

V. "On the Cause of the Light Border frequently noticed in Photographs just outside the Outline of a Dark Body seen against the Sky; with some Introductory Remarks on Phosphorescence." By Professor G. G. STOKES, Sec. R.S.
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An observation I made the other day with solar phosphori, though not involving anything new in principle, suggested to me an explanation of the above phenomenon which seems to me very likely to be the true one. On inquiring from Captain Abney whether it had already been explained, he wrote: "The usual explanation of the phenomenon you describe is that the silver solution on the part of the plate on which the dark objects fall has nowhere to deposit, and hence the metallic silver is deposited to the nearest part strongly acted upon by light." As this explanation seems to me to involve some difficulties, I venture to offer another.

1. I will first mention the suggestive experiment, which is not wholly uninteresting on its own account, as affording a pretty illustration of what is already known, and furnishing an easy and rapid mode of determining in a rough way the character of the absorption of media for rays of low refrangibility.

The sun's light is reflected horizontally into a darkened room, and passed through a lens,* of considerable aperture for its focal length. A phosphorus is taken, suppose sulphide of calcium giving out a deep blue light,† and a position chosen for it which may be varied at pleasure, but which I will suppose to be nearer to the lens than its principal focus, at a place where a section of the pencil passing through the lens by a plane perpendicular to its axis shows the caustic surface well developed. A screen is then placed to intercept the pencil passing through the lens, and the phosphorus is exposed to sunlight or diffuse daylight, so as to be uniformly luminous, and is then placed in position; the screen is then removed for a very short time and then replaced, and the effect on the phosphorus is observed.

Under the circumstances described there is seen a circular disk of blue light, much brighter than the general ground, where the excitement of the phosphorus has been refreshed. This is separated by a dark halo from the general ground, which shines by virtue of the

* The lens actually used was one of crown glass which I happened to have; a lens of flint glass would have been better, as giving more separation of the caustic surfaces for the different colours.

† The experiments were actually made, partly with a tablet painted with Balmain's luminous paint, partly with sulphide of calcium and other phosphori in powder.

original excitement, not having been touched by the rays which came through the lens.

2. The halo is due to the action of the less refrangible rays, which, as is well known, discharge the phosphorescence. Their first effect, as is also known, is however to cause the phosphorus to give out light; and if the exposure were very brief, or else the intensity of the discharging rays were sufficiently reduced, the part where they acted was seen to glow with a greenish light, which faded much more rapidly than the deep blue, so that after a short time it became relatively dark.

3. This change of colour of the phosphorescent light can hardly fail to have been noticed, but I have not seen mention of it. In this respect the effect of the admission of the discharging rays is quite different from that of warming the phosphorus, which as is known causes the phosphorus to be brighter for a time, and then to cease phosphorescing till it is excited afresh. The difference is one which it seems important to bear in mind in relation to theory. Warming the phosphorus seems to set the molecules more free to execute vibrations of the same character as those produced by the action of the rays of high refrangibility. But the action of the discharging rays changes the character of the molecular vibrations, converting them into others having on the whole a lower refrangibility, and being much less lasting.

4. Accordingly when the phosphorus is acted on simultaneously by light containing rays of various refrangibilities, the tint of the resulting phosphorescence, and its more or less lasting character, depend materially on the proportion between the exciting and discharging rays emanating from the source of light. Thus daylight gives a bluer and more lasting phosphorescence than gaslight or lamplight. I took a tablet which had been exposed to the evening light, and had got rather faint, and, covering half of it with a book, I exposed the other half to gaslight. On carrying it into the dark, the freshly exposed half was seen to be much the brighter, the light being, however, whitish, but after some considerable time the unexposed half was the brighter of the two.

Again, on exposing a tablet, in one part covered with a glass vessel containing a solution of ammonio-sulphate of copper, to the radiation from a gas flame, the covered part was seen to be decidedly bluer than the rest, the phosphorescence of which was whitish. The former part, usually brighter at first than the rest, was sure to be so after a very little time. The reason of this is plain after what precedes.

A solution of chromate of potash is particularly well suited for a ray filter when the object is to discharge the phosphorescence of sulphide of calcium. While it stops the exciting rays it is transparent for nearly the whole of the discharging rays. The phosphorescence is

accordingly a good deal more quickly discharged under such a solution than under red glass, which along with the exciting rays absorbs also a much larger proportion than the chromate of the discharging rays.

5. I will mention only one instance of the application of this arrangement to the study of absorption. On placing before excited sulphide of calcium a plate of ebonite given me by Mr. Preece as a specimen of the transparent kind for certain rays of low refrangibility, and then removing the intercepting screen from the lens, the transmission of a radiation through the ebonite was immediately shown by the production of the greenish light above-mentioned. Of course, after a sufficient time the part acted on became dark.

6. I will mention two more observations as leading on to the explanation of the photographic phenomenon which I have to suggest.

In a dark room, an image of the flame of a paraffin lamp was thrown by a lens on to a phosphorescent tablet. On intercepting the incident rays after no great exposure of the tablet, the place of the image was naturally seen to be luminous, with a bluish light. On forming in a similar manner an image of an aperture in the window shutter, illuminated by the light of an overcast sky reflected horizontally by a looking-glass outside, this image of course was luminous; it was brighter than the other. On now allowing both lights to act simultaneously on the tablet, the image of the flame being arranged to fall in the middle of the larger image of the aperture, and after a suitable exposure cutting off both lights simultaneously, the place of the image of the aperture on which the image of the lamp had fallen was seen to be *less* luminous than the remainder, which had been excited by daylight alone. The reason is plain. The proportion of rays of lower to rays of higher refrangibility is much greater in lamplight than in the light of the sky; so that the addition of the lamplight did more harm by the action of the discharging rays which it contained on the phosphorescence produced by the daylight, than it could do good by its own contribution to the phosphorescence.

7. The other observation was as follows:—The same tablet was laid horizontally on a lawn on a bright day towards evening, when the sun was moderately low, and a pole was stuck in the grass in front of it, so as to cast a shadow on the tablet. After a brief exposure the tablet was covered with a dark cloth, and carried into a dark room for examination.

It was found that the place of the *shadow* was *brighter* than the general ground, and also a deeper blue. For a short distance on both sides of the shadow the phosphorescence was a little feebler than at a greater distance.

This shows that, though the direct rays of the sun by themselves alone would have strongly excited the phosphorus, yet acting along

with the diffused light from all parts of the sky, they did more harm than good. They behaved, in fact, like the rays from the lamp in the experiment of § 6. The slightly inferior luminosity of the parts to some little distance on both sides of that on which the shadow fell, shows that the loss of the diffuse light corresponding to the portion of the sky cut off by the pole was quite sensible when that portion lay very near the sun.

All this falls in very well with what we know of the nature of the direct sunlight and the light from the sky. In passing through the atmosphere, the direct rays of the sun get obstructed by very minute particles of dust, globules of water forming a haze too tenuous to be noticed, &c. The veil is virtually coarser for blue than for red light, so that in the unimpeded light the proportion of the rays of low to those of high refrangibility goes on continually increasing, the effect by the time the rays reach the earth increasing as the sun gets lower, and has accordingly a greater stretch of air to get through. Of the light falling upon the obstructing particles, a portion might be absorbed in the case of particles of very opaque substances, but usually there would be little loss this way, and the greater part would be diffused by reflection and diffraction. This diffused light, in which there is a predominance of the rays of higher refrangibility, would naturally be strongest in directions not very far from that of the direct light; and the loss accordingly of a portion of it where it is strongest, in consequence of interception by the pole in front of the tablet, accounts for the fact that the borders of the place of the shadow were seen to be a little less luminous than the parts at a distance.

8. The observations on phosphorescence just described have now prepared the way for the explanation I have to suggest of the photographic phenomenon.

It is known that, with certain preparations, if a plate be exposed for a very short time to diffuse daylight, and be then exposed to a pure spectrum in a dark room, on subsequently developing the image it is found that while the more refrangible rays have acted positively, that is, in the manner of light in general, a certain portion of the less refrangible have acted in an opposite way, having undone the action of the diffuse daylight to which the plate was exposed in the first instance.

It appears then that in photography, as in phosphorescence, there may in certain cases be an antagonistic action between the more and less refrangible rays, so that it stands to reason that the withdrawal of the latter might promote the effect of the former.

Now the objective of a photographic camera is ordinarily chemically corrected; that is to say, the minimum focal length is made to lie, not in the brightest part of the spectrum, as in a telescope, but in the part which has strongest chemical action. What this is, depends

more or less on the particular substance acted on; but taking the preparations most usually employed, it may be said to lie about the indigo or violet. Such an objective would be much under-corrected for the red, which accordingly would be much out of focus, and the ultra-red still more so.

When such a camera is directed to a uniform bright object, such as a portion of overcast sky, the proportion of the rays of different refrangibilities to one another is just the same as if all the colours were in focus together; but it is otherwise near the edge of a dark object on a light ground. As regards the rays in focus, there is a sharp transition from light to dark; but as regards rays out of focus, the transition from light to dark though rapid is continuous. It is, of course, more nearly abrupt the more nearly the rays are in focus. Just at the outline of the object there would be half illumination as regards the rays out of focus. On receding from the outline on the bright side, the illumination would go on increasing, until on getting to a distance equal to the radius of the circle of diffusion (from being out of focus) of the particular colour under consideration the full intensity would be reached. Suppose, now, that on the sensitive plate the rays of low refrangibility tend to oppose the action of those of high refrangibility, or say act negatively, then just outside the outline the active rays, being sharply in focus, are in full force, but the negative rays have not yet acquired their full intensity. At an equal distance from the outline on the dark side the positive rays are absent, and the negative rays have nothing to oppose, and therefore simply do nothing.

9. I am well aware that this explanation has need of being confronted with experiment. But not being myself used to photographic manipulation, I was unwilling to spend time in attempting to do what could so much better be done by others. I will, therefore, merely indicate briefly what the theory would lead us to expect.

We might expect, therefore, that the formation of the fringe of extra brightness would depend:—

(1.) Very materially upon the chemical preparation employed. Those which most strongly exhibit the negative effect on exposure to a spectrum after a brief exposure to diffuse light might be expected to show it the most strongly.

(2.) Upon the character of the light. If the light of the bright ground be somewhat yellowish, indicating a deficiency in the more refrangible rays, the antagonistic effect would seem likely to be more strongly developed, and, therefore, the phenomenon might be expected to be more pronounced.

(3.) To a certain extent on the correction of the objective of the camera. An objective which was strictly chemically corrected might be expected to show the effect better than one in which the chemical

and optical foci were made to coincide, and much better than one which was corrected for the visual rays.

It is needless to say that on any theory the light must not be too bright or the exposure too long; for we cannot have the exhibition (in the positive) of a brighter border to a ground which is white already.

P.S.—Before presenting the above paper to the Royal Society I submitted it to Captain Abney, as one of the highest authorities in scientific photography, asking whether he knew of anything to disprove the suggested explanation. He replied that he thought the explanation a possible one, encouraged me to present the paper, and kindly expressed the intention of submitting the question to the test of experiment.

I have referred to the photographic action of the more and less refrangible rays as antagonistic. This is practically true so far as the explanation I have ventured to offer is concerned, inasmuch as the more refrangible rays convert a salt of silver which is not developed into one which is developable, while the less refrangible convert the latter into one which is not developable. But Captain Abney has pointed out to me that though the first and third salts cannot be distinguished by appearance, nor by the action of the developing solution, they are nevertheless not the same, so that the two actions of the rays are not, rigorously speaking, antagonistic, inasmuch as the one is not strictly the reverse of the other. Thus with bromide of silver the explanation of the observed phenomena, according to Captain Abney, is that the undevelopable bromide is converted, chiefly by the action of the more refrangible rays, into a subbromide, which is developable; and this again is converted, chiefly by the action of the less refrangible rays, into an oxybromide, which is undevelopable. As however under the ordinary circumstances for obtaining a good picture the action of the light is chiefly of the first kind, and a much longer exposure would be required to bring out prominently the second kind of action, the explanation I have suggested is not virtually affected, though the two actions could not be prolonged indefinitely, as in the illustrative experiment in phosphorescence described in § 6.

June 10.

The Society adjourned over the Whitsuntide Recess to Thursday, June 15th.