

PHOSPHORESCENCE PATTERNS IN DIAMOND

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1. INTRODUCTION

THAT some diamonds continue to shine for a while in darkness after exposure to sunlight has long been known and to this phenomenon is applied the term phosphorescence. The brightness of the phosphorescence varies considerably for different diamonds, and this variation is closely related to the strength of emission of visible light under ultraviolet irradiation which in general is known as fluorescence. Brightly phosphorescent diamonds are also brightly fluorescent. However, there is a striking difference in this respect between yellow-fluorescent and blue-fluorescent diamonds (Raman, 1943). The former have a short-lived and scarcely noticeable phosphorescence while the latter have a bright glow lasting for several minutes. The colour in both types of diamond is greenish yellow. By viewing the diamonds through a suitable violet filter, Sir C. V. Raman discovered that for a short duration of a few seconds, there is blue light accompanying the greenish yellow glow in the case of brightly blue-fluorescent diamonds. But it is the latter that carries most of the energy emitted.

Researches carried out at this Institute (Raman, 1943) have revealed that cleavage plates of diamond often exhibit patterns of fluorescence due to variations in *intensity* of the emitted light from various parts of the plate, and in many cases also variations of *colour*. A detailed investigation of these patterns appears in a paper by G. R. Rendall (1946) in the proceedings of the symposium. The results of the investigation show that while some diamonds exhibit only blue or yellow fluorescence patterns, others exhibit both, and these patterns may be entirely different. Visually it is noticed that cleavage plates which exhibit fluorescence patterns also exhibit phosphorescence patterns, that is, variations of the intensity of the phosphorescence. The object of the present investigations was to photograph such patterns so that they could be studied at leisure and compared in detail with fluorescence patterns. The main difficulty in obtaining such patterns is the feebleness of the phenomenon requiring long exposures of more than several hours if a phosphoroscope and a camera are used. This has been successful

overcome by the use of the ingenious method of contact photography suggested by Mr. Hermann Yagoda in a letter to Sir C. V. Raman. The method consists in placing the luminous plate of diamond in direct contact with a sensitive photographic plate in the dark and developing the plate subsequently. The records obtained by this method are presented in this paper. The interesting result has emerged that the yellow phosphorescence emission corresponds to the blue-fluorescence pattern, and that the yellow-fluorescence patterns are not recorded in phosphorescence.

2. EXPERIMENTAL TECHNIQUE

The technique used in getting the phosphorescence patterns was extremely simple. The best source for exciting the phosphorescence in diamond was found to be sunlight between 10 A.M. and 2 P.M. Sunlight was reflected by a heliostat into a hollow brass tubing fixed in one of the walls of a dark room. Close to this tubing was fixed a lens of aperture 10 cms. and focal length 15 cm. Just in front of the lens was placed a Corning glass filter (3" × 3"), which allows only the ultraviolet light between 3500 and 4000 Å and a little red light above 7000 Å to pass through. The filter also served the useful purpose of cutting off the long-wave radiations which would otherwise heat the diamond. The specimens used in these experiments were cleavage plates of diamond in the collection of Sir C. V. Raman. A hypersensitive panchromatic HP3 plate was kept in readiness inside a darkened chamber. The cleavage plate was held for about a minute in the path of the ultraviolet beam and transferred quickly into the chamber and placed in contact with the sensitive side of the photographic plate. After half an hour, by which time the glow would have practically disappeared for even the most intensely blue-luminescent specimens, the diamond was removed and the photographic plate was developed. A photograph showing great wealth of detail was obtained which may be called the phosphorescent pattern of the diamond, as the prints show at a glance the large variations in the intensity of the evanescent light over the different portions of the same diamond.

In the case of moderately luminescent specimens, the diamonds were placed in contact with a mirror silvered on the front and after excitation dropped along with the mirror on the photographic plate. Thus, a nearly fourfold increase in intensity was obtained as the phosphorescence is doubled up in intensity and the mirror reflects half the phosphorescent light back to the photographic plate. The clarity was not, however, lost as the diamonds were very thin, being rarely more than 1 mm. thick. Another method of obtaining an increase in intensity of the glow—employed especially for big

cleavage plates—was to hold the diamonds at the focus of the ultraviolet light and oscillate the diamonds quickly so that the whole area of the plate is excited uniformly to the maximum possible activation.

One of the possible methods of obtaining the patterns in weakly luminescent diamonds would be to increase the aperture of the lens beyond $f/1.5$ used in the experiments. Alternatively, a big concave mirror could be used. But the best method would be to make an arrangement by which the diamonds could be replaced in exactly the same position on the photographic plate. By this method the procedure can be repeated a number of times and each time the exposure need only be for a short time of 2 or 3 minutes, as weakly phosphorescent diamonds have a short-lived glow.

In the case of the intensely blue-fluorescent diamond N.C. 79, it was dropped on the photographic plate half a minute after excitation (Fig. 1 in Plate XXII). Also to show that the glow is mainly yellow and not blue, two more photographs of the glow were obtained by placing two thin gelatin filters respectively between the diamond and the HP3 plate. One of the filters was yellow and transmits wavelengths above 5000 \AA , while the other was a violet filter transmitting wavelengths below 5000 \AA and above 6300 \AA . From Fig. 2 in Plate XXII which was obtained with the yellow filter, it is clearly seen that the energy of phosphorescence is almost entirely in the yellow. In the picture obtained with the violet filter (not reproduced), the outline of the diamond was barely visible.

The contact method of photography used in the present investigations might be suitably adapted for taking fluorescent patterns in very feebly fluorescent diamonds. Between the diamond whose pattern is required and the photographic plate a thin cellophane filter, which cuts off the ultraviolet light completely might be placed, ultraviolet light alone being incident on the diamond. Thus the fluorescence pattern alone will be recorded on the photographic plate.

3. DESCRIPTION OF THE PATTERNS

The phosphorescence patterns of 12 cleavage plates of diamond of different size and shape are reproduced in Plates XXII and XXIII and the prints have been made of the same size by a suitable enlargement of the negatives. All the diamonds are strongly fluorescent, N.C. 79 being the most intense blue-fluorescent one. The others exhibit varying colours in fluorescence due to mixing of the blue and yellow fluorescence in different proportions. N.C. 110 and N.C. 107 are triangular and N.C. 85 is rod-shaped. N.C. 80 and N.C. 108, are circular, N.C. 106, N.C. 107 and N.C. 114 are very small and thin, while B1, B2, B3 and B4 are large plates.

In most cases, geometric patterns of phosphorescence are obtained. N.C. 110 shows nearly parallel bands, N.C. 80, N.C. 85, N.C. 107 and N.C. 114 exhibit triangles, while B. 1, B. 2, B. 3 and B. 4 show hexagons. N.C. 108 shows an interesting pattern which resembles a spider's web.

4. COMPARISON OF PHOSPHORESCENCE AND FLUORESCENCE PATTERNS

The comparison of phosphorescence with the fluorescence patterns in the same diamond confirms the observation that brightly blue-fluorescent portions have bright phosphorescence. Thus in the case of purely blue-fluorescent diamonds, both the patterns are exactly analogous. As an example the case of N.C. 79 (old number D. 34) might be cited. The bright blue patch comes out brightly in the phosphorescence patterns also. The fluorescence patterns of this and of N.C. 85 and N.C. 106 (old numbers D. 42 and D. 186 respectively) are given in the paper by Sunanda Bai (1944) in the earlier symposium.

In the case of diamonds showing the mixed type of fluorescence, however, the phosphorescence patterns were compared with the blue and yellow fluorescence patterns recorded separately in the paper by Rendall (1946) which appears in the present symposium. There, the fluorescence patterns of N.C. 80, N.C. 108, N.C. 110, N.C. 114 and B. 1 are represented. The comparison at once reveals that it is the blue and not the yellow pattern that is recorded in the phosphorescence pattern in spite of the fact that the glow is yellow. Striking examples are N.C. 110 and N.C. 114 which show entirely different patterns in the yellow and blue as might be seen in the abovementioned paper. In the yellow fluorescence patterns of these diamonds there are straight parallel bands. In the blue, N.C. 110 exhibits curved bands and a portion at the left bottom is comparatively weakly luminescent. The phosphorescence pattern is identical with the blue-fluorescence pattern. In the blue, N.C. 114 exhibits a patch at the right while the parallel bands appearing in the yellow are entirely missing. The phosphorescence pattern of this diamond shows a bright portion at the right and resembles the blue pattern. However a small portion at the bottom of the bright patch in the blue fluorescence is not recorded in phosphorescence. These observations confirm the finding that yellow fluorescence has only a feeble and short-lived phosphorescence accompanying it. As further confirmation of this, a brightly green-fluorescent diamond was tried and gave an extremely feeble picture showing only the bare outline (not reproduced).

N.C. 80 exhibits nearly the same patterns both in blue and yellow fluorescence and the phosphorescence pattern is similar to both. N.C. 108 has a bright central spot in the blue fluorescence surrounded by a spiral,

while in the yellow the spot is absent. In phosphorescence the central bright spot along with the spiral comes out.

In all the photographs the edges of the diamond come out strongly as they have bright blue-fluorescence and hence strong phosphorescence. In the case of the phosphorescence pattern of B. 1, there is a bright patch in the middle of the hexagon, while in the blue fluorescence pattern this is entirely absent. In the cases of B. 2, B. 3 and B. 4, a larger number of concentric hexagons are obtained in phosphorescence than in fluorescence patterns. In these cases and that of N.C. 114 referred to above, therefore, there are light departures from the exact identity of the phosphorescence patterns with the blue-fluorescence pattern.

In conclusion the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for suggesting the problem and for the invaluable guidance given during the investigations.

SUMMARY

Phosphorescence patterns in a dozen cleavage plates of diamond revealing the variations in intensity of phosphorescence in different portions of the same diamond have been successfully recorded by the method of contact photography. Comparison of these with the fluorescence patterns in the same diamond shows that the yellow phosphorescence emission corresponds to the blue fluorescence patterns, and that the yellow fluorescence patterns, if present, are not recorded in phosphorescence. Geometric patterns such as parallel bands, triangles, hexagons and spirals have been obtained in many cases.

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