care is required that one side only of the paper be wetted, which is by no means difficult to effect, the fluid is so greedily absorbed by it; all that is necessary being a broad shallow vessel to allow of the paper touching the fluid to its full width, and that it be drawn over it with a slow steady movement. When thus wetted it is to be quickly dried by a warm, but not too bright fire; of course daylight must be carefully excluded. Papers thus iodidated do not lose their sensitiveness for many days.

29. There are many inconveniences attending the use of fluid mercury, particularly to travellers; I therefore propose a plan by which this may be avoided, and the mercurialization very much facilitated. It is this: the box used for vaporization is so made as to admit of a piece of copper, rather more than half the size of the paper or plate, being placed upon the iron bottom. When required for use, the copper is rubbed over with the nitrate of mercury, washed, dried, and fixed in its place. As soon as the copper gets hot, which is very quickly, the mercury on its surface is volatilized, and the action on the photograph effected. I find this plan occupies only half the time of the original, with a capsule of mercury.

30. The drawing is now to a certain extent complete, but I have found the use of the hyposulphite of soda to remove the iodine objectionable, on the ground of its tendency to darken the mercurial deposit. A warm solution of the muriate of soda is more efficacious.

31. I have now to call particular attention to a phenomenon of a most remarkable character, opening a wide field for inquiry. The singular manner in which the mercurial vapour arranges itself on DAGUERRE's tablets has excited much attention, and given rise to numerous speculations, but even this appears to me far less curious than the following discovery.

If one of the above papers, when removed from the mercurial vapour, be dipped into a solution of the bichloride of mercury, the drawing disappears, but after a few minutes it is seen, as if by magic, unfolding itself, and gradually becoming far more beautiful and whiter than before—delicate lines, before invisible or barely seen, are now distinctly marked, and a rare and singular perfection of detail given to the drawing.

It may appear at first sight that the bichloride of mercury dissolves off the metal and deposits it again in the form of chloride (calomel). But this does not account for the fact, that if the paper has been prepared with the nitrate of silver, the mercury disappears, and the drawing vanishes, the deposit taking place only on those parts upon which light has acted but feebly, as, for instance, on the vernations of leaves, leaving those portions of surface exposed to full luminous influence without a particle of quicksilver. When the paper has been either a chloride or iodide, the effect is as above, and the thickness of the deposit is as the intensity of the light has been; consequently the semi-tints are beautifully preserved. If the drawing remains too long in the solution, the precipitate adheres to the dark parts and destroys the effect. The singularity of this operation will be more striking if the picture has been soaked for some time in a solution of the hyposulphite of soda, and then dipped into the bichloride of mercury. As the drawing disappears, a series of circles, formed of a white powder, appear to arise from the paper, generally commencing at the centre, and slowly extending over its whole surface: the powder is afterwards deposited, and the sheet is buried in the precipitate; but on taking the paper from the liquid and passing a stream of water over it, the precipitate is entirely removed from all the parts,

except the lights of the picture. To explain the rationale of this definite arrangement of a dense precipitate, is beyond my power.

32. Sir JOHN HERSCHEL has recently shown that corrosive sublimate obliterates the ordinary photographic drawings, and that they may be restored by the hyposulphite of soda. An equally singular effect is produced upon some of the papers above-mentioned. If the ordinary muriated photographic paper darkened (7. 8.) be used to procure a drawing by the process which occupies our attention, on being treated with a solution of the bichloride of mercury, the dark parts of the picture are whitened, and it of course becomes of the negative variety; but it is speedily rendered positive, or the lights and shades corrected, by the hyposulphite of soda. We have it thus in our power to produce upon the same sheet two very marked varieties of photographic drawings.

Devonport, May 5, 1840.

POSTSCRIPT.

(*a.*) I find the invisible photographic image, on the papers prepared by sulphuration, becomes evident without the aid of mercurial vapour, by simply soaking for some time in a solution of corrosive sublimate. The picture thus formed is extremely faint, but the fact is worthy of notice, as it may ultimately lead to the discovery of a process, by which the disengagement of the light-created picture may be effected by more simple means than at present.

(*b.*) If papers saturated with starch prior to being washed with the salt of silver and exposure to the sulphuretted hydrogen gas, the silver being applied on one side only, be, when completed, placed between the leaves of a printed book and subjected to some little pressure, the printing is faithfully copied off on the *unsilvered* side. It is with difficulty the letters can be made out when the paper is taken from the volume, but by immersing it in a solution of iodine they become a deep blue, verging on a black, whilst the ground remains of a yellow colour, which by the continued action of the fluid changes to a light violet. On drying, the ground becomes considerably darker, and the printing, though evident, indistinct, appearing in some positions the lightest, in others the darkest portions of the paper. These, and the facts above-mentioned, render it probable that we may eventually succeed in copying prints, &c. by mere juxtaposition.

R. H.

May 19, 1840.