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XXXVIII. On the use of hydriodic salts as photographic agents

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a dilute solution of sulphocyanide of potassium, the sulphocyanogen is precipitated of a light yellow colour, and does not subside readily. I have ascertained, by experiment, that this light yellow substance is not sulphocyanogen, but hydrothiocyanic acid. It is, however, more difficult to convert sulphocyanogen into this acid by chlorine, than by nitric acid; chlorine consequently gives the purer substance.

In conclusion, I would state, that these experiments have been performed in Prof. Graham's laboratory, to whom and to his late assistant Mr. Fownes, I am happy in acknowledging myself indebted for their suggestions during this research.

University College, June 25, 1840.

XXXVIII. *On the Use of Hydriodic Salts as Photographic Agents. By Mr.* Robert Hunt.

[Continued from p. 211, and concluded.]

38. *On the darkening of the Photograph.*

Mr. TALBOT first directed attention, at the last meeting of the British Association, to a peculiarity possessed by some of these kinds of photographs, namely, that they were neither fixed nor otherwise; but that on exposure to sunshine they changed in their dark parts from a red to a black, the lights of the picture being unaffected by the light.

39. This singular effect I have proved to be entirely dependent on the influence exerted by the less refrangible rays of the solar spectrum in exalting the oxidation of the silver; but a brief statement of some effects produced by the dissevered rays, will place the matter in a much clearer light.

40. By allowing a very intense prismatic spectrum, formed by a flint-glass prism, to fall upon any of these photographs which blacken by white light, it will be found that the darkening process commences in the red ray, at which point it goes on with the greatest intensity, and is gradually shaded off to the lowest edge of the extreme red; the shading is also continued through the orange and yellow rays being sharply cut off at that line of the spectrum where the pure green is visible.

41. As it was not possible to pursue my inquiry on the effects of the spectrum with any degree of satisfaction without a heliostat, an instrument I have not the means of procuring,

in alkali, the sulphocyanogen is first dissolved, leaving the acid. This explains why sulphocyanogen prepared by nitric acid becomes yellow when treated with alkali, which is not the case with that prepared by chlorine.

I turned my attention to the effects produced by the light which had permeated coloured media, the absorptive powers of which were carefully analysed.

The media I was induced to adopt transmitted rays in the following order.

BLUE. *Ammonia-Sulphate of Copper.*—The whole of the most refrangible rays, from the edge of the green to the extremity of the violet.

GREEN. *Nitro-muriate of Copper.*—Those rays which have place between the extreme upper edge of the blue, and a line which would accurately divide the pure yellow.

YELLOW. *Bi-chromate of Potassa.*—That portion of the spectrum which would lie between a line drawn below the orange, rather within the red ray, and through the lower edge of the pure green ray.

RED. *A strong Solution of Carmine in Ammonia.*—A portion of the orange and all the rays below it.

42. The most remarkable effects were produced upon the papers *a*, *b*, *c*, *d*, and *n* (13). They have been subjected to similar influences, prepared with all the hydriodates I have mentioned (20—27); but I do not feel myself warranted in occupying your pages with any statement of the results on any, but those prepared with the pure hydriodate of iron and the hydriodate of baryta. These drawings were all well washed with hot water, and when quite dry, arranged under the different fluids, and exposed in a window which faces the south. I will name the papers from the salt used, and the colour shall indicate the rays.

43. *Hydriodate of Iron*, *Muriate of Ammonia.*—BLUE. The picture nearly destroyed by the browning of the yellow lights, at the same time as the darker parts have much faded.

GREEN. The dark parts nearly all faded out; the few remaining spots much reddened, but no change in the yellow of the light parts.

YELLOW. Looking through the paper, the lights appear darkened by a blueish-green tinge; the dark parts, originally a red brown, are changed to a blue-black.

RED. The lights yellower than before; the darks a deep black.

44. *Chloride of Sodium.*—BLUE. The lights darkened, and the dark parts faded and reddened. GREEN. Picture entirely obliterated; the yellow unchanged. YELLOW. The lights tinged a decided blue; shadows darkened.

RED. The lights of a green tinge; but I consider this to arise from the deepening of the yellow hue; the dark parts blackened.

45. *Muriate of Strontia.*—Blue. These are more permanent than any other variety of the hydriodic photographs. Under this influence the shadows are browner than before; the lights scarcely changed. Green. The yellow much increased in depth; the dark parts faded slightly and become very red. Yellow. The lights very little tinged with blue; the darks without any apparent change. Red. The lights deepened; the shadows a fine black.

46. *Muriate of Baryta.*—Blue. The yellow parts are become brown; the dark portions faded and reddened. Green. Lights unchanged; the dark parts very red. Yellow. Lights unchanged; shadows tinged green, over a very decided blackening which has taken place. Red. The yellow much heightened; the dark parts much tinged with green.

47. *Hydrochloric Acid.*—Blue. Faded out: lights darkened. Green. Faded out; yellow much increased. Yellow. The lights rendered very yellow; darks unchanged. Red. Yellow become very strong; the shadows are very much blackened.

48. *Hydriodate of Baryta.*—Under this head it will only be necessary to name the effects on three kinds of photographs, the others being very similar in all their changes to those just mentioned.

49. *Muriate of Ammonia.*—In my paper on the influence of coloured media, vol. xvi. p. 270 of your Journal, I have already mentioned the singular change which ensues upon exposing this kind of drawing to light under media such as we are now considering. To that paper I refer you.

50. *Muriate of Baryta.*—Blue. Faded in the dark parts, which are become a brick red; the yellowness of the lights increased. Green. The lights unchanged; the shadows suffused with a pink hue. Yellow. Lights unchanged; shadows much darkened and strongly tinged with a light blue. Red. Lights unchanged; dark parts a deep blue. These singular effects, which, although they are traceable on nearly all those photographs which blacken by after exposure to sunshine, are much more decided when the salts of baryta in one or other of the processes have been used. I communicated these facts with others to Sir John Herschel, who has paid me a very high compliment by inserting my communication in his valuable memoir "On the Chemical Action of the Solar Spectrum." I the less regret my inability to pursue my observations on the effects of the pure prismatic rays on the hydriodic preparations, finding that the subject is one which, among others equally curious and important, is engaging the attention of this eminent philosopher.

51. *Muriate of Strontia.*—Blue. Lights but very little

changed; darks faded and reddened. GREEN. Lights unchanged; shadows less faded, not so red. YELLOW. Lights unchanged; dark parts a blue-black. RED. Lights unchanged; dark parts become very black.

52. From a careful perusal of these results it will appear that this curious darkening of the finished picture is most evident under the influence of red light, but that this property extends up to the green rays, beyond which a different power is exercised; the *deoxidizing* influence appearing to be greatest in the blue rays, whilst the yellow iodide of silver suffers decomposition in the most refrangible rays.

53. *The fading of Hydriodic Photographs.*—I have before noticed (30.) the want of absolute permanence in these pictures. The study of the *modus operandi* of solar light in its action on them opens some very remarkable facts in relation to the iodide of silver, which when first observed, led me to believe the existence of two distinct salts, whereas I now entertain a different opinion. The drawing fades first in the dark parts, and as they are perceived to lose their definedness, the lights are seen to darken, until at last the contrast between light and shadow is very weak.

54. If a dark paper is washed with an hydriodate and exposed to sunshine, it is first bleached, becoming yellow; then the light again darkens it; if, when quite dry, it is put away in the dark, it will be found in a few days to be again restored to its original yellow, which may be again darkened, but not so easily as at first, and the yellow colour is again restored in the dark. The sensitiveness to the influence of light diminishes after each exposure, but I have not been enabled to arrive at the point at which this entirely ceases.

55. If a dark paper, bleached by an hydriodate and light, be again darkened, and then placed in a bottle of water, the yellow is much more quickly restored, and bubbles of gas will escape freely, which examination will show to be oxygen.

56. By inclosing pieces of hydriodated paper in a tube to darken, we discover, as might have been expected, some hydrogen is given off. If the paper is then well dried and carefully shut up in a warm dry tube, it remains dark; moisten the tube or the paper, and the yellowness is speedily restored.

57. Take a photograph thus formed and place it in a vessel of water, in a *few days* it will fade out, and bubbles of oxygen will accumulate around the side. If the water is examined, there will be found no trace of either silver or iodine; thus it is evident the action has been confined to the paper.

58. We see that the iodide of silver has the power of sepa-

rating hydrogen from its combinations. I cannot regard this singular salt of silver as a definite compound: it appears to me to combine with iodine in uncertain proportions. In the process of darkening the liberation of hydrogen is certain; but I have not in any one instance been enabled to detect free iodine; of course it must exist either in the darkened surface, or in combination with the unaffected under layer; possibly this may be the iodide of silver, with iodine in simple mixture, which, when light acts no longer on the preparation, is liberated, combines with the hydrogen of that portion of moisture which the hygrometric nature of paper is sure to furnish, and as an hydriodate again attacks the darkened surface, restoring thus the iodide of silver. This is strikingly illustrative of the fading of the photograph. The picture is light iodide of silver and dark oxide of silver; as the yellow salt darkens under the influence of light it parts with its iodine, which immediately attacks the dark oxide, which is gradually converted into an iodide, oxygen, as I have shown, being liberated. The following experiments go not only to prove this position, but also serve to illustrate in some measure the action of light on this compound.

59. *Iodide of Silver.*—Precipitate with any hydriodate, silver from its nitrate in solution, and expose the vessel containing it, liquid and all, to sunshine, the exposed surfaces of the iodide will blacken; remove the vessel into the dark, and after a few hours all the blackness will disappear: we may thus continually restore and remove the blackness at pleasure.

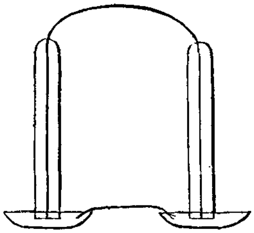
60. If we well wash and then dry the precipitate it blackens with difficulty, and if kept perfectly dry it continues dark; but moisten it and the yellow is restored after a little time.

61. In a watch-glass, or any capsule, place a little solution of silver; in another, some solution of any hydriodic salt; connect the two with a filament of cotton, and make up an electric circuit with a piece of platina wire, expose this little arrangement to the light, and in a very short time it will be seen that iodine is liberated in one vessel, and the yellow iodide of silver formed in the other, which blackens as quickly as it is formed.

62. Place a similar arrangement to the above (61.) in the dark, iodine is slowly liberated. *No iodide of silver formed,* but around the wire a beautiful crystallization of metallic silver.

63. A piece of platina wire was sealed into two glass tubes; these when filled, the one with hydriodate of potassa in solution, and the other with a solution of the nitrate of silver, were reversed into two watch-glasses containing the

same solutions, the glasses being connected with a piece of cotton, as in the adjoining figure.



A few hours of daylight occasioned the hydriodic solution in the tube to become quite brown with liberated iodine; a small portion of the iodide of silver was formed along the cotton, and at the end dipping in the salt of silver. (The glasses were kept purposely wide apart to prevent a quick formation.) *During the night the hydriodic liquid became again colourless and transparent, and the dark salt along the cotton was as yellow as at first.*

64. A curious illustration of the action I have endeavoured to elucidate, may be had by operating with chlorine. Its first action on one of these hydriodic photographs is the separation of iodine, which, when exposed to the light, is seen to act on the edges first, and gradually over the whole extent of the darkened portions. This curious action may be repeated until all the iodine is removed from the paper.

I think it will now be evident, that before we can expect to have quite permanent and well-finished hydriodic photographs, we must have at command the means of removing all the iodide of silver without injuring the dark oxide.

65. *On the Action of the dissevered Rays of the Solar Spectrum on dark photographic Papers washed with an hydriodate Liquid.*—Sir John Herschel, in his valuable memoir before-mentioned, has clearly shown, "that the total effect of a ray of white light on iodic preparations, is in fact the difference of two opposing actions, either of which may be exalted or enfeebled at pleasure by circumstances under our command, but difficult to reproduce exactly at our pleasure. When these opposing actions," I still quote Sir John's words, "exactly neutralize each other, the paper is insensible. When either preponderate, it is positive or negative in its character, according to that of the preponderant action; nay, it may at one and the same moment be positive to light incident under certain circumstances, insensible under others, and negative under a yet different illumination."

66. These singular facts were noticed by me in a very early stage of my inquiries; and you may perhaps remember my forwarding to you, with some specimens illustrative of my paper on "The Chemical Action of the Solar Spectrum," an hydriodated photograph, which exhibited the effects of coloured media in determining the action*.

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* See Sir John Herschel's memoir "On the Chemical Action of the Rays of the Solar Spectrum," Phil. Trans. 1840, Part i. page 43.

67. It is essential to a right understanding of the following results, that the absorptive power of the media I used in my experiments be set forth. Into a frame were fixed four coloured glasses.

A PURPLE GLASS, cutting off all the rays below the green, a portion of the green being also absorbed.

A GREEN GLASS, admitting the permeation of those rays only which lie between the least refracted extremity of the blue and the extreme orange. A portion of the yellow rays are absorbed.

A PALE AMBER GLASS, shortening the spectrum by the violet and indigo rays only.

A RED GLASS, absorbing all the most refrangible rays, permitting those only which lie below the blue to permeate.

68. If any of the sensitive darkened photographic papers (*a*, *b*, *c*, *d*, *o*,), washed with a good hydriodic solution, be placed in close contact, face to face, with an engraving which has been rendered transparent by being well soaked in water, and exposed to sunshine with the above frame superposed, we produce (to use Sir J. Herschel's nomenclature) a positive and a negative photograph on the same sheet. Beneath the blue glass the picture is copied as perfectly, but not quite so quickly, as under a colourless glass, the lights of the engraving being correctly copied on the photograph.

Beneath the green glass the lights and shadows of the photograph are completely reversed. In all the parts which correspond with the lights of the engraving the oxidation is much exalted, the paper having assumed a defined blackness. The darker parts of the engraving are copied in lights not simply formed by the contrast of the original brown of the paper with the induced blackness, but by a positive brightening of the parts.

Beneath the yellow glass the results are singularly uncertain. Often on the same sheet, with the same hydriodic solution, two experiments will give totally different results. I send you two specimens in proof of this, prepared in every way alike, and both executed within the same half-hour.

Under the red glass a reversed picture is formed, *not by the darkening of the oxide*, which retains its original colour, but by the eating out of strong lights under the dark parts of the engraving.

69. From these results it is evident that the blackening action on the wet hydriodidated paper is dependent on a different class of rays from those which blacken the finished drawings: in the wet process I ever find the maximum of darkness beneath the green glass, or rather within the limits of the green and yellow rays, little or no darkening effect being evident in the red rays; whereas on the dry picture

the maximum of effect is in the red rays (42—50.). I am inclined, however, to believe, that examination of these phænomena by a fixed spectrum will prove a shifting of the actions according to the kinds of paper used; but I am satisfied the entire action will be confined in the one instance to the green and yellow rays, and in the other to the orange and red rays.

70. The very curious brightening of those parts of the photograph corresponding with the darks of the engraving, attracted my attention powerfully. My first impression was, that the carbonaceous matter of the ink used in printing exerted a kind of catalytic action in directing the formation of an iodide of silver. I think I have proof of this to some extent.

71. Most printed pages, unless they are very old, when placed in juxtaposition *in the dark* with an hydriodidated photographic paper, leave an impression after some hours, and I have succeeded in partially copying some engravings thus. However, the result is uncertain; the copy, at all times faint, is often very imperfect, being sometimes bleached in circles, of which a letter or two form the centres; at other times the letters are copied, but all of them shaded from an extension of the bleaching action.

72. From effects I noticed from the accidental contact of some carbonate of iron, I was sanguine of being enabled to copy a written page. In this I was disappointed. I have not, with any of the numerous kinds of writing ink which I have tried, succeeded in obtaining the slightest trace of a letter on the photographic paper.

73. From the rapidity with which this effect is produced when the photograph and engraving are exposed to light, it is evident some other cause than the one I have just considered was in active operation. A careful examination of the photographs formed under the before-mentioned glasses, particularly under the red glass, convinced me that the quickening agent was to be sought for in the calorific rays, which are absorbed and retained with greater force by the dark parts of the engraving.

74. To put this notion to the test, I placed a printed page in contact with a paper wetted with an iodidated solution, over which I placed a glass, and then a plate of copper, which I made hot by rubbing it with a heated iron. The passage of the heat through the glass was sufficient to effect as fair a copy as is produced under the red glass by the influence of light.

75. These researches, which were pursued with a view

alone to an explanation of the peculiar mode of operation exhibited by the hydriodic salts on different preparations of silver under the influence of light, have thus opened a new and unexpected field of interesting inquiry, which may possibly end in the establishment of the new art of THERMOGRAPHY.

I shall pursue this subject with the same interest by which I have been led forward in my inquiries on Photography since the publication of Mr. Talbot's processes and those of Daguerre. For a few interesting applications and curious discoveries which I have made I merit not, nor do I seek praise. To every inquirer there is a mine of discovery, of which the few specimens I have gathered on the surface will, I trust, show the richness of the yet buried treasure.

I remain, Gentlemen, yours, &c.

Devonport, July 4, 1840. ROBERT HUNT.

XXXIX. *On the Form of Rutile.* *By* W. H. MILLER, *Esq., Professor of Mineralogy in the University of Cambridge.*

THE following values of the angles between normals to the faces of rutile were obtained from two extremely perfect crystals, for which I am indebted to Mr. Brooke. The instrument used as a goniometer was a twelve-inch theodolite. The coincidences of the signals were observed with a telescope having a power of about twelve. Each result is the mean of two observations made with the signals interchanged, in order to eliminate the error arising from the imperfect centring of the crystal. In one the faces p'', p''' (fig. 1.) gave double images, those in p''' being close and ill-defined. The observed values of $p'\,p'''$ were $65^\circ\ 33'\ 0''-30''-8''$; those of $p\,p''$ $65^\circ\ 32'\ 22''$, or $65^\circ\ 34'\ 26''$, according as one or the other of the images was made to coincide with the signal seen by direct vision. In the second and more perfect

Fig. 1.

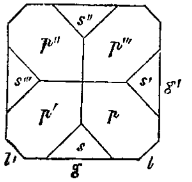

Fig. 2.