INFRA-RED RADIATIONS WITH SPECIAL REFERENCE TO THEIR QUENCHING EFFECTS UPON ZINC SULPHIDE PHOSPHORS.

By G. G. BLAKE, M.I.E.E., F.Inst.P.,

Physics Department, Sydney University.

(Communicated by Professor O. U. Vonwiller.)

(With Plates III-V.)

(Manuscript received, June 21, 1939. Read, July 5, 1939.)

Much work has been done in study of fluorescence and phosphorescence. Already a number of books have been written on the subject. Consequently the author is able to quote only a few necessary historical facts having special reference to this work, before describing his own contribution to the subject.

HISTORICAL.

Fluorescence and Phosphorescence.

Many important facts and theoretical considerations were recorded at a discussion on luminescence by members of the Faraday Society at Oxford in October, 1938; fluorescence and phosphorescence were defined (for practical purposes) as follows:

A, B, C, Plate III, Fig. 1, is a time curve of luminescence. A substance may be said to be "fluorescing" whilst it is being subjected to an exciting radiation. As soon as the exciting radiation is removed, the luminescence of the substance commences to decrease as depicted from B to C, and during this period the substance may be said to be "phosphorescing".


It was pointed out by N. Riehl that, in addition to the "phosphorescence" which is strongly affected by temperature and can be "frozen", there is an accompanying "afterglow" which is uninfluenced by temperature. Whilst "phosphorescence" can be increased only to the limit of "saturation excitation" afterglow can be increased practically without limit by increasing the exciting radiation. When the afterglow has died out there remains a certain amount of residual energy which can be stored up for any length of time until it is liberated by heat. This energy corresponds to phosphorescence.

Since the early investigations of E. Becquerel with his phosphroscope, and of P. Lenard, a great deal of work has been carried out. Copious references are given in Handbuch der Experimental Physik (see 1). In this work the effect of temperature on phosphorescence has been dealt with very fully. In this connection particular reference should be made to the work of F. Schmidt in 1920, who, amongst many other things, investigated the effect of changing the temperature of a phosphor whilst it was under illumination from a Nernst lamp.

Much information on the chemical side will also be found in these two volumes re the preparation of zinc sulphide phosphors and phosphors containing selenium. The effects of magnetic and electric fields also have been studied.

Becquerel and others have shown that a large number of phosphors have only a momentary duration of phosphorescence.

According to Le Bon (1 "The Evolution of Forces") at a temperature below 0° C. varying with different substances, a body does not visibly phosphoresce. As the temperature rises, up to about 100° C., phosphorescent intensity increases. Above this temperature it decreases and reaches zero at about 500° C.

The same authority gives the following general law: "After a certain emission of light at a given temperature a phosphor indefinitely retains a residual phosphorescence as long as its temperature is not raised again."

---

3 See also "Zine Sulphide Phosphors", J. Chem. Phys., 6, 454-461, 1938, which deals with the theory of phosphorescence and copper-activated phosphors, also J. Chem. Phys., 7, 4-7, 1939.

K—July 5, 1939.
According to Houston, fluorescence is explained on Bohr's theory as follows: "If, when an atom is raised to a higher state by absorption of light, it returns to the normal state by stages emitting light, in the process fluorescence takes place. Owing to the nature of the process, the emitted frequencies must be smaller than the absorbed frequency in accordance with Stokes' law."

**The Work of the Author.**

The present paper deals only with some effects observed with zinc and calcium, sulphide phosphors.

**Phosphorescent Screens.**

In order to study their properties, screens were prepared first as described by Le Bon. The ZnS or CaS was ground in a mortar and then passed through a fine silk sieve; finally it was mixed with bronzing varnish, the proportion of the phosphor being not less than 30%. After thoroughly mixing, it was poured (without being allowed to settle) on to a sheet of cardboard or glass laid flat. Screens made in this way dried and were ready for use in about fifteen minutes.

These screens answered fairly well, but did not phosphoresce so brilliantly as the original phosphors from which they were made.

It was next decided to employ a solution consisting of equal parts of amyl acetate and acetone, in which was dissolved sufficient celluloid to give it the viscosity of a thick varnish. Thoroughly powdered zinc sulphide or calcium sulphide was mixed into this and the mixture was poured on to cardboard or glass in similar manner to the bronzing varnish mixture of Le Bon. It dried in about the same time, and was found to possess a considerable increase of luminosity.*

The two following symbols are freely employed by the author for convenience of denotation. ZnS denotes that a zinc sulphide screen at ambient temperature has not been exposed to exciting radiations, i.e. that it is not phosphor-

---


* It should be possible under pressure, or in some other manner, to manufacture a far more perfect screen, having a glazed surface similar to the calcium tungstate intensifying screens used in radiography. With a really well-finished screen, far more brilliant photographic results could be obtained.
escing; ZnS denotes that the screen at ambient temperature has been exposed to exciting light radiations and is phosphorescing.

Photographic impressions (contact prints) from phosphorescing screens are spoken of as phosphorographs.

Fluorescent Screens.

Fluorescent screens have been in use for radiography for many years. Röntgen first employed screens of barium platinocyanide for visual X-ray examinations, and the now general employment of "intensifying screens" when taking radiographs is due to a suggestion made by A. A. Campbell Swinton.⁵

A screen of calcium tungstate or other fluorescent material is placed in contact with an X-ray plate or film between the latter and the X-ray tube. The X-rays having penetrated the subject, cause the intensifying screen to fluoresce with an actinic light to which the plate is at least ten times more sensitive than it is to the X-rays. All intensifying screens make use of the part of the curve of luminescence between A and B, Pl. III, Fig. 1, and every endeavour is made to reduce phosphorescence to a minimum.

In order to obtain photographic records of the effects of various visible and infra-red radiations upon a phosphorescent screen, Le Bon and others have made contact prints by placing a photographic plate in contact with the screen for a few seconds after the required visible effect has been obtained and while the screen is still phosphorescing.

The Quenching of Fluorescence by Infra-red Radiation in the Region A to B, Pl. III, Fig. 1.

The author has found that the quenching effects of infra-red rays are far less apparent during fluorescence than they are after the exciting radiation has been removed and phosphorescent decay has commenced. Phosphorographs A and B, Plate V, each show the images of the filaments of two 100 W. incandescent metal filament electric lamps. (see also Pl. III, Fig. 2.)

⁵ Jour. Roy. Soc. Arts, 44, 1896. At this lecture, Campbell Swinton said, "It appears to me that the sensitiveness of photographic plates to these rays might very probably be very largely increased by treating them with fluorescent materials or even arranging a fluorescent screen to be in contact with the film during exposure." KK—July 5, 1939.
A Zn S Cu screen (green fluorescence) was first energized by an exposure of 10 seconds to a 500 W. D.C. arc between steel electrodes; it was then placed in the position shown in Fig. 2 and the images of the two filaments F and F' were simultaneously projected on to it.

The light from L' was filtered by means of a trough containing cupric ammonium sulphate so that only blue rays were transmitted. The image of the lamp, therefore, increases the phosphorescence of the screen and shows as a bright line, B, on Pl. V., phosphorographs A and B.

The light from the other lantern was filtered by means of a sheet of black glass which cut out all visible radiations and transmitted only infra-red. These latter radiations quenched the phosphorescence of the screen and show as dark lines, Q, in the phosphorographs.

By increasing the intensity of the quenching radiations or by reducing the intensity of the blue energizing rays (by the employment of a diaphragm, additional blue filters, or a series resistance R) control was obtained of the effects produced on the Zn S screen—either the energizing or the quenching radiations were made to predominate at will. In phosphorograph A, Pl. V., blue radiations predominate, and in phosphorograph B of the same Plate quenching radiations are the stronger (note specially the point of intersection of the two filament images).

Plate III, Fig. 3 illustrates another experiment to show this effect; in this case a transparent Zn S Cu screen (glass backing in lieu of cardboard) was employed.

The diffused blue rays from lamp L cause it to fluoresce weakly. As soon as the quenching rays from lamp L' are simultaneously projected on to the other side of the screen the fluorescence is extinguished (where the projected image of lamp L' falls upon the screen). The extinguishing action of infra-red rays upon fluorescence is comparatively weak, but as soon as the exciting radiations are removed and phosphorescence has commenced the quenching effects are relatively powerful.

The Quenching of Phosphorescence by Infra-red Radiations in the Region B to C, Pl. III, Fig. 1.

Pl. V., phosphorograph C, is a contact print from a Zn S Cu screen (green) on a panchromatic plate. The screen was first energized by an exposure of 10 seconds to a 500 W. D.C. arc. A strip of tinfoil, N, having a circular hole at its centre, was laid across it. Both screen
and foil were then covered by 24 thicknesses of thin black paper (selected) and placed near to a 100 W. incandescent metal filament electric lamp. When the black paper was removed from the screen (in the dark) the phosphorescence of the latter had been quenched everywhere except where it was shielded by the tinfoil, thus showing the transparency of the paper to infra-red radiations and the powerful extinguishing action of the latter in the region of the phosphorescent decay curve B and C, Pl. III, Fig. 1.

Chromatic Aberration and Astigmatism.

The employment of a Zn S screen in place of an ordinary photographic plate reveals defects not seen on the latter.

The general scheme of this experiment can be obtained by reference to Pl. III, Fig. 2; in this case, however, only one lamp, L1, was employed. Its light was unfiltered and the image of the filament was focussed through lens Y1 on to a flat surface S. (Y1 was set at an angle to the rays as indicated by the dotted line Y2). First an ordinary photographic plate was placed at S and a rapid exposure given. The photographic image obtained is seen in photograph D, Pl. V.

A Zn S screen was then placed at S and another exposure was made; see the contact print (or phosphorograph) made from the screen after this exposure (upon a panchromatic plate), phosphorograph E, Pl. V. D and E are similar to F and G, but in the latter cases a diaphragm was employed covering 3 of the lens Y1.

At the bottom of phosphorographs E and G the visible rays have caused increased phosphorescence and are at sharper focus (owing to the glass lens having different refractive indices for visible and infra-red radiations) than the quenching radiations which have given us the black lines on either side of the white phosphorescent line. In the absence of any visible rays the quenching effect would show up as a broad line covering the whole of the space occupied by the narrow and sharper focussed line of phosphorescence.

As the experiment was performed during fluorescence the unfiltered visible rays from the lamp were able to overcome the quenching completely. Reference to Pl. V, phosphorographs A and B, will show by the absence of dark shadows on either side of the filament image that the
filter employed had entirely absorbed the quenching radiations.

On the left-hand side of phosphorographs E and G, Pl. V, it will be observed that quenching has taken place only on the left-hand side of the filament image. This indicates that the lens is astigmatic; it has bent the visible rays towards the right in the vertical plane, whereas in the horizontal plane it has acted symmetrically.

Comparison of the Relative Focal Length of a Glass Lens to Blue and to Quenching Infra-red Radiations.

The light from a 100 W. metal filament lamp L, Pl. III, Fig. 4, was first scattered by means of a sheet of frosted glass placed between it and a narrow slit. On the other side of the slit filters of black and of blue glass were employed each covering half of the slit as depicted.

By means of a glass lens Y, the image of the blue half of the slit was brought to a sharp focus at position A on to a Zn S Cu screen (green). H, Pl. V, is a phosphorograph of the effect produced.

The screen was then re-energized and moved further from the lens until the quenching radiations gave a sharply defined image of the slit. Phosphorograph I, Pl. V, shows the effect produced.

A comparison of phosphorographs H and I shows that (1) when the blue rays were in focus, although the quenching rays were out of focus, they were not scattered appreciably; (2) whereas, when the quenching rays were in focus, the blue rays were not only out of focus but also were scattered strongly. A comparison of phosphorograph H with the filtered blue image of the filament seen in A and B, Pl. V, shows that the blue glass used in our present experiment was an imperfect filter and allowed the quenching radiations to operate on each side of the blue image of the slit. In order to bring the quenching rays to a sharp focus, the screen had to be moved approximately $2\frac{1}{32}$ inches further from the lens.

Given the refraction index of the latter and an accurate optical bench, it should be possible to calculate the wavelength of the quenching rays.
Scattering.

Further comparative tests of the scattering of visible and infra-red radiations were made as follows:

1. A ZnS screen (Pl. III, Fig. 5) was placed in the shadow of a lip or shield $P$. Normally using a blue glass filter the light from lamp $L$ was sufficiently scattered by a sheet of ground glass that it caused an increase in the brilliance of the phosphorescence of the screen.

2. Still retaining the blue glass filter, when the frosted glass was removed the blue rays passed right over the ZnS screen and did not affect it.

3. Using a black glass filter instead of the blue and leaving the frosted glass in position, it was not possible to obtain any evidence of scattering of the infra-red radiations.

4. Evidence of scattering was obtained however in the following manner:

Pl. III, Fig. 2. The image of an incandescent lamp filament was projected by infra-red radiation through a black glass filter on to a ZnS (green) screen. Brightly burnished thin sheet ebonite, or clear glass, could be placed in any position in the path of the rays without destroying the definition of the image, but unpolished ebonite or ground glass dispersed the image unless placed in contact with the ZnS screen.

A Reversal of Image Effect and its Interpretation.

Phosphorographs J and K, Pl. V, show the effects of a small heating unit, illustrated in Pl. III, Fig. 6, upon a ZnS screen.

The heater coil $R$ was enclosed within a metal shield $M$ and when heated to about 45° C. it was placed in contact with the back of a ZnS screen (on cardboard).

The latter phosphoresced more brightly under the action of the heat, but a few seconds after the heater had been removed the bright patch (seen on phosphorograph J) gradually disappeared, and, as one watched, a dark patch gradually developed in its place (see phosphorograph K, Pl. V). This effect must not be confused with the well-known phenomenon of "photographic reversal". A certain definite amount of energy was stored within the zinc sulphide during its energizing exposure to light. Under normal conditions a certain amount of this energy would be gradually dispersed as phosphorescent light, following a decay curve as shown from B to C, Pl. III, Fig. 1. The effect of the heat has been to sharpen and
shorten this curve, i.e. energy was expended more rapidly, hence the increase of luminosity. This was followed on cooling by a deficiency of phosphorescence as compared with the rest of the screen, whose phosphorescence was decaying at its normal speed, and on the duration of the decay curve.

Phosphorograph L, Plate V, shows the speeded decay of luminescence, due to placing a small coin straight from one's pocket, at body heat about 36° C. (only 14·25 degrees above ambient temperature) on to the surface of a Zn S screen (green).

The Earliest Appearance of Quenching Radiations.

The heater unit F illustrated in Pl. III, Fig. 7 controlled by a variable series resistance R was fitted in an open-ended metal cylinder E, and the latter was fitted with a cardboard cover C, in the end of which was an orifice D. This was pushed over the cylinder until the cardboard end almost touched the heater coil. A Zn S screen (green) was then placed tightly against D and the heater coil was gradually raised in temperature from room temperature through dark heat to white heat. As the temperature increased the fluorescent image of the orifice grew in luminosity, but as soon as the heater reached a barely visible red heat (about 400° C.) quenching set in, which steadily increased in intensity with additional rise in temperature until the heater fused.

Another experiment was made in the following manner: The image of a bunsen gas flame was projected by means of a lens upon a Zn S screen (green). No quenching was observed, but after the introduction of a short length of iron wire into the flame, quenching occurred along the image of the wire as soon as the latter glazed at dull red heat.

Shift of Spectral Distribution Effect.

Pl. III, Fig. 8 represents a 100 W. metal filament electric lamp L controlled by means of a variable series resistance R. This was first set with its sliding contact at a position B, and a Zn S screen (green) was exposed to the unfiltered light from lamp L at this setting. The Zn S screen thus energized was then covered with a sheet of metal provided with a small slit as shown in the figure.

The slider was then moved back to a position A and another exposure was given through the slit at this new
setting. This resulted in a quenching of the phosphorescence. The slit was then moved across to another part of the $\Phi$ screen, and the slider of the resistance was moved to a position C, thus increasing the brightness of the lamp, and another exposure was made. This time an increase of luminosity resulted. The phosphorograph M, Pl. V, is a contact-print on a panchromatic plate from a $\Phi$ Zn S screen after the three foregoing exposures.

The position B of the slider could be chosen at random at any point along the resistance; an increase of current through the lamp (i.e. an increase of filament temperature) always caused increased luminosity, whilst a decrease always caused quenching.

That this effect was due to a shift of spectral distribution and not to an alteration of light-intensity was shown as follows: Having energized the screen at any selected setting of the resistance, the former was removed to a greater distance from the lamp L. In this way we obviously decreased the intensity of the light according to the inverse square law but no quenching action occurred.

Infra-Red Radiographs.

Le Bon\(^1\) showed that printer’s ink is very opaque to infra-red radiations. He wrapped a printed sketch in black paper, placed it in an envelope in an ebonite box and obtained a good impression of the sketch upon a $\Phi$ Zn S screen by means of the quenching radiations from a paraffin lamp.

N, Pl. V, is an infra-red radiograph taken in this manner of a newspaper cutting wrapped in black paper (selected) within an ordinary white paper envelope. The whole packet was opaque to visible light, but when it was placed upon a $\Phi$ Zn S (green) screen and exposed to the quenching radiations from an ordinary otherwise unscreened 100 W. incandescent electric lamp for 10 seconds, the infra-red rays passed right through the packet as X-rays pass through an opaque body, and quenched the screen in varying degree in accordance with its varying densities. The ink being almost entirely opaque, prevented all quenching.

The phosphorograph N, Pl. V, here reproduced is a contact-print on a panchromatic plate from a $\Phi$ Zn S screen after such a radiographic exposure.
A New Photographic Process.
(Positive and Negative Photographic Phosphorescent Impressions on Screens.)

Further consideration of the "shift of spectral distribution effect" showed that we had here a method of obtaining at will either a photographic positive or negative.

Phosphorographs.

Experiments were made and it was found that an ordinary finished photographic negative could be imprinted upon a ZnS screen. O and P, Pl. V, are a positive and a negative photograph respectively. Both are contact-prints on panchromatic plates made from phosphorescent impressions on ZnS screens.

In one case a finished negative was placed in contact with a ZnS screen and an exposure was made to the light of a 100 W. metal filament electric lamp, and in the other case a ZnS screen was employed in contact with the same finished photographic negative and an exposure was made to the same lamp, but this time the visible radiation was filtered out by the employment of a thin sheet of ebonite.

Control of Contrast.

By making use of the "shift of spectral distribution" (see Pl. III, Fig. 8) we can obtain complete control of contrast, the greater the distance we move our sliding contact away from point B on either side, the greater will be the contrast obtained in printing from any negative. Contrast is also enhanced by the employment of filters.

Intensification by Heat.

By reference to Pl. V, phosphorograph JK, it is seen that heat increased the brilliance of the phosphorescence at the loss of its duration.

Phosphorograph Q, Pl. V, is a contact-print from a purposely under-exposed phosphorescent picture on a ZnS screen. The central portion has been intensified by heat. The procedure was as follows.

After a ZnS screen covered by a finished photographic negative had been (under) exposed to a weak blue light, and had imprinted upon it a weak phosphorescent print, a short strip of copper heated to 45° C. was placed underneath and in contact with it, as depicted. As soon as the brilliance of the picture had increased to the required
degree, a contact print was made by placing a panchromatic plate on to the screen while it was still on the hot metal plate. This method is applicable, of course, whether one is making a positive or a negative print.

A Spectrographic Comparison of Zn S and Ca S Phosphors.

Pl. IV is the result of a spectrographic examination showing in which parts of the spectrum fluorescence commences and where quenching ends. Langley has shown that infra-red radiation extends from \(0.4 \mu\) to beyond \(7\mu\).

There is no need to dwell upon this as Langley, Le Bon and others have already made similar spectrographic investigations. It is interesting to note that Zn S (green) commences to fluoresce just on the green side of the F spectral line. Zn S (yellow) commences to fluoresce well down in the yellow, and Ca S commences to fluoresce in the purple end of blue.

The spectrograph employed was one manufactured by Griffin & Tatlock, in which the spectrum was obtained by means of a 6 V. incandescent electric lamp and a defraction grating. A sheet of red glass transparent to the quenching radiations was employed as a screen, to filter out the otherwise interfering secondary spectrum.

The wave-lengths of the phosphorescent light appear to be very sharply defined.

The Selective Properties of Zn S Phosphors.

A screen was made containing Zn S, green and yellow mixed in equal proportions. It was placed in front of the spectrograph and when viewed in the dark the selectivity of the phosphors was apparent. At the blue end of the spectrum only the Zn S (green) crystals were phosphorescing, whereas at the yellow end yellow phosphorescence was seen.

The experiment was also carried out in another way. A \(50/50\) green and yellow Zn S screen was exposed to an electric light, one half being covered by a green glass filter and the other by blue glass. On removal of the filters in the dark, where covered by the blue glass it was phosphorescing with green light, and under the green glass the phosphorescence was yellow.
In another experiment a sheet of red glass was placed over a brightly phosphorescing ZnS screen (green). This completely cut out all visible radiations.

A test was made to see if the phosphorescence of one ZnS screen could be transmitted to another by contact; but the result was negative, both in the case of green to green, green to yellow, and vice versa, or yellow to yellow and yellow to green and vice versa.

Depth of Phosphorescence.

A tube was filled with powdered crystals of ZnS (green) and its open end was closed by a thin skin of celluloid dissolved in amyl acetate and acetone. When dry this end of the tube was exposed to light; it phosphoresced brilliantly, but as expected the phosphorescence was only on the surface. Apparently only the crystals actually exposed to the exciting radiation became luminous.

Fluorescence Preceding Quenching.

Working at a temperature of 19°C, it was observed that when the image of the filament of an electric lamp was projected by infra-red rays through a black glass filter on to a ZnS screen, in the case of ZnS (yellow) the quenching was very obviously preceded by a short period of increased luminosity. In the case of ZnS-Cu (green) the same effect was present, but it was more difficult to observe. The author found that it could be seen best if the ZnS screen was kept in slow motion. These and other similar investigations are still proceeding.

ACKNOWLEDGMENTS.

In conclusion the author wishes to express his thanks to Professor O. U. Vonwiller and members of the staff of the Physics Department of Sydney University for the helpful facilities they have afforded during these investigations, which have been made, for the most part, in the Physical Laboratories.

**View This Item Online:** [https://www.biodiversitylibrary.org/item/174130](https://www.biodiversitylibrary.org/item/174130)

**DOI:** [https://doi.org/10.5962/p.360269](https://doi.org/10.5962/p.360269)

**Permalink:** [https://www.biodiversitylibrary.org/partpdf/360269](https://www.biodiversitylibrary.org/partpdf/360269)

**Holding Institution**
Smithsonian Libraries

**Sponsored by**
Biodiversity Heritage Library

**Copyright & Reuse**
Copyright Status: In Copyright. Digitized with the permission of the rights holder
Rights Holder: Royal Society of New South Wales
License: [http://creativecommons.org/licenses/by-nc-sa/3.0/](http://creativecommons.org/licenses/by-nc-sa/3.0/)
Rights: [https://www.biodiversitylibrary.org/permissions/](https://www.biodiversitylibrary.org/permissions/)

This document was created from content at the Biodiversity Heritage Library, the world's largest open access digital library for biodiversity literature and archives. Visit BHL at [https://www.biodiversitylibrary.org](https://www.biodiversitylibrary.org).

This file was generated 27 June 2023 at 09:08 UTC