

SOME STUDIES IN SHORT DURATION
PHOSPHORESCENCE.

BY CHAN. W. WAGGONER.

THE experiments which follow deal with the decay of phosphorescence in certain compounds after excitation by the ultraviolet light from the iron spark. Messrs. Nichols and Merritt¹ have studied the decay of phosphorescence in sidot blend and other long-time phosphorescent compounds throughout a certain range. They find that the decay curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas is a straight line for small values of t , and that it changes to a curve concave toward the axis of t as t increases; but for still larger values of t , the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words, the decay curve consists of two straight portions which gradually merge into each other.

Werner,² using a photographic method, and working with a long-time Sr—Zn—CaF₂ phosphorescent compound, found when the results were plotted with $I^{-\frac{1}{2}}$ as ordinates and corresponding times as abscissas the same kind of curves as were obtained by Nichols and Merritt. In the method used by the latter experimenters it was not possible to obtain points on the decay curve closer than four tenths of a second after the exciting light was shut off; and the first point in the curve given by Werner is twenty-one seconds after shutting off the exciting light. The study of the decay curve immediately after excitation has ceased was suggested to the writer by Professor Merritt, who had designed a phosphoroscope for this work. It was found, however, that even when operating the phosphoroscope at its slowest speed, the decay of sidot blend was too slow to be measured with accuracy and ease.

¹ PHYS. REV., Vol. 21, p. 247, 1905; Vol. 22, p. 279, 1906.

² Ann. der Phys., Vol. 24, p. 164, 1907.

Only by the use of infra-red rays was it possible to increase the decay sufficiently to determine the shape of the curve for the initial decay.

The limits of the operations of the phosphoroscope being fixed, it was found necessary to prepare phosphorescent compounds whose decay was very rapid and still of sufficient intensity to measure. A number of these compounds were prepared and studied along with several specimens of willemite whose decay was suitable.

METHODS OF PREPARING THE PHOSPHORESCENT COMPOUNDS.

In preparing the compounds, the methods given by Wiedemann and Schmidt¹ and Andrews² were followed. The ease with which these compounds may be prepared, and the intensity of the phosphorescent light given off when they are excited by the spark, seems to warrant a rather detailed account of their preparation.

A salt of manganese, in this case $MnSO_4$, was used as the active agent. Lenard and Klatt³ found that the intensity of the compound is less affected by varying percentages of manganese, than with any of the other active agents. The compound consists of an inactive salt, an active salt, such as manganese, and a flux.

$ZnCl_2 + MnSO_4$.—Some zinc chloride prepared from metallic zinc was dissolved in a small quantity of distilled water. A small trace (usually less than one per cent.) of $MnSO_4$, dissolved in water, was added to the $ZnCl_2$ solution and the whole brought to the boiling point. An equal volume of sodium silicate, as the flux, was then added and the whole evaporated to dryness. On being exposed to the spark, faint green phosphorescence could be seen. It was then placed in a porcelain crucible and heated to a bright red for two hours. When cool it showed pale green fluorescence when exposed to the spark and when the exciting source was cut off, it was found to have considerable bright green phosphorescence. A sample of the powder at this point was kept and marked $ZnCl_2$ no. 1. The remainder of the powder was heated to a bright red for three hours and when cool showed both fluorescence and phosphorescence of greater intensity than did $ZnCl_2$ no. 1. A sample of

¹ Wied. Ann., Vol. 54 p. 604, 1895.

² Science, Vol. XIX., March, 1904.

³ Ann. der Phys., Vol. 15, p. 243, 1904.

this was saved and marked no. 2. The remaining powder was heated two hours at a bright red and on examination when cool, it was found to have lost some of its original phosphorescent intensity. This was marked $ZnCl_2$ no. 3.

$CdCl_2 + MnSO_4$.—Substituting $CdCl_2$ for $ZnCl_2$ but giving it exactly the same treatment it was found that it was necessary to heat the compound at a bright red for three hours before the phosphorescence color was very intense, and that subsequent heating had no marked effect on its phosphorescence intensity when exposed to the spark. The fluorescence color was pink, and the phosphorescence dark red.

$CdSO_4 + MnSO_4$.—Some $CdSO_4$ was dissolved in water with a small trace of $MnSO_4$ and the whole heated to dryness without adding the flux. The resulting white powder showed pale yellow fluorescence and an orange-yellow phosphorescence of much longer duration than the zinc compounds.

$ZnSO_4 + MnSO_4$.— $ZnSO_4$ substituted for $CdSO_4$ and treated in the same way resulted in a white powder which showed pink fluorescence and bright red phosphorescence, but the intensity was too small to be measured by the method used.

Some "chemically pure" calcium sulphide was purchased with the view of trying to prepare compounds of CaS and $MnSO_4$, but it was found to be already an active phosphorescent compound having a brownish-red color.

Two large pieces of willemite, showing brilliant green phosphorescence with the iron spark were studied. It was found that their rates of decay were not the same. The sample having the slowest decay was marked willemite no. 5. The sample having the very rapid decay was crushed into a fine powder, a sample made into a screen and marked willemite no. 1. A part of the powder was heated to a bright red heat in a porcelain crucible for forty-five minutes. This was marked willemite no. 2. The remainder of the powder was heated for two hours at a bright red, and marked willemite no. 3.

One $ZnCl_2 + MnSO_4$ sample made by W. S. Andrews, Schenectady, N. Y., was also studied.

For purposes of study, screens were made by placing the phos-

phorescent powder on small squares of heavy dark brown cardboard, the cards having been covered first with white "Zapon" varnish.

METHODS OF MEASUREMENT.

The phosphoroscope used in these measurements is shown in Fig. 1. It consists of a disc *D*, fastened to a cylinder *L*, rotating

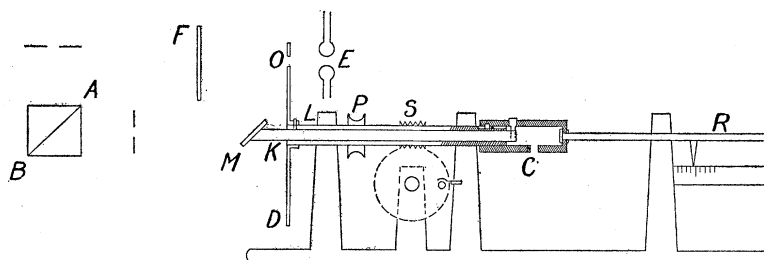


Fig. 1.

about a horizontal axis. On the inside of *L* is a shaft *K* which rotates at the same speed as the cylinder. On the end of *K* is a plane mirror, placed 45° to the axis of the shaft, and by use of the mechanism at *C* the position of the mirror, relative to any point on the disc *D* may be shifted while the disc is rotating. The disc has an opening at *O*, through which the light from the spark *E*, may pass each successive revolution, and excite the specimen placed at *F*. Now if the mirror is in the position shown it will reflect into the slit of a spectrophotometer the light which comes from the phosphorescent screen *F*, while it is being excited by the spark. By moving the rod *R*, the mirror is turned so as to reflect the light from the screen *F* into the spectrophotometer some time after excitation, and in this way the intensity of the phosphorescence after successive excitations may be measured by the spectrophotometer *AB*. The cylinder *L* is driven by a motor belted to it over the pulley *P*. *S* is a worm driving a cog wheel, which serves as a device for recording the speed by making an electric connection with a chronograph once in every hundred revolutions of the disc. Current operating the motor was taken from a direct-current source having a special device for maintaining constant voltage, and the speed of the motor was found to remain almost constant. The

disc D has a second half-disc fastened to the first (not shown in the figure) by which it was possible to change the size of the opening at O . The essential advantage of this phosphoroscope over others is that the decay of the phosphorescent light may be studied without changing the time of excitation. Another feature of this method is that settings on the spectrophotometer for any curve may be repeated as often as desired and the time taken for the determination of each setting may be as long as desired. The results shown in the curves that follow were determined from two different settings of the spectrophotometer for each point, and the plotted point represents the average.

The source of excitation was the spark between iron terminals. An induction coil was connected to a source of alternating current of 60 cycles frequency; a small condenser being connected in multiple with the spark gap. In order to study the effect of decreased time of excitation, it was found necessary to increase the frequency of the spark, this being accomplished by connecting it to a source of alternating current giving 140 cycles. With this higher frequency the chances of the spark exciting the screen at each turn of the disc is greater; also the higher frequency could be used as a check on the curves taken at the lower frequency.

An incandescent lamp connected to a constant potential source was used as a comparison source in the spectrophotometric measurements.

DISCUSSION OF RESULTS.

The curves shown in Fig. 2 are decay curves typical of three substances studied. They are plotted with $I^{-\frac{1}{2}}$ as ordinates and corresponding times as abscissas. It will be seen that the curves have the same general characteristics as those for long-time phosphorescent substances, *i. e.*, the curve consists of two straight lines merging into one another. Curve A shows a very rapid decay, and it is quite difficult on account of the small intensity of the light to follow the second straight portion of the curve very far.

It will be seen that in each curve one point has been plotted to the left of the zero on the ordinates. This observation is made on the fluorescent light, *i. e.*, it is the intensity of the light coming from the screen when the mirror is in position to reflect the light which

comes from the screen during excitation. The zero point, or the point where the exciting light fails to be reflected into the spectrophotometer, was determined by placing a piece of white paper in place of the screen.

On examination of the time of excitation it will be found that there can be at most only 120 sparks per second and during the time of excitation given in the curves in Fig. 2 it will be seen that three sparks per revolution of the disc is the maximum number that could pass while the screen is being excited. In fact it is highly improbable that this number really do pass during excitation, and it

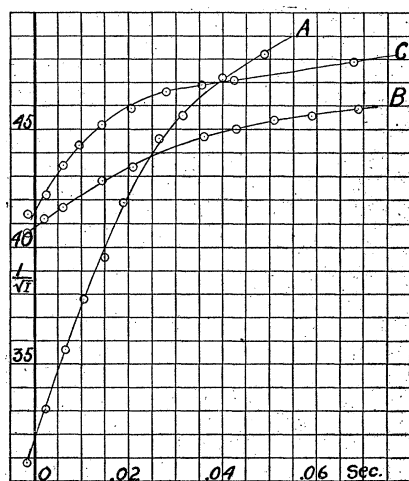


Fig. 2.

Decay curves.

- Curve *A*. Willemite No. 5, time of excitation .026 sec.
 " *B*. Andrews $ZnCl_2$, " " " .027 "
 " *C*. $ZnCl_2$ No. 3, " " " .026 "

would seem then that the excitation may vary. However, it will be remembered that these excitations follow each other very rapidly; for example, in curve *B*, Fig. 2, the rotating disc makes a complete revolution in .108 sec., and as something like 10 to 20 seconds were taken to make the setting of the spectrophotometer, whatever changes take place in the spark during successive excitation, the reading is an average value of the intensity at that point. In

order to make sure of this, readings were taken starting with the lowest intensity and ending with the highest: then starting with the highest and following the decay to the lowest value of intensity, the points plotted being an average of the two settings for each point on the curve.

A question might also arise, as to how the decay curve for a substance would vary if the points on the curve were determined by observing the decay after a single excitation, instead of by noting the time for the intensity to fall to a fixed value and then re-exciting to determine the next point, and so on. Messrs. Nichols and Merritt¹ have shown that the curves taken on sidot blend with the spectrophotometer for the first seven seconds of the decay are straight lines when plotted with $I^{-1/2}$ as ordinates and corresponding times as abscissas. These curves were taken by noting the

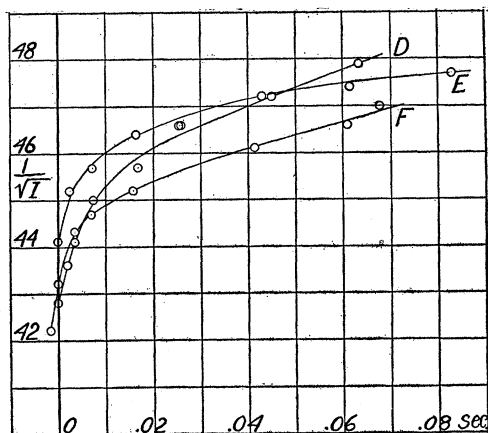


Fig. 3.

Showing the decay in different substances.

Curve *D*. CaS, time of excitation .033 sec.

“ *E*. CdSO₄, “ “ “ .032 “

“ *F*. CdCl₂, “ “ “ .031 “

time required for the intensity to fall to a fixed value, then re-exciting and noting the time to fall to a different intensity. Comparing the curves taken in this way, with the curves they give for the decay of the total intensity, by noting the intensity at different

¹PHYS. REV., Vol. XXI., p. 247, 1905, and Vol. XXIII., p. 37, 1906.

times after one excitation, it can be seen that the curves are similar in shape so far as those taken with the spectrophotometer have been carried.

It will be noted that in practically all the substances studied, the measurable portion of the decay is over in .07 second. Some of the substances may, however, be seen in a dark room for a very much longer time.

The curves shown in Fig. 3 indicate a much slower decay than those shown in Fig. 2. The initial decay, however, is quite rapid. These

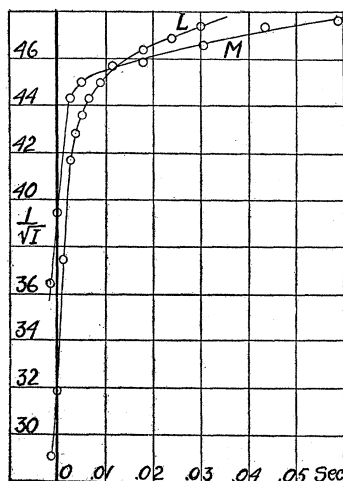


Fig. 4.

Showing effect of heat treatment.

Curve L. Willemite No. 1, time of excitation .022 sec.

" M. " " 2, " " " .022 "

curves were more difficult to obtain than those shown in Fig. 2 since the maximum wave-length, the one observed in every case, lies in the yellow-red, while the curves in Fig. 2 all have their maximum in the green. This difficulty, aside from the fact that the decay is less rapid, makes the points on these curves less certain than those of Fig. 2. It will be seen, nevertheless, that the curves have the same general shape and consist of the two straight lines merging into each other.

All of the substances mentioned are excited to fluorescence by

kathode rays to some extent, the CdSO_4 being especially brilliant, giving a very intense yellow. They were also found to be excited somewhat by X-rays, the CdSO_4 again showing the greatest intensity. In all cases the phosphorescence excited by X-rays was too small to be measured with the present apparatus.

The curves given in Fig. 4 show the change in the decay of willemite when heat-treated. Curve *L* shows the decay of the untreated willemite. Curve *M* shows the decay after heating the willemite for forty-five minutes at a bright red heat. It is clear from the

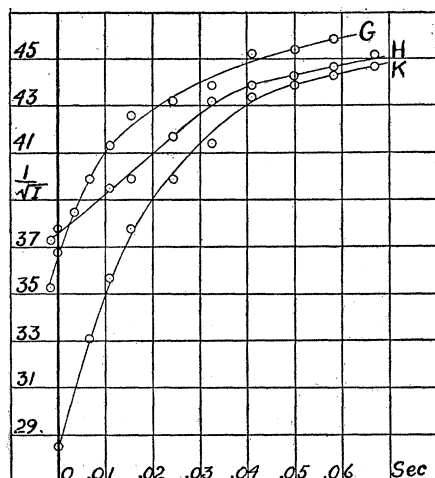


Fig. 5.

Curves showing effect of heat treatment.

Curve *H*. ZnCl_2 No. 1, time of excitation .031 sec.
 " *K*. " " 2, " " " .031 "
 " *G*. " " 3, " " " .031 "

curves that the heat treatment has decreased the initial intensity and made the decay less rapid; both these changes may be observed by the eye alone if the two screens are excited in a dark room. Willemite no. 3 which had been heated two hours was found to give a curve whose points fell so nearly on curve *M* that it was not plotted.

The curves given in Fig. 5 show the decay in $\text{ZnCl}_2 + x \text{MnSO}_4$ as affected by heat treatment. Curve *H* represents the decay in a sample of the substance taken as a dry powder, which resulted from the mixture in preparing and heating it only two hours at a bright

red. Curve *K* represents the decay of a sample heated five hours and curve *G* after seven hours heating. The curves show that the first heating was not sufficient to bring out the initial brightness and longer decay of the substance, and that there is a time limit to the heating necessary to produce maximum intensity; for on heating beyond this the initial intensity becomes less. From the behavior of this artificial compound it would seem that the natural willemite shown in Fig. 4 had reached a maximum heat treatment already, for further heating decreased its initial intensity. The slope of the curves in Fig. 5 seem to indicate little change in the rate of decay

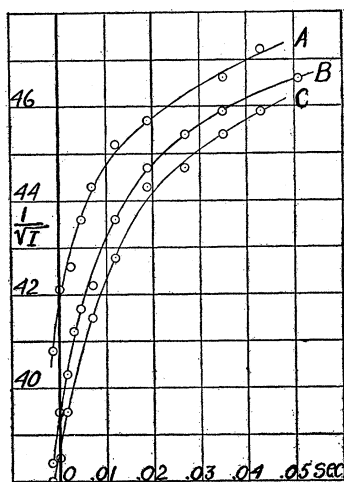


Fig. 6.

Showing the effect of changing the time of excitation.

Curve *A*. ZnCl₂ No 3, time of excitation .013 sec.

“ *B*. “ “ “ “ “ .024 “

“ *C*. “ “ “ “ “ .058 “

after the initial drop; unfortunately the intensity becomes so small that it was found impossible to carry the curves farther, and the readings in this region represent the average of a number of settings.

The curves given in Fig. 6. show the effect of decreasing the time of excitation in ZnCl₂ no. 3. This was accomplished by making the opening of the disc in Fig. 1 smaller. It was found that when 60-cycle current was used for the spark, the curves taken with decreased time of excitation were more or less irregular. This

was no doubt due to the fact that with the small opening of the disc the irregularities of the spark were more pronounced. However, on the 140-cycle current the curves were quite regular and could be duplicated very closely. The curves given in Fig. 6 were taken with the spark operated from the 140-cycle current and it will be noted that a decrease in the time of excitation brings about a more rapid decay.

The curves in Fig. 6 also serve to confirm, somewhat, the curves taken with the 60-cycle current; for it will be seen that they have the same general shape as those given for $ZnCl_2$ no. 3 in Fig. 2.

THE EFFECT OF INFRA-RED ON THE INITIAL DECAY OF SIDOT BLEND.

The effect of infra-red on long-time phosphorescent substances has been studied,¹ and it was natural to suppose that short-time substances would be affected in somewhat the same way. The method of experimentation followed was to allow the light from the arc to fall on the phosphorescent screen through a piece of very

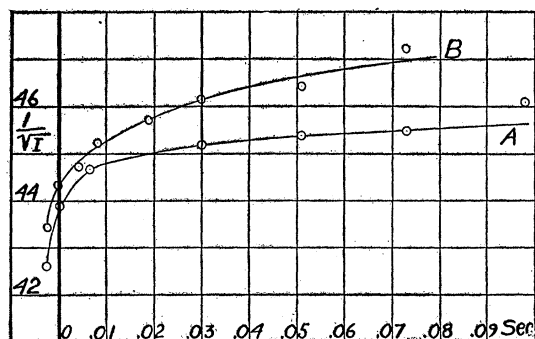


Fig. 7.

Curves showing the effect of infra-red on the initial decay of sidot blend.

Curve *A*. Without infra-red, time of excitation .04 sec.

“ *B*. With “ “ “ “ .04 “

dense ruby glass, and compare the shape of the decay curves taken with and without the infra-red. It was found, however, that none of the short-time substances were affected in measurable amount.

¹ Nichols and Merritt, *PHYS. REV.*, Vol. XXV., p. 362, 1907.

There was a slight indication of some change in the shape of the latter portion of the decay curve, but the error in setting the spectrophotometer in this region where the light is so faint would account for the changes in the curves.

While the effect of infra-red on the decay of short-time phosphorescent compounds is so small that it cannot be readily measured, the effect of infra-red on sidot blend is quite marked.

In Fig. 7 curve *B*, showing the decay under the action of the infra-red, is the average of a number of determinations and the shape of the curve is fairly definite. However, this cannot be said of curve *A*, which is also the average of a number of trials, since the total intensity, over the range of time available, is very small. There is some doubt also as to the shape of the curve during the first hundredth of a second. It was necessary to change the position of the disc on the shaft of the phosphoroscope in studying the effect of infra-red and it is possible that the zero given may be incorrect, *i. e.*, the points on the zero ordinate and perhaps the one following may be in the fluorescent light, and therefore the real phosphorescent decay started at some later time than the zero given. This possible error in the zero only applies to the curves taken in studying the infra-red and in no way affects the other curves.

There is no question as to the effect of infra-red on the initial decay of sidot blend, but owing to the very slow decay, the shape of the curves may be more or less in error.

DECAY CURVES FOR DIFFERENT WAVE-LENGTHS.

The phosphorescence spectrum of each substance was studied and curves of decay taken for different wave-lengths to determine if all parts of the band, characteristic for each substance, decayed at the same rate. In all the substances studied the phosphorescence spectrum at room temperature consisted of a single band. The extent of each being as follows :

CaS ₁	.53 to .64 μ with max. at .575 μ .
CdCl ₂	.545 " .65 μ " " " .59 μ .
CdSO ₄	.514 " .623 μ " " " .565 μ .
ZnCl ₂ no. 1	.49 " .585 μ " " " .52 μ .
Andrews ZnCl ₂	.49 " .545 μ " " " .52 μ .
Willemite no. 1	.46 " .56 μ " " " .52 μ .

In order to determine the rate of decay of different parts of the band for any substance, two methods were used. One was to take a number of decay curves at different wave-lengths of the band and plot a curve showing the intensities at a fixed time after excitation, and the wave-lengths. The second method was to fix the axle of the phosphoroscope so as to reflect the light from the screen a certain time after excitation; then, by shifting the telescope of the spectrophotometer, to determine the intensity of the phosphorescence for the different wave-lengths; then adjust the phosphoroscope to give the decay at a later period, and in the same way measure the intensity for different wave-lengths. Both of these methods gave the same results, *i. e.*, that all portions of the band seemed to decay at the same rate. The curves shown in Fig. 8 are typical for all the substances studied.

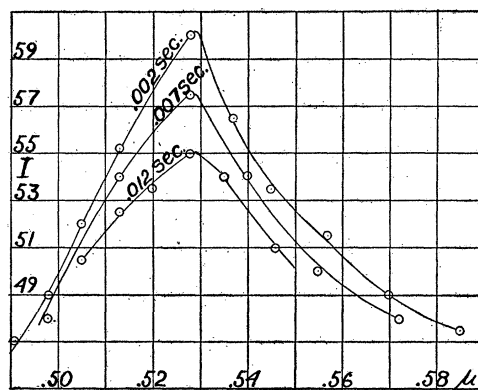


Fig. 8.

Curve showing the phosphorescent spectrum of $ZnCl_2$, no. 1, at different times after the exciting light was removed.

In none of the substances was there an indication of a shift of the maximum of the curve as the decay went on. If any change occurs during the decay it is too small to be detected by the method used.

SUMMARY.

The most important points brought out by the experiments here described may be briefly stated as follows :

1. The decay curve when plotted with the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas consists of two straight lines gradually merging into each other. In this respect the short-time and long-time phosphorescent compounds seem to be similar.

2. The transition from fluorescence to phosphorescence is gradual, *i. e.*, the curve shows no sign of discontinuity.

3. The shape of the decay curve and the intensity depend upon the time of excitation.

4. The effect of heat treatment is such as to change both the intensity and the rate of decay of phosphorescence.

5. The effect of infra-red on short time decay substances, if it exists at all, is very slight; but its effect on the initial decay of sidot blend is quite marked.

6. The experiments indicate that all portions of the phosphorescence band present at ordinary temperatures decay at the same rate.

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PHYSICAL LABORATORY,
CORNELL UNIVERSITY.