Development of cathodoluminescent phosphors

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Phosphors are solid materials that have the ability to convert one or more forms of energy into visible or near-visible radiation; luminescence is the generic term for the phenomenon of this conversion. There are a number of excellent books and review articles covering the theoretical aspects of luminescence and the various phosphor systems that have been studied.[1-10] Some of these treat cathodoluminescence in detail,[1,2,3,10] and one is written with practical commercial development problems as its main theme.[9] None of them, however, deals specifically with the problems associated with the commercial development of cathodoluminescent materials, the subject of this article.

PHOSPHORS have been commercially important for a much longer period of time than other electronically active solids.[11] However, despite the long history associated with them and the very extensive literature on the subject of luminescence, their theoretical basis is not nearly as well understood as that of the more recently developed semiconductors, such as transistors. Things have not changed much since an introductory paper presented in 1954 stated that the manufacture of phosphors is largely an experimental science, if not a craft.[12] Research, development, and technology of phosphors is today still a combination of art, intuition, and fundamental knowledge.

RCA's present interest in luminescence is centered primarily on cathodoluminescent phosphors, i.e., those materials that have the ability to transform the energy of an electron beam into visible or ultraviolet radiation, because this energy transformation is the basis of RCA's extensive cathode-ray-tube business. Color-television tubes provide by far the greatest dollar volume in the tube market; for this reason, phosphor research and development done by the Materials Group at Lancaster is slanted heavily toward support of this item.

A large number of compounds are known to be luminescent, but the specific requirement thay they be economically useful in a cathode-ray device immediately imposes a series of design parameters which narrows the field of investigation to a surprisingly few chemical systems. These stringent design requirements also make the invention of a new commercial phosphor extremely difficult, for not only must the proposed material have exceptional luminescent properties, but it must also possess the combination of chemical and phsyical properties which will make it suitable as a screen material for cathode-ray tubes. Although characteristics of a phosphor can be varied within moderate limits, there is usually an interaction between the variables so that as one is improved, another is degraded. The result is that any phosphor represents a compromise in which the variable considered most important in a given application is optimized.

Design requirements

The design requirements of commercial cathodoluminescent phosphors can be divided into two broad categories; those dealing with luminescent characteristics and those dealing with physical-chemical properties. The first considers phosphors simply as energy converters and sets their operational requirements in a particular device. The second category views phosphors as tube components which must remain stable during the manufacturing process.

Luminescent characteristics

A phosphor must convert the energy of an electron beam into emitted radiation efficiently. This requirement

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may seem obvious, but there are many phosphors that are efficiently excited by ultraviolet radiation but not by an electron beam and therefore are useless in cathode-ray tubes. On the other hand, there are literally thousands of chemical combinations that luminesce under electron bombardment but have an efficiency of conversion of electron-beam energy into light that is too low to make them commercially useful. The most efficient and practical cathodoluminescent phosphors have been estimated to convert, at best, only 20% of beam power into radiant energy[13]. Sometimes the tube designer is willing to accept less than optimum conversion efficiency if some other characteristic, such as a unique decay property, is his major concern. Under any circumstance, however, conversion efficiency always has a high priority among the requirements. Unfortunately, there is little theoretical knowledge to guide the optimization of this parameter because the mechanism by which beam energy is dissipated in a crystal and transformed by a luminescent center into visible emission is but superficially understood. The closing of this knowledge gap is, today, the greatest challenge in the field of phosphor development. An advance in information in this area could revolutionize cathodoluminescence.

Another luminescent characteristic required of a phosphor is that it emit in some predetermined portion of the spectrum. Cathode-ray tubes are used in a wide variety of applications, and the phosphors used in them must emit in an area of the spectrum suitable to a specific application.

Although most tubes manufactured are used in the black-and-white or color television entertainment area, there are a number of industrial applications in which screens are coupled to a particular photographic film type or photosensitive surface. In these uses, the output of the phosphor is tailored to match, as closely as possible, the response characteristics of the system. Because the phosphors developed by RCA are used principally for color television, the major interest is in rather narrow regions of the spectrum comprising the three primaries used in color TV: red, blue, and green. Colorimetry of the phosphors is of paramount importance because the gamut of hues obtainable in a color picture is defined by the coordinates of the three primaries[14-16].

In addition to efficient energy conversion and emission, the persistence (the phosphorescence or decay rate) of a phosphor must be of the proper magnitude. The requirements in this category vary widely. In tubes designed for industrial or military applications, the range may be from 10^{-8} second (or less) to several seconds duration, depending on end use. A medium-short persistence is desirable for entertainment tube types because the decay must be fast enough to insure that there is no smearing of the image in rapid action, yet slow enough so that flicker does not become objectionable. In multiple-phosphor screens, such as those used in color television tubes, the persistence of the three phosphors must be reasonably matched or color trailing (image blur) becomes noticeable.

It is desirable that the light output of each phosphor in a multi-color screen vary linearly with power, and each with the same slope, so that high and low brightness areas of a picture will be properly shaded. Because the total output of the screen is dependent on beam power (the product of beam voltage and beam current) it is important that the voltage and current characteristic of each of the phosphors be stable. As the voltage of the tube is usually fixed, the variation in output characteristics of the phosphor with variable current becomes the major concern. In some systems, such as sulfides, the light output of the phosphor does not always increase with current in the linear manner desired, but begins to drop off at some intermediate operating current. This phenomenon is known as current saturation, or "droop-on-drive".

Another equally undesirable characteristic is known as color shift, a change of hue of emission with increased current. The higher the current, the more pronounced is the color shift. Color shift manifests itself in the appearance of a new, spurious emission band (usually at lower wavelengths) superimposed on the desired emission band. The phenomenon frequently occurs simultaneously with current saturation of the main band. Both main-band saturation and color shift are detrimental to color picture tube quality because they noticeably distort the hue in the highlights of the picture.

Physical-chemical characteristics

Commercially, phosphors are applied to a tube faceplate to form a screen by a variety of application techniques. Settling, slurrying, and dusting are the methods commonly employed. The method used dictates the average particle size and distribution of the phosphors to be used. Ideally, the phosphor chemist should develop preparation processes that are flexible enough to produce the variety of particle sizes required for the different application techniques. This condition is frequently difficult to achieve, however, because the high temperatures required to develop optimum luminescent characteristics simultaneously causes crystal growth. The phosphor developmental engineer must therefore make suitable compromises to obtain the brightest material that can be applied in a reasonable manner.

A phosphor must also be chemically compatible with the application media. Most application methods involve aqueous systems which are pH sensitive. The phosphor must, therefore, be stable in water to the extent that it does not decompose to form basic or acidic constituents. Such constituents would alter the properties of the slurry formulation and its application characteristics. Of course, the phosphor should be inert so that its intrinsic luminescent properties are preserved. If the phosphor is not inert, it will suffer severe loss of efficiency during tube processing.

The surface properties of a phosphor must fit the screening techniques so

Phosphor slurry being dispensed.

that the phosphor can be well dispersed in the medium, yet bond well to the glass substrate. A variety of "coatings," which might be thought of as a "cement", is designed to facilitate bonding in the particular application technique used. Colloidal silica, silicates, and phosphates are the most frequently used chemical coatings, presumably because they form surfaces which bond well to glass, the most common substrate to which phosphors are applied. The laws governing surface properties are at present not completely understood.

Because phosphors are used in a vacuum, they must not decompose or evaporate during processing or under electron bombardment. Organic luminescent materials cannot be used because of their instability under these conditions. Their decomposition products could then poison the electron-emitting cathode or raise the gas pressures that would destroy the usefulness of the tube. Even when a material has a vapor pressure low enough to withstand a vacuum, the energy of the electron beam itself can cause crystal changes that destroy the luminescence of the materials. Halide phosphors, particularly the fluorides, have notoriously poor tube life because the chemical reducing power of the beam causes permanent crystal damage and ultimately destroys screen efficiency.

A phosphor must be able to maintain its important physical properties during tube processing; i.e., it must demonstrate chemical, thermal, and vacuum stability. During outgassing, a tube is subjected to temperatures of about 400 to 450°C. At these temperatures, the organic binders used in screen deposition are decomposed and yield a combination of gaseous reaction products, including CO, CO_2, and H_2O. Although the phosphor may be unaffected by these individual gases at room temperature and atmospheric pressure, the combination of gases and elevated temperature could prove disastrous.

Phosphor cost

One of the more important commerical considerations not yet mentioned is phosphor cost. It must be possible to manufacture a phosphor in a reproducible manner at a reasonable cost; a rather high unit cost can be tolerated provided some outstanding characteristic can be obtained. The red phosphor now used in RCA's color tubes is a case in point. It costs substantially more per tube than any previous phosphor but its outstanding efficiency makes the added cost worthwhile in tube and set performance.

Group organization and responsibilities

The RCA engineering group devoted to the achievement of the phosphor characteristics described above, the Materials Group, is located in Lancaster, Pa. Its activities range from Applied Research through Development and into Pilot Plant production. When necessary, factory assistance is given and close liaison exists between Laboratory and Factory Engineering personnel.

Laboratory engineering

Laboratory Engineering has the ability to follow an idea from its basic conception through factory production and, in addition, makes its staff available to Marketing and Sales as field engineers. Laboratory Engineering then is involved in the whole gamut of the business enterprise. The general philosophy of the Laboratory Engineering group is to concentrate on phosphor technology and to leave testing and analyses to other groups more knowledgeable in those areas. Laboratory Engineering does, however, draw heavily on these supporting specialists and the well-instrumented laboratories available to them.

Analytical group

The Analytical Group performs a wide variety of services. Of particular note are the spectrographic and X-ray diffraction work which is relied upon heavily in purity and compositional studies of phosphors. Particle size analysis is another function of considerable importance. Because some work involves the interaction of many variables, the aid of a statistician is enlisted occasionally in setting and interpreting statistically designed experiments.

Colorimetry group

The Colorimetry Group is essential to the phosphor development operation, for it is they who make the necessary

Microscopic screen inspection.

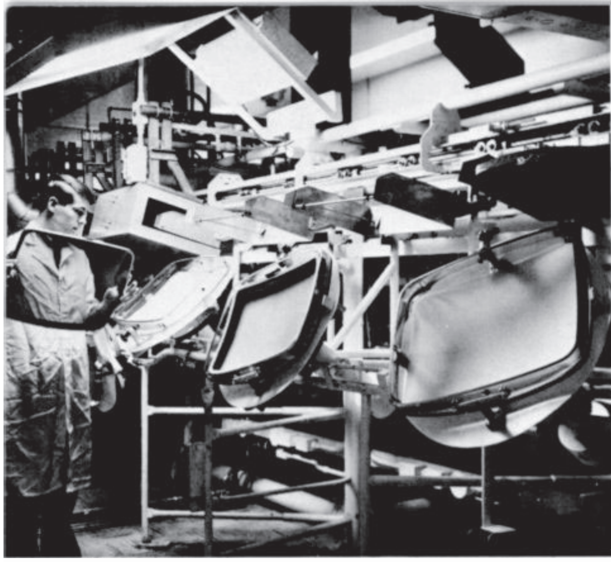
efficiency, persistence, and color-coordinate measurements.

Applied research

The worker in the phosphor field is often accused of alchemy because he sometimes uses rather unorthodox methods to achieve rather unusual results. His background should be in either inorganic or physical chemistry and, ideally, should include a very broad spectrum of experience; a surprising number of disciplines are necessary in the successful development of a commercial phosphor. (A sense of humor has also been known to help.)

The role of Applied Research in phosphor development is twofold. First, its efforts are directed toward the achievement of a basic understanding of those processes which are used in synthesizing the blue and green-emitting sulfide phosphors. Second, it carries on a search for new phosphor systems and new ways of using older systems. The approach to each type of research is quite different.

Efforts in the first area might be called purely scientific in that the approach, at least, can be well organized according to basic principles. Because the blue and green-emitters are sulfides precipitated from aqueous solutions, such fundamental properties as the kinetics of the precipitation and the role of the precipitating conditions on the final characteristics of the phos-



Inserting the shadow mask after phosphor application.

phor are being studied. The influence of the flux and flux systems, including phase diagram studies, and diffusion as it affects particle growth, are also under investigation. Much of the work in this first area is conducted along classical lines where chemical theory is well developed and mathematical models exist. All theory and models must of course be interpreted with a view toward fulfilling present needs. Note that the researcher must be conversant with a wide variety of chemical knowledge, for he deals with solution chemistry as well as with high-temperature and solid-state chemistry. His life is orderly though complex. He seeks new knowledge, but more or less within the framework of existing procedure.

The second area of research, that of new systems, is quite different. Here, intuition and art are as important as fundamental knowledge. There is no guiding theory and much of the work is empirical. The chemist's work in this area is frustrating in large part because thousands of samples may be prepared before one of even moderate promise is found. Many of the chemical systems have been worked and reworked, not only within RCA, but in a large number of laboratories throughout the world. Statistically, the chances of finding a completely new phosphor are exceedingly low. The researcher must not only consider a compound as such, but he must be concerned about the way that compound is synthesized, for often success or failure is due to some unique preparatory scheme which imparts just the right amount of crystalline irregularity necessary for an efficient phosphor. Consideration must also be given to the "antique" compounds, known to be luminescent, but never tested under modern cathode-ray conditions.

Development

The job of the chemist who devoleps phosphors is reasonably straightforward; he develops new phosphors and their manufacturing processes to a fine degree. His interaction with other groups is much more varied than the research man and includes an occasional assignment as a technical field representative with Sales and Marketing. (RCA enjoys a very substantial share of the market for zinc and zinc-cadmium sulfide phosphors used in cathode-ray tubes throughout the industry.) His knowledge must be very broad in the field of inorganic physical chemistry because he tackles problems as diverse as ultra-purification of materials, high-temperature syntheses, control of crystal growth, and surface properties of materials. It is generally he who must attempt to satisfy all the criteria listed in the earlier part of this article, or at least determine the optimum compromise.

Pilot plant

The Pilot Plant has proven to be an invaluable aid in the phosphor development operation in that it performs a variety of functions including scale-up of developmental procedures, rough cost analyses, manufacture of phosphors used in small quantities in either lab or factory, and investigations leading to new or improved processes. The equipment used in the Pilot Plant more closely approximates factory size than does the lab equipment, therefore, such items as firing time and temperature are developed best in this plant. The engineering in the Pilot Plant is then true chemical engineering as distinguished from the pure chemistry of the other groups. Pilot Plant personnel must have a knowledge of production-type equipment and its capabilities, a talent for process simplification, and a healthy respect for costs. It is up to them to render a phosphor process practical from the viewpoint of production. Frequently, the Pilot Plant has been the initial production unit for a new material and has sold its product to the tube factory. In the early stages of phosphor development, reasonable cost estimates can be made, scrap potentials discovered and corrected, and process reproducibility assessed. Interaction with other groups is, of course, greatest with the development engineers and factory personnel, but some liaison with Applied Research is also necessary. Vendor relationships through Purchasing are also important, not only in equipment areas, but in materials as well. Prior to acquisition of the Pilot Plant, the Phosphor Factory itself had to do its own scale-up and process development. This procedure was undesirable and led to much delay because tests had to be squeeezd into existing production schedules.

Technical progress

Table I is a modified, up-dated version of previously published data[11,16]. The listings within each color are chronological in time of commercial color-television usage and show how the improvement in phosphors has contributed to the advances in color tube performance.

Table I—Commercially used phosphors

Types of emitters	*Phosphor notation*	*Powder colorimetric data*[1] *x*	*y*	*Y (Lumens/W)*
Blue				
Calcium Magnesium Silicate : Titanium	$CaO:MgO:2SiO_2:Ti$	0.169	0.134	8.7
Zinc Sulfide: Silver: Chloride[2]	ZnS : Ag : Cl	0.146	0.052	7.5
Zinc Sulfide: Silver: Chloride[2]	ZnS : Ag : Cl	0.150	0.059	9.1
Green				
Zinc Silicate : Manganese	$2ZnO:SiO_2:Mn$	0.218	0.712	31.1
Zinc Cadmium Sulfide: Silver: Chloride[3]	(ZnCd)S : Ag : Cl	0.242	0.529	56.0
Zinc Cadmium Sulfide: Silver: Chloride[3]	(ZnCd)S : Ag : Cl	0.303	0.587	70.3
Red				
Cadium Borate : Manganese	$2CdO:B_2O_3:Mn$	0.630	0.370	10.7
Zinc Phosphate: Manganese	$\beta 3ZnO:P_2O_5:Mn$	0.674	0.326	7.0
Zinc Selenide : Copper	ZnSe : Cu	0.652	0.347	17.0
Zinc Cadmium Selenide: Copper: Chloride	(ZnCd) Se: Cu: Cl	0.662	0.338	11.0
Zinc Cadmium Sulfide: Silver: Chloride[3]	(ZnCd)S : Ag : Cl	0.663	0.337	12.6
Yttrium Vanadate : Europium	$YVO_4:Eu$	0.675	0.325	9.5
Yttrium Oxysulfide : Europium	$Y_2O_2S:Eu$	0.660	0.340	13.8

1. This notation defines color in accordance with that established by the Commission Internationale de l'Eclairage (C.I.E.).
2. The differences between these two phosphors are in silver content, flux composition, and firing temperature.
3. These phosphors differ primarily in their cadmium content.

Early phosphors

The listing under the color red illustrates how RCA's research and development activity operates in seeking to optimize all design specifications. The first phosphor on the list—cadmium borate: manganese — satisfied all requirements except one of the most important: quality of emission. The emission of the borate phosphor was much too orange. For that reason it was relpaced by zinc orthophosphate: manganese whose color was ideal. The lower lumens/watt value of the phosphate results from its redder color and a somewhat lower intrinsic conversion efficiency, a severe handicap that led to much research to find a replacement. The phosphate was commercially acceptable, however, and was used as RCA's standard red in those early years when color was trying to get off the ground.

Zinc selenide: copper

The next phosphor to receive considerable attention was zinc selenide: copper. This phosphor is almost a classic example of one whose initial promise was very high but which was subsequently found to lack many of the required characteristics. Zinc selenide: copper has an outstanding lumens/watt value, although its hue is a bit too orange.

Zinc cadmium selenide: copper

An improved red emission is obtained by addition of cadmium selenide to form solid solutions of zinc cadmium selenide. When this is done, however, the lumens/watt value of the compound is significantly decreased; the percentage decrease is greater than should be expected on the basis of color change alone. It has been concluded, therefore, that the solid solution has an intrinsic lower conversion efficiency than zinc selenide alone. Although disappointing in some characteristics, the zinc cadmium selenide has a final lumens/watt value that is still much higher than the phosphate it was designed to replace. A major disadvantage of zinc-cadmium selenide is its process instability; in water, at room temperature, a slow decomposition occurs. At the elevated temperatures of tube and screen bakes, the water vapor evolved during decomposition of the organic binder attacks the phosphor at such an accelerated rate that an efficiency loss of approximately fifty per cent occurs. Although a coating capable of slowing decomposition was developed, the close controls required in both manufacture and screen processing forced RCA to drop zinc-cadmium selenide as a commercial product.

Silver-activated zinc-cadmium sulfide

A silver-activated zinc cadmium sulfide of high cadmium content eventually replaced the zinc orthophosphate: manganese, primarily because of its higher conversion efficiency, but also because its persistence matched that of the other two sulfides more exactly. All of the brightness gain indicated in Table I was not realized because the sulfide suffered mild degradation during tube processing and showed a slight color shift on drive, a drawback not present in the phosphate. The plus features of the sulfide were considered to far outweigh its disadvantages, and for many years it was the standard red component in RCA color tubes.

Europium-activated yttrium vanadate

The europium-activated yttrium vanadate replaced the sulfide for reasons not readily apparent from Table I. Again, it was adopted on the basis of a series of compromises, the sum total of which made it superior to the sulfide. One prime disadvantage was its cost, some ten times that of the sulfide. Advantages included no color shift with high current and no current saturation; persistence was in line with the green and blue sulfides. The lumens/watt values shown in Table I appear to put the vanadate at a disadvantage in relation to the sulfide. After processing into tubes, however, the vanadate shows a very slight improvement over the sulfide, because the sulfide efficiency is degraded during processing while the vanadate is not. This is a good example of why the acceptance of a phosphor must be based on its performance in the tube and not on a simple powder test.

Europium-activated yttrium oxysulfide

Shortly after the yttrium vanadate: europium went into production, RCA's research efforts led to the discovery of europium-activated yttrium oxysulfide, a phosphor with a much higher efficiency than the vanadate. The oxysulfide is as stable as the vanadate in all respects, has processing stability, shows no color shift on drive, and no current saturation.

A new process compatible with factory equipment had to be invented for the production of the oxysulfide (here the staff of the David Sarnoff Laboratories helped considerably). Firing conditions capable of yielding proper color and particle size had to be developed, rigid control procedures established, and impurity levels discovered. The Pilot Plant went into production of the material to establish production routine, and actually made many hundreds of pounds of product without a single reject lot, to determine reliability, costs, and other commercial considerations.

Future improvements

From RCA's viewpoint, a phosphor is not a commercial success until it has performed satisfactorily in a marketable cathode-ray tube. To perform satisfactorily a phosphor must fulfill two categories of design parameters, one dealing with intrinsic luminescent properties, the other with application characteristics. Future improvements exclusive to RCA will become increasingly difficult because intense competition has increased not only the number of investigators throughout the world, but the sophistication of the approach to the discovery of new phosphors.

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