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# Uniform Luminescent Materials[1]

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THE PHENOMENAL INCREASE in the production of luminescent materials in Britain since the advent of fluorescent lighting has raised manufacturing problems of a type not usually associated with inorganic preparations. These problems are due to the difficulties which arise when attempts are made to produce large quantities of material having uniform luminescent characteristics.

There are several properties of luminescent material, or phosphore, which may be considered its luminescent characteristics. The physical properties of all crystalline solids can be divided into two classes: those which are the same for any two specimens of the same material, and those which are influenced by the past history of the particular sample. The "structure sensitive" properties which form the second class are often very sensitive to the presence of small amounts of impurity. Luminescent characteristics of inorganic solids which fall into this class are as follows:

(1) *Excitation spectrum.* Most materials are excited by a broad band of wave lengths in the ultraviolet, having one main, and possibly subsidiary maxima. The position of the band usually coincides with the long-wave length edge of the fundamental crystal absorption, but the details will depend on the method of preparation (Fig. 1).

(2) *Emission spectrum.* The energy distribution of the emitted light is often the most important characteristic of the material, because it determines the color. In certain cases this is very difficult to control. In commercial phosphores it consists of one or more bands from 500 to 3,000 angstroms wide, and it may extend considerably into the ultraviolet.

(3) *Efficiency.* No absolute value can be given to the efficiency of any luminescent material which will be significant in all its applications, because of the complexity of the phenomena involved. For practical purposes, therefore, it is customary to compare the relative efficiencies of different materials under conditions of excitation similar to those met with in use. In excitation by ultraviolet light the quantum efficiency is a significant figure; but this must be coupled with the wave lengths of excitation, and emission of the energy conversion is required (since the energy of one quantum E, of wave length $\lambda$, is $hc/\lambda$), and finally, the sensitivity of the eye to light of different wave lengths must be considered if the light output is to be estimated from any absolute physical measurements.

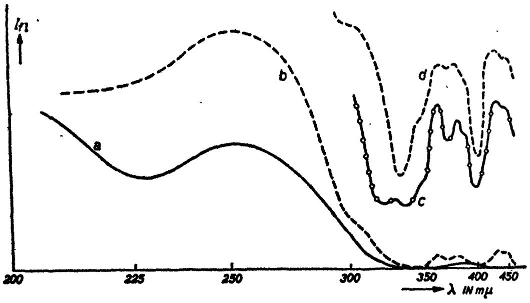

FIG. 1. Excitation spectra of zinc silicate phosphores at room temperature: *a.* $Zn_2SiO_4$—Mn 1‰; *b.* $Zn_2SiO_4$—Mn 5%; *c.* $Zn_2SiO_4$—Mn 2% (band system enlarged); *d.* $Zn_2SiO_4$—Mn 5% (band system enlarged).
(*After* Kroger, *F. A. Physica,* 1939, **6**, 764.)

In cathode-ray tubes the efficiency of the luminescent material is often a function of the electrical characteristics of the tube, the thickness of the layer of material and the nature of its support, while in the case of X-ray screens the efficiency is largely determined by the absorptive power of the material and so will vary with the wave length of the radiation used.

(4) *Phosphorescence.* Of the total energy which is absorbed during the excitation of a phosphore, a part is emitted immediately (fluorescence), a part is degraded into heat, and a third part may be stored for a period within the crystal, to be liberated later by either of the above processes. The phosphorescent characteristics of the material are determined by the total amount of energy which is stored within it and the rate at which part of this energy is re-emitted as light. It is difficult to specify these characteristics absolutely, and for practical purposes relative measurements are used. The requirements of various applications differ widely. Some may require

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[1] Acknowledgments are due to Mr. J. A. M. vanMoll and the Directors of Philips Lamps, Ltd., for permission to publish this paper.

complete extinction within a few milliseconds, while others may need a continuous glow lasting several hours.

In addition to these specifically luminescent characteristics there are all the usual physical and chemical properties of any pigment, such as particle size and stability. The control of each brings its own problems.

### THEORETICAL FRAMEWORK

Only a very brief outline can be given here of the theoretical framework by which these properties are related to each other and to the composition and method of preparation of the phosphores. Several reviews have been published in recent years which deal with the matter in greater detail (*1*).

The electrons of an atom in a gas, as is well known, occupy certain discrete energy states and can be excited, by various means, into other states of higher energy provided that these are not already occupied. Such transitions are accompanied by the absorption or emission of practically monochromatic radiation. When a large number of atoms are brought together to form a crystal, the energy levels of the outer valence electrons are profoundly modified, owing to the development of the binding forces which hold the crystal together.

The sharp levels of the individual atoms broaden out into bands (Fig. 2). Each broad band of allowed energies is made up of discrete states, but these are so dense, being equal to the number of ions in the crystal, that they can be considered as continual. It is no longer possible to say that any particular electron is associated with any one particular ion; they are all shared by the whole lattice. The electron population of any band is limited by the fact that each of its component levels can be occupied by only two electrons having opposite spins. In all ionic crystals there is a filled band in which every allowed level is fully occupied, separated by a gap of several electron volts from the next band above it, which is normally empty.

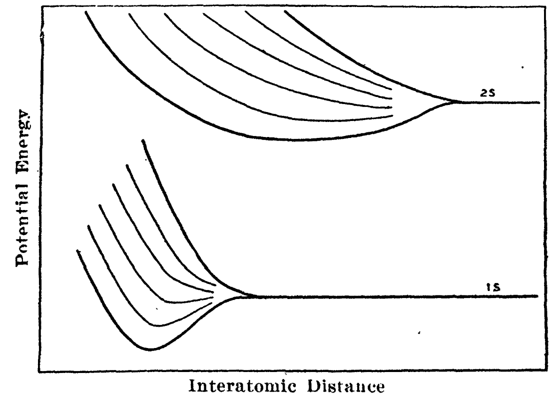

FIG. 2. (*After* Shockley, *West. Bell System Tech. J.*, 1939, 18, 645.)

Electrons may be excited into this upper band by the absorption of a quantum of radiation of sufficiently short wave length, and once there, in a perfect crystal, they would be free to move under the lattice under the influence of an applied electric field. An excited electron will eventually return to the lower band, either by a direct transition with the emission of a quantum of radiation, or by a more complex mechanism, connected with the thermal vibrations of the lattice by which the energy is lost as heat. For most pure substances, at ordinary temperatures, the latter is the case.

If, however, the energy gap between the two bands is bridged here and there by other allowed energies, light emission is more likely to take place. This is just what may happen when a small amount of an impurity ion is introduced into the crystal lattice. The discrete levels of the impurity ion, which remain localized in its neighborhood, may fall within the forbidden energy gap. The excited electrons may then fall from the upper band to one of these levels, emitting a band of wave lengths, the position of which will depend on the size of the energy gap between the bottom of the band and the impurity level.

When the impurity ion possesses a large number of closely spaced levels in this region, there is even less chance of a visible emission than for the pure substance, as transitions between these levels will result only in the emission of very small quanta in the infrared. These two possibilities correspond to the action of "activators," without which many materials will not luminesce strongly at room temperatures, and "poisons," the presence of which kills luminescence which would otherwise be evident.

Theory at present gives little indication of the concentrations at which activators should be used, but empirical data show that optimum concentrations vary for different methods of excitation of the same material, apart from wide variations between different materials (Fig. 3).

The introduction of the activator produces strains in the lattice, and these result in local disturbances of the energy bands. Similar effects are also produced by a number of other types of lattice defect which are present in all normal crystals. They are usually due to the displacement of lattice ions from their normal positions. Electrons excited into the empty band may become trapped in the neighborhood of these defects, to be liberated later by thermal vibrations. These electrons account for the very long phosphorescence of certain materials. The number and type of defect can be controlled to some extent by the heat treatment given to the material.

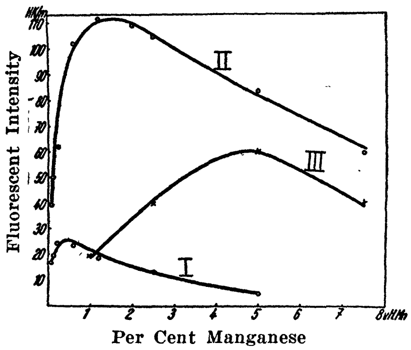

FIG. 3. Effect of manganese concentration on the fluorescent intensity of zinc silicate excited by (I) 740 A.U., (II) 2,537 A.U., and (III) 3,650 A.U.
(*After* Ruttenauer, *A.Z. Tech. Phys.*, 1938, **19**, 148.)

## PRACTICAL ASPECTS

The mechanism of luminescence gives some explanation of the necessity for extremely careful control of every stage in the manufacture of a phosphore. There is, however, a considerable variation in the tolerances which can be allowed as between one phosphore and another. In one case the emission spectrum may be invariable and the efficiency sensitive only to the heat treatment and the purity, while in another case the emission spectrum may be sensitive to very slight changes in the composition and the firing schedule.

For certain purposes the particle size must be controlled within narrow limits at about a two-inch diameter. Normal methods of comminution can seldom be used freely, because of the destructive effect of grinding on the luminescence, so that efforts have been made to produce the material with the correct particle size in the first place.

Below are details of the preparation of three luminescent materials which are suitable examples of the three most important chemical classes: the silicates, the tungstates, and the sulphides. For this purpose it is assumed that the two first are to be used in a normal fluorescent lamp and that the sulphide is to be a component of a white television screen.

*Zinc beryllium silicate.* This material, which is activated by manganese, can be prepared so as to fluoresce with any color between a very greenish yellow and a deep orange. The first step in its preparation is the purification of its constituent oxides. Various methods can be used to purify the zinc, beryllium, and manganese, most of which rely on well-known reactions of analytical chemistry. The purification is sufficient in this case when the copper, iron, and nickel content are all below 0.001 per cent and that of all other heavy metals is less than 0.01 per cent (*2*). The silica can be purified by distillation of an organic compound, such as ethyl silicate, which is hydrolized to give a silica gel (Brit. Pat. 498,556). Suitable proportions of the oxides (depending on the required color) are mixed with the silicon compound, which is then hydrolized and the mixture dried and pulverized. Useful luminescent materials can be prepared in which the ratio of $SiO_2$ to metal oxides differs widely from that indicated by the orthosilicate formulas, $Zn_2SiO_4$ and $Be_2SiO_4$. Materials in which the proportions vary as follows have been patented (Brit. Pat. 5131584):

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|---|---|---|---|
| ZnO | 10—60% | $SiO_2$ | 11—88% |
| BeO | 1—40% | Mn | 1—15% |

The dry powder is then fired in a silica vessel to a temperature between 1,000° and 1,250° C., held there for up to two hours, and finally cooled, either in air or by immediate quenching in cold water. The precise details of this heat treatment have a considerable effect on the emission spectrum and the phosphorescent behavior of the resulting material. It is therefore necessary to control them as closely as possible, and to ensure that the whole of each batch reaches the same temperature in the furnace.

The material is then ground to the desired size, and in some cases a second firing may be given after the grinding to restore the efficiency. If this is done, special care must be taken to avoid sintering of the powder. Various special techniques have been suggested for avoiding this, such as blowing the powder through the furnace as a cloud of dust (U. S. Pat. 2,196,082).

*Magnesium tungstate.* No activator is required for this material, which invariably fluoresces with a blue-white color. Its efficiency and stability, however, are very dependent on the purity of the materials used. The magnesium oxide may be purified by standard chemical methods. The tungstic oxide is passed through a cycle, familiar in the preparation of pure tungsten for lamp filaments, in which ammonium tungstate is recrystallized and converted into tungstic acid and the acid dissolved in ammonium hydroxide and recrystallized as ammonium tungstate. The cycle is repeated until the material is sufficiently pure, the limits in this case being of the order of 0.005 per cent for iron and copper (Brit. Pat. 5131584).

The oxide for carbonate of magnesium is mixed as a wet paste with the tungstic acid, dried, ground, and fired at 1,000° C. for one hour (Brit. Pat. 469,732). As in the case of the silicate, a second firing may be necessary after the material has been ground to size.

*Zinc sulphide: copper.* Pure amorphous zinc sulphide is first obtained by precipitation with hydrogen sulphide from a purified zinc solution. The tolerated amounts of heavy metal impurity are very much smaller than for the silicates, quantities of 0.0001 per cent of iron or nickel having a marked effect on the luminescent characteristics. The dried precipitate is then mixed with about 2 per cent of sodium chloride and 0.1 per cent of copper chloride (Brit. Pat. 550,800). The mixture is fired in an atmosphere of nitrogen for two or three hours at 1,100° C., after which any sodium chloride remaining is washed out with water. The resulting material has a strong green emission, while its phosphorescent properties will depend on the details of the heat treatment. The role of the sodium chloride in this preparation is to increase the rate of crystallization and to lower the temperature necessary for rapid diffusion of the activator into the lattice. Fluxes of this sort are also used to control the particle size of the product.

Sulphides differ from the other types of phosphore, in frequently exhibiting the emission spectrum of more than one activator at the same time. All zinc sulphides emit a blue band, which can be attributed to interstitial zinc atoms. The distribution of the emitted energy between this and the added activator band is influenced by the concentration of the activator and also by the intensity of the excitation. This causes slight changes in the fluorescent color as the intensity is altered, and similar changes may occur during the phosphorescence, as each band decays independently of the other.

In each of these examples it is essential that both the color and the efficiency of the materials should be constant from batch to batch, because in each case the color is not required for itself alone but as a component of a mixture which fluoresces white. Any changes in either of these factors will necessitate changes in the proportions of the components of the mixture if the white is not to be altered, and such adjustments are most undesirable in a manufacturing process.

### CONCLUSION

The techniques for the large-scale production of luminescent materials are still largely experimental, but there can be little doubt that when their development has been completed, they will influence a wide field of chemical manufacturing processes outside their own immediate sphere.

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# Another Chain Reaction

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TWICE IN THE PAST THIRTY YEARS the nations of the world have been placed in situations from which there has been no escape except by war. Now, with the advent of the atomic bomb, the problem of what to do to prevent the recurrence of this takes on an urgency that has never existed before. Time after time we have seen aggressive, organized minorities force large numbers of people to conform to their wishes with disastrous consequences. What the world has never yet seen is an equally well-organized effort on the part of people of good will for constructive purposes.

Professor Smyth's report, *Atomic energy for military purposes,* makes it clear that protection against the destructiveness of the atomic bomb is futile. No countermeasures offer any hope except international agreement by all nations that this instrument shall not be used again for war. The difficulty will be to get the agreement. Moreover, it will take time and meanwhile an international race for atomic bomb supremacy may get started that will leave each country no alternative except to inflict upon its citizens the waste of human and material resources required to meet this threat. In addition to agreement by the governments of the world, a very extensive program of education will be necessary to insure the support of the governed if enforcement is to be practical.

It is clear that the leaders in the development of the atomic bomb are fully aware of the potentialities of what they have brought into being and are doing everything possible to keep the race for supremacy from starting. On the part of the rest of us scientists, however, two attitudes of mind are quite common, both of which seem to me equally to be regretted. The first of these is represented by deep dismay, coupled with a generally hopeless feeling that there is nothing that we can do about it. The second expresses the conviction that scientists must pursue their unfettered way in quest of truth regardless of consequences and that responsibility rests elsewhere to pre-