



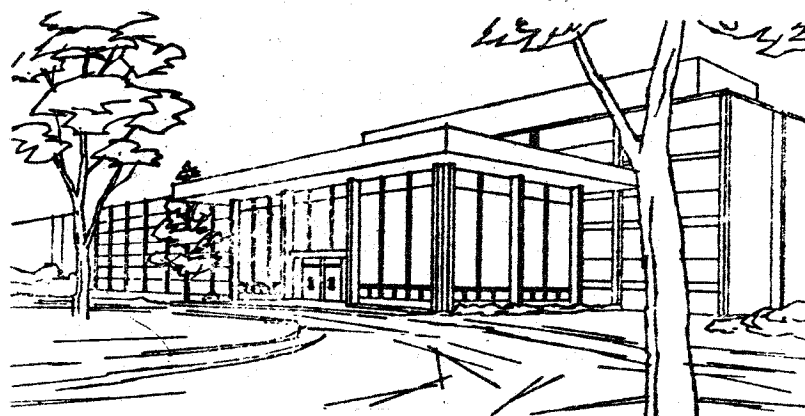
Cathode-Ray-Tube Phosphors: Principles and Applications

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DAVID SARNOFF RESEARCH CENTER

Cathode-Ray-Tube Phosphors: Principles and Applications

SIMON LARACH AND AUSTIN E. HARDY

Abstract—Principles and applications of phosphors in cathode-ray tubes are discussed. Among the basic parameters covered are: back-scattering, secondary emission, penetration, electronic transitions, dead voltage and energy, and optical efficiencies. Various relevant aspects of television kinescopes are discussed, including commercially used phosphor characteristics and screening techniques, radar tubes, image tubes, voltage-dependent color displays, flying-spot and beam-indexing tubes, projection, printing, and infrared stimulation systems. Colorimetry and photometry, as applied to phosphors, are discussed, including the CIE and UCS systems.

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CATHODOLUMINESCENCE

THE WORD *luminescenz* (luminescence) was used first by E. Wiedemann in 1888, in "all these phenomena of light which are not solely conditioned by the rise in temperature," and *luminescence* has been defined more recently [1] as a "process whereby matter generates nonthermal radiation which is characteristic of the particular luminescent material." Light emission due primarily to the temperature of a source is termed *incandescence*. While incandescence emission is the result of a statistically averaged effect over all atoms of the source, the nature of impurity luminescence emission is determined by the physicochemical character of dis-

crete volumes or elements. In such luminescence, therefore, the basic time constant involved in transient responses is determined primarily by the luminescence center rather than by the bulk of the containing material, whereas in incandescence, the basic time constant for transient effects is determined by the thermal inertia of the source [2]. A detailed discussion of the early history of luminescence can be found in Harvey [3].

The average time of duration of the excited state in light emission from excited monotonic gases at low pressure is of the order of 10^{-8} s. *Fluorescence* is the term which has been adopted for light-emission processes capable of this response time. The emission of light from slower processes is sometimes referred to as *phosphorescence*. This latter term is also applied to the emission which is detectable after removal of the excitation source.

Luminescence thus involves excitation and the emission of radiant energy, and luminescence is often classified by the type of excitation required to excite the luminescence.

Cathodoluminescence is the excitation of solids to luminescence by the direct impact of electrons. Excitation energies can vary from a fraction of an electronvolt to millions of electronvolts. Garlick [4] and Leverenz [1] have discussed various aspects of cathodoluminescence.

Cathodoluminescence is a rather complex process, involving several processes between the initial excitation and the final emission of light from the phosphor. With a beam of electrons incident on phosphor particles, there is a finite probability of reflection of the primary beam. A fraction of the electrons will penetrate the phosphor, and scattering will occur, with concomitant formation of charge carriers, which can transfer energy to emitting centers. There are, however, competing nonradiative processes, which tend to decrease the final radiative emission efficiency. Garlick [4] has discussed several of these fundamental processes. The backscattering of electrons, due primarily to Coulomb interaction, is of importance in cathodoluminescence. Tomlin [5] gives the following relation between the backscattering coefficient η and the atomic number Z

$$\eta = \frac{1}{6} \ln Z - \frac{1}{4}. \quad (1)$$

By using weighted mean atomic numbers, η for zinc sulfide has been calculated as being about 26 percent [4].

Those primary electrons which penetrate the phosphor, and are not backscattered will undergo energy loss through inelastic scattering. Garlick [6] has derived the following relation from the Bethe [7] nonrelativistic equation of charged particle interaction with matter:

$$-\frac{dE}{dX} = \frac{2\pi NZe^4}{E} \ln \left(\frac{E}{E_i} \right) \quad (2)$$

where dE/dX is the specific energy loss, E is the residual primary electron energy at the penetration depth X , N is the number of bound electrons in cm^{-3} of the solid, Z is the (mean) atomic number of the solid, e is the electronic charge, E_i is the ionization energy averaged over all the electrons.

A limitation of the Bethe relation is that scattering effects on particle range for electron excitation is not taken into account. For the range 300–3000 eV, the effective electron range can be taken as varying as $E^{1.4}$. A frequently encountered relation is the Thomson-Whiddington law

$$X = a(V_0^2 - V^2) \quad (3)$$

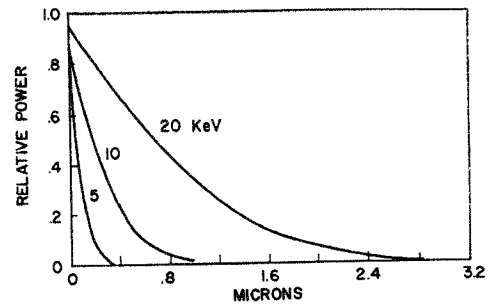


Fig. 1. Relative power per unit area for 5-, 10-, and 20-keV electron beams through ZnS.

where V is the potential at penetration depth X , V_0 is the incident electron potential, a is a constant roughly proportional to inverse density of the solid [5].

Kingsley and Prener [8] have recently investigated the voltage dependence of the cathodoluminescence efficiency of ZnS:Cu phosphors, on which were deposited nonluminescent ZnS coatings. They found that the efficiency was governed by the power loss of the electron beam in the coating, using the formula of Makhov [9] that the electron beam power per unit area at depth X could be given approximately by:

$$P(X, j_0, V_0) = j_0 V_0 \exp(-X^2 - X^{0.9}) \quad (4)$$

where j_0 is the beam current density at the surface, V_0 is the accelerating potential, and where X is a normalized depth, given by:

$$X(X, V_0) = X/\rho^{-1}CV_0^n = X/R(V_0) \quad (5)$$

where ρ is the density of the material, and $R(V_0)$ is referred to as the electron range.

Fig. 1, after Kingsley and Prener [8], shows, for 5-, 10-, and 20-keV electron beams through ZnS, the relative power per unit area.

Borodenko [10] has carried out investigations of the coefficient of transmittance τ for primary medium energy (1–10 keV) electrons impinging on metallized luminescent screens. He reports that τ depends on the material and thickness of the film, and on the primary beam energy, such that $\tau = CE_n^n$, where C is a constant characteristic of the material.

Investigations of electron energy-loss spectra of ZnS, ZnSe, and ZnTe have been reported recently by Hengehold and Pedrotti [11], both by electron-reflection and electron-transmission techniques. A series of three peaks was found, the first associated with the excitation of a surface plasmon, the second an interband transition from the d band, and the third, the excitation of a bulk plasmon.

Since in cathodoluminescence, excitation is by a beam of primary electrons, these tend to charge the crystallite negatively. The phosphor, therefore, must lose at least an equal number of electrons, by conduction or by emission, to prevent electrostatic repulsion of further primary electrons. The secondary-emission ratio R_s thus becomes of interest, and is defined as the ratio of the number of emitted secondaries to the number of absorbed primary electrons. As seen in Fig. 2, R_s rises to a first unity intercept (first crossover voltage) at 50–200 V, and falls to a second unity intercept (second crossover voltage) at about 1000 V and higher. Leverenz [1] describes the first slow rise of R_s as occurring in the surface layers, where much of the excitation energy is dissipated as heat; the portion where $R_s > 1$ is in the medium voltage range,

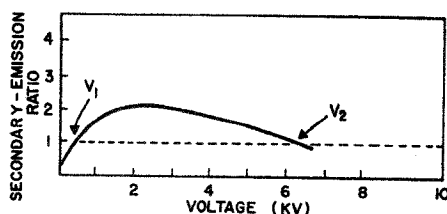
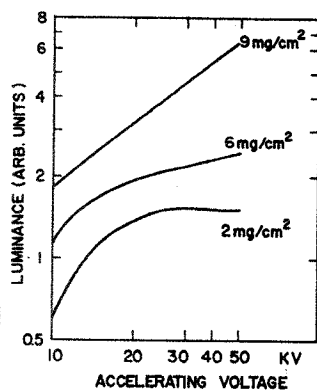


Fig. 2. Secondary emission rates as a function of voltage.

Fig. 3. Cathodoluminescence of aluminized screens of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ as a function of primary electron accelerating potential.

the final portion occurring in the high-voltage region, where there is a low probability of escape for the deep internal secondaries. Specific values of R_s as a function of voltage depend on the physicochemical parameters of the phosphor particles, together with their surround, such as coatings, adhesives, electrolytes, etc. Typical second-unity intercepts have been given by Knoll [12] as 2.5 kV for ZnO , and greater than 60 kV for $\text{Zn}_2\text{SiO}_4\text{:Mn}$.

From Fig. 2, we can see that at beam voltages below the first-unity intercept and above the second-unity intercept, phosphor screens will require conducting paths to the anode. Between the two unity intercepts, phosphor screens may be used without such aids, since the screen is maintained at the applied voltage by R_s being ≥ 1 . At voltages greater than about 10 kV, phosphor screens are coated, on the gun side with a thin (several thousand Angstrom) layer of reflecting aluminum, which serves to act as a conducting path, and to provide a light reflecting surface for back-scattered photons. This technique is treated in more detail later in this paper.

Fig. 3 shows the cathodoluminescence of aluminized screens of $\text{rbhdi-Zn}_2\text{SiO}_4\text{:Mn}(0.3)$ as a function of acceleration potential of primary electrons, for three thicknesses of phosphor layer [13]. It is of interest that small amounts of certain transition group elements can markedly decrease the emission intensity of cathodoluminescent materials. Fig. 4 demonstrates such "poisoning" of cathodoluminescence by minute amounts of iron, cobalt, and nickel in ZnS:Ag [14].

We have discussed qualitatively absorption, excitation, backscattering, secondary electron emission, and the next essential link in the chain is the transfer of energy to the emitting centers. Various theoretical aspects of luminescence have been treated by Curie [15], Williams [16], and others. A schematic energy-level diagram is shown in Fig. 5.

In part I of Fig. 5 there are shown three ways for photons to be absorbed by a phosphor crystal.

Excitation 1 indicates the relatively low-energy photon which owes its absorption to defects. In excitation 2, we have

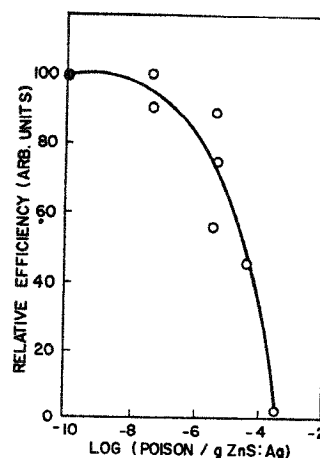
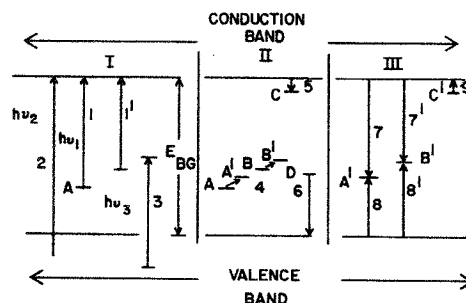
Fig. 4. Poisoning of cathodoluminescence of ZnS:Ag by iron, cobalt, and nickel.

Fig. 5. Electronic transitions in a luminescent material.

the case of a higher energy photon, at least of band-gap magnitude, which directly affects the host crystal atoms. When the photon energy is more than that just sufficient to place an electron into the conduction band, the excess is almost instantaneously (10^{-12} s) lost to the lattice as heat. Transition 3 involves electronic transitions which do not directly involve either the valence or conduction band. These usually arise from ions of elements whose electrons within the so-called incomplete shells are not shared with those of neighboring lattice atoms and can make transitions independently of them. Thus the spectra arising from such an impurity ion in different hosts are frequently similar. The location of the level of the unexcited atom (ion) is usually not known and is placed in this figure primarily to show that $h\nu_3 < E_{BG}$.

In part II of Fig. 5, events are shown that occur subsequent to the absorption process. The lattice in the neighborhood of the A and B defects adjusts to the change in the balance of forces caused by the electron excitation. This, in turn, reacts on the defects to reduce the energy which is released when the electron returns to its "original" site. This is signified in the diagram by locating the return state (A' , B') at a different level. Transition 4 can be thought of as an internal readjustment (releasing energy through radiation or heat transfer to the lattice). Other defects frequently lead to levels C , easily excited (even by lattice vibration) and therefore frequently available as a temporary "resting place" or trap for the electrons excited from lower energy levels (transitions 1 and 2). Still other defects D (or even other A levels), can supply to the valence band an electron to replace the one lost by transition 2. These levels are then called "hole traps." Part III of Fig. 5 shows the transitions responsible for the observed

luminescence. (Transition 8 is shown to illustrate one effect of temperature on luminescence. At sufficiently high temperature the probability of transition 8 is large enough to significantly reduce the number of levels A' and, therefore, reduce the number of radiative transitions 7.)

In a real phosphor, at any instant of time, a variable number of the processes are going on at interrelated rates. The major factors which determine these rates are: the instantaneous number of occupied traps, unoccupied traps, occupied (unexcited) centers (of each kind), unoccupied centers, free electrons, free holes, and the rate of absorbed (exciting) photons, if any. In many cases, the temperature plays a significant role in determining occupancy. Because of these interrelations, the emission intensities of many phosphors under steady-state conditions (constant excitation for long periods) are found not to respond in a linear (proportional) manner to the excitation intensity.

The time-intensity behavior of the emission during the early stages of excitation, and after (as well as during excitation), is also determined through the interrelation of these processes, especially by the transitions 5 and 9.

It is important also to consider that an important factor in producing secondary electrons is the limiting energy of secondaries at which still more secondaries can be produced [4]. Shockley [18] has estimated that the mean energy E for producing a free electron-hole pair, for the effective masses of the two carriers being equal, is $1.5 E_g$. Due to the discrepancy between hole and electron masses in ZnS, Garlick [4] has given $E \sim 3E_g$.

In attempting to calculate the maximum possible energy-conversion efficiency of a cathodoluminescent material, one has to deal with: the backscattering coefficient; the ratio of the minimum ionization energy to the energy of the band gap; the relative numbers of emitting radiative and nonradiative centers, with the appropriate recombination statistics and the radiative recombination center efficiency. If, as treated by Garlick [4], we analyze ZnS:Ag, where $\eta = 0.26$, and $E/E_g = 3$, then the overall efficiency can be given by:

$$\epsilon = (1 - \eta) \frac{E_g}{E} \left(\frac{h\nu}{E_g} \right). \quad (6)$$

Since for ZnS, $E_g = 3.7$ eV, $h\nu = 2.63$ eV, then $\epsilon \approx 18$ percent. Brill and Klasens [19], in their experimental determination of cathodoluminescence efficiencies, obtained a value of 21 percent for ZnS:Ag. Values of some representative phosphors are given in Table I, from their paper.

Hersh and Forest [20] have recently proposed a mechanism of cathodoluminescence in oxygen-dominated phosphors, wherein hot carriers (excitons) are generated by the electron beam, with an excited host center acting as an energy source, and resonance-transferring energy to the activator, which then emits radiatively.

Meyer [21] has measured the absolute efficiency of various phosphors, under cathode-ray excitation, as a function of voltage and current density. He reports that assuming intrinsic efficiency independent of voltage may not be feasible unless the energy exceeds the K X-ray levels of the host material.

In plotting brightness versus voltage, most phosphors have a threshold between 1–2 kV, referring to extending the nearly linear portion of the curve to the abscissa, as shown in

TABLE I

Phosphor	Emission Color	Energy Efficiency	Optical Efficiency (lumens watt ⁻¹)
ZnS:Ag:Cl	blue	212	7
0.52ZnS:0.5CdS:Ag:Cl	yellow	19.5	98
ZnS:Cu:Al	green	23	92
Zn _{0.55} O:Mn	green	8.5	42

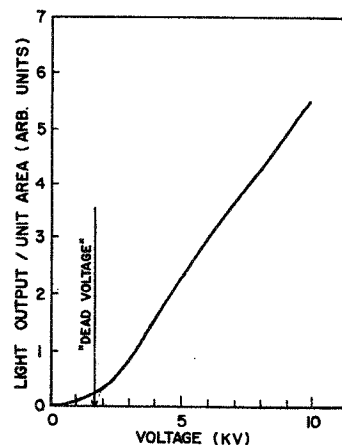


Fig. 6. Brightness-voltage curve.

Fig. 6. This voltage threshold is often referred to as *dead voltage*, which implies a rather inert shell which is exterior to an efficient core of phosphor material. Gergely [22] has suggested that carriers diffuse to surface traps, where nonradiative recombination can take place. Prener and Kingsley [23] report interesting results in experiments wherein cobalt, as a poison, is diffused into a phosphor for various thicknesses. They report that the dead voltage is a function of the thickness of the poisoned region, the thickness and dead voltage being related by: $d(\text{cm}) = 7.3 \times 10^{-7} V_0^{1.77} (\text{kV})$.

COLOR TELEVISION

Phosphors are used in a large variety of cathode-ray devices. In most instances it has been possible to optimize and improve the performance of the devices significantly by improving the phosphors themselves. Probably the best example of improved device performance through the use of better phosphors, is the color-television picture tube. As of this writing at least 18 different phosphors have been developed and used commercially to some degree. There have been 10 red emitters, 5 green emitters, and 3 blue emitters. These 18 phosphors are listed in Table II by color in the approximate chronological order in which they were used commercially.

Although many of these phosphors are closely related chemically they do represent, in most cases, important advances in certain characteristics. Some of the recent red phosphors give essentially equal performance and the actual choice by a tube maker depends on the screening process or salvage facilities he prefers to use.

As a result of continuous and intensive phosphor development effort, the basic screen efficiency has risen from 15 lm/W in 1951 to 35 in 1973. This improvement plus major tube design innovations such as the matrix or black surround principle has increased the device efficiency of the color picture tube as a producer of white light from approximately 0.6 lm/W in 1951 to 8 lm/W in 1973. This represents an average increase

TABLE II
CHRONOLOGICAL LIST OF COLOR-TELEVISION PHOSPHORS

Red	1	Cadmium Borate:Manganese
	2	Zinc Orthophosphate:Manganese
	3	Zinc Selenide:Copper
	4	Zinc Cadmium Selenide:Copper
	5	Zinc Cadmium Sulfide:Silver
	6	Yttrium Orthovanadate:Europium
	7	Yttrium Orthovanadate:Bismuth:Europium
	8	Yttrium Oxy-sulfide:Europium
	9	Yttrium Oxide:Europium
	10	Cadolinium Oxide:Europium
Green	1	Zinc Orthosilicate:Manganese (low concentration)
	2	Zinc Orthosilicate:Manganese (high concentration)
	3	Zinc Aluminate:Manganese
	4	Zinc Cadmium Sulfide:Silver
	5	Zinc Cadmium Sulfide:Copper:Aluminum
Blue	1	Calcium Magnesium Silicate:Titanium
	2	Zinc Sulfide:Silver
	3	Zinc Sulfide:Magnesium (copper resistant)

due to all factors of more than 0.3 lm/W/year. Thus color-picture performance has progressed from a 100-in² picture at no more than 20-fL brightness to a picture size in excess of 300 in² and brightness levels well over 100 fL.

The color-television picture tube history is more dynamic than any other device based on the use of luminescent materials. The first commercial color-television system was basically a black and white tube with a red, blue, and green sectored filter disk rotating in front of the tube. The color purity or saturation was good but the brightness was low. In addition, the system was mechanical and not compatible with black and white signal transmission. This system was soon replaced by an all electronic compatible system using the so-called tricolor shadow mask tube. This principle is still in use today. It uses red, blue, and green phosphor elements deposited on the inner surface of the picture tube faceplate in a certain geometric pattern or mosaic. Three electron guns in the tube can selectively excite the three color phosphors.

For many years the red phosphor was the least efficient of the three which accounts for the large number of changes in the red phosphor. For example, the cadmium borate phosphor which was the best red available initially was quite orange in its emission. In order to improve its redness it was proposed that Didymium glass be used as a filter and safety glass in front of the tube. Didymium glass has a very strong and narrow absorption band in the orange region and does indeed result in a good red color when used with the cadmium borate. However, the cost of the glass was unattractive. In 1951 a better red phosphor, zinc orthophosphate:manganese, was developed and became the industry standard [24]. The chromaticities of the primary phosphors as specified by the National Television Standards Committee (NTSC) merely represented what was available. In the case of the blue primary two chromaticities were allowed, the deep blue zinc sulfide:silver and calcium magnesium silicate:titanium. The reason for this odd situation was that blue zinc sulfide was so susceptible to copper contamination which changed the emitting color from blue to green, that some companies were forced to use the more stable silicate. Soon the copper contamination was reduced to manageable levels and the sulfide was used exclusively. Eventually, the susceptibility of the blue zinc sulfide:silver to copper contamination was drastically reduced and today most companies use so-called copper resistant blues.

Another milestone was the all-sulfide screen in 1961 [25]. This combination offered a 50-percent or more increase in white brightness and also provided shorter persistence than the silicate-phosphate system. As a result smearing or color trailing on fast moving objects was eliminated.

The red-emitting sulfide had an orange body color which presented major screen deposition problems. These were successfully solved and the all-sulfide screen was the industry standard for over four years. The green sulfide in this screen represented a major departure in chromaticity from the NTSC value. Side-by-side comparisons of actual pictures on tubes with the saturated silicate green versus the desaturated sulfide green revealed very little subjective difference. This observation is explained largely by two facts. First, there are very few highly saturated greens in nature and second the physiological effect known as color contrast tends to enhance perceived color saturation. In any case the 50-percent increase in brightness outweighed the objective color errors that occurred.

In late 1964, a new family of red emitters, the rare-earth europium-activated compounds, were applied to color television [26]. Up to the advent of rare-earth phosphors, all previous commercially used materials were broad-band emitters—that is the spectral energy emission curves are essentially bell shaped. The rare-earth phosphors on the other hand are basically line emitters. The yttrium orthovanadate:europium was the first rare-earth phosphor to be used. It offered only a modest 6-percent increase in white-light output, but it did ease the screen deposition problems of the red sulfide and brought the relative red, blue, and green currents for producing white closer to unity. In less than two years after the vanadate, an improved rare-earth phosphor, yttrium oxy-sulfide:europium was introduced [27]. This phosphor is the commonly used red emitter in the world today.

In 1968 a copper-activated green sulfide was introduced [28] which has now completely replaced the older silver-activated zinc cadmium sulfide. A small brightness increase was realized from this change plus the benefit of a more nearly white body color and greater stability to tube processing.

As a result of the many improvements in the red phosphor it is now the green that requires the most beam current in the mixture of red, blue, and green to produce white. Consequently, the research and development going into discovering and improving the green far outweighs the work on blue or red.

As long-range objectives, the color-television picture tube industry needs a more efficient green, a green which is more saturated colorimetrically and a red with the present efficiency but a deeper hue. Of course, increased efficiency of any of the phosphors is always welcome but the above objectives have the highest priority.

Spectral-energy distribution curves for the color-television picture tubes phosphor most widely used at the present time are given in Figs. 7–9.

Some important colorimetric and photometric characteristics of key color-television phosphors are given in Table III. Column headings are discussed later in the paper.

BLACK AND WHITE TELEVISION

The history of the development of phosphors for black and white television has not been as glamorous as for color television. Nevertheless, the story is quite interesting especially when one considers that the earliest experimental screens consisted only of green-emitting willemite which was obtained as the naturally occurring mineral in Franklin County, New Jersey. The brightest chunks, as examined under a short wavelength ultraviolet lamp, were broken up with a hammer and ground down to a fine powder suitable for use in making a viewing screen.

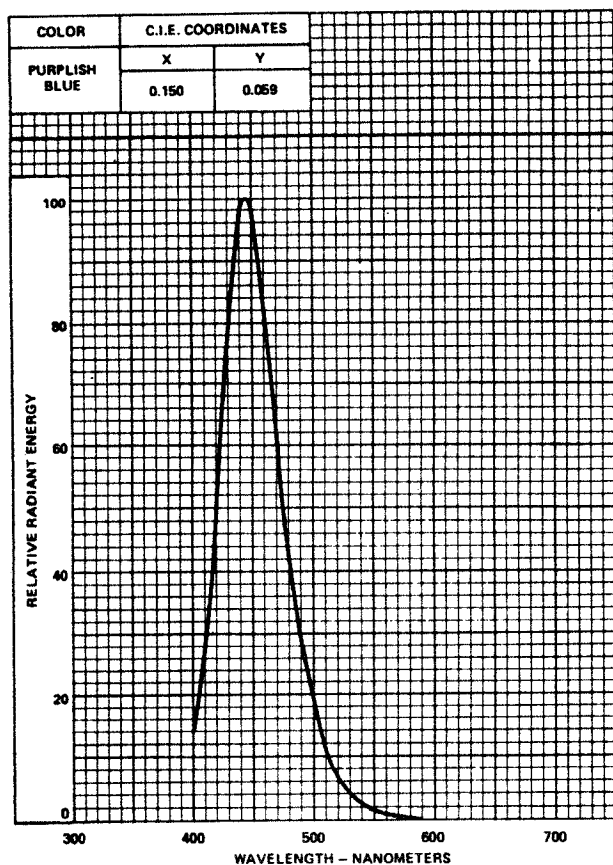


Fig. 7. Color TV blue ZnS:Ag.

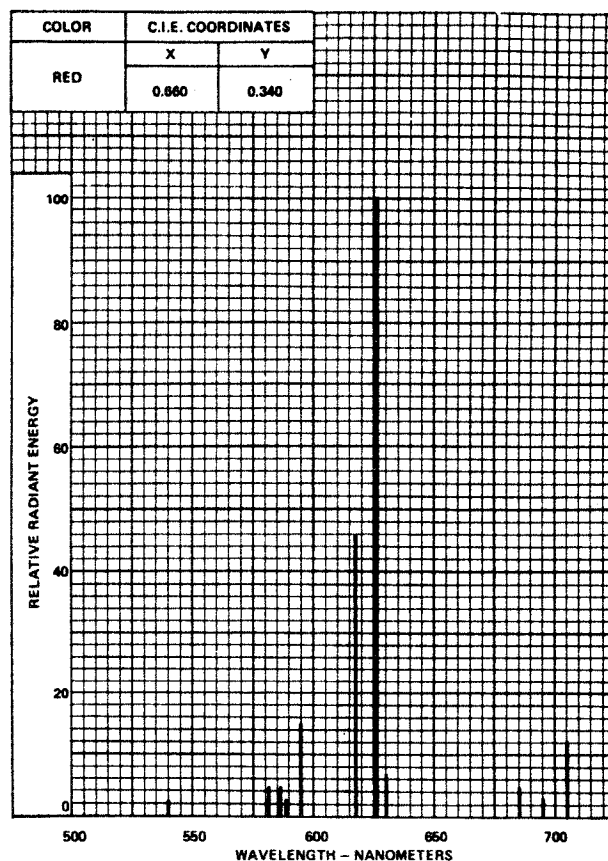
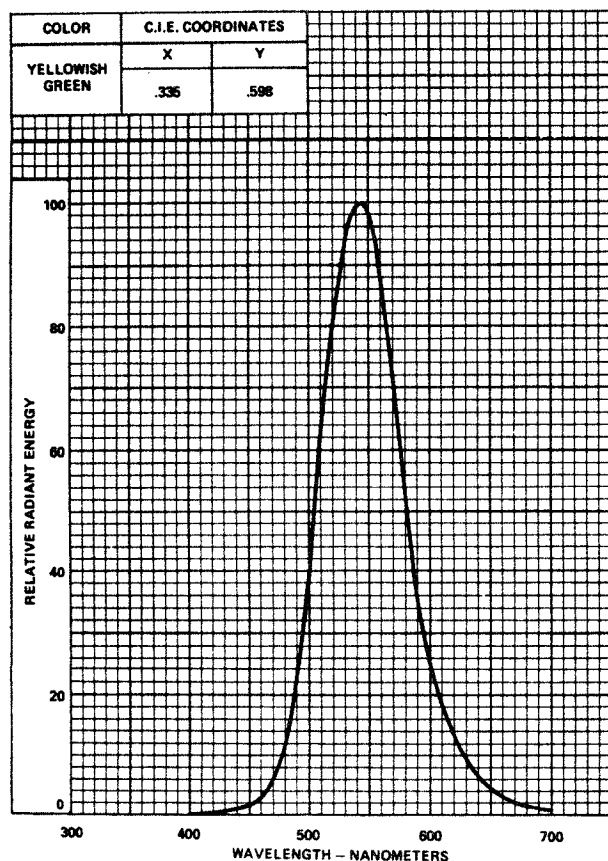
Fig. 9. Color TV red Y₂O₃S:Eu.

Fig. 8. Color TV green ZnCdS:Cu:Al.

TABLE III
SOME IMPORTANT CHARACTERISTICS OF PHOSPHORS

Phosphor	Color	CIE x	CIE y	Luminous Efficiency lm/W	S	Luminous Equivalent	Power Efficiency	Dominant Wavelength	Percent Saturation
Zn ₃ (PO ₄) ₂ :Mn	Red	.674	.326	7.0	21.5	162	0.05	613	100
Zn ₂ SiO ₄ :Mn	Green	.218	.712	31.1	43.7	520	0.06	537	87
ZnS:Ag	Blue	.154	.068	7.5	110	57	0.15	464	87
ZnCdS:Ag	Red	.663	.337	8.6	25.5	119	0.12	609	100
ZnCdS:Ag	Green	.285	.595	46.0	77.3	434	0.14	548	72
YVO ₄ :Eu	Red	.675	.325	9.5	29.3	135	0.06	613	100
Y ₂ O ₃ S:Eu	Red	.644	.350	17.1	48.9	265	0.06	605	100
ZnCdS:Cu:Al	Green	.335	.598	65.1	108.9	514	0.13	556	84

The first commercial tubes had white-emitting screens. White emission was obtained by mechanically mixing a blue-emitting phosphor with a yellow-emitting phosphor which by the principle of color addition combine to produce the sensation of white light. Fig. 10 is a spectral-energy distribution of a typical present-day black and white picture tube screen. The blue phosphor used initially and still used today is a silver-activated zinc sulfide. The early yellow component was from the zinc beryllium silicate:manganese series. Different shades of yellow could be obtained by varying the zinc-to-beryllium ratio. The shade of white was adjusted by controlling the relative amount of blue and yellow phosphors in the mixture. The sulfide-silicate still finds limited use in black and white projection systems. For direct view tubes, however, the yellow silicate was long ago replaced by a yellow-emitting zinc cadmium sulfide:silver activated phosphor. At first it was thought that the all-sulfide black and white screen would be too difficult to manufacture because of its great sensitivity to

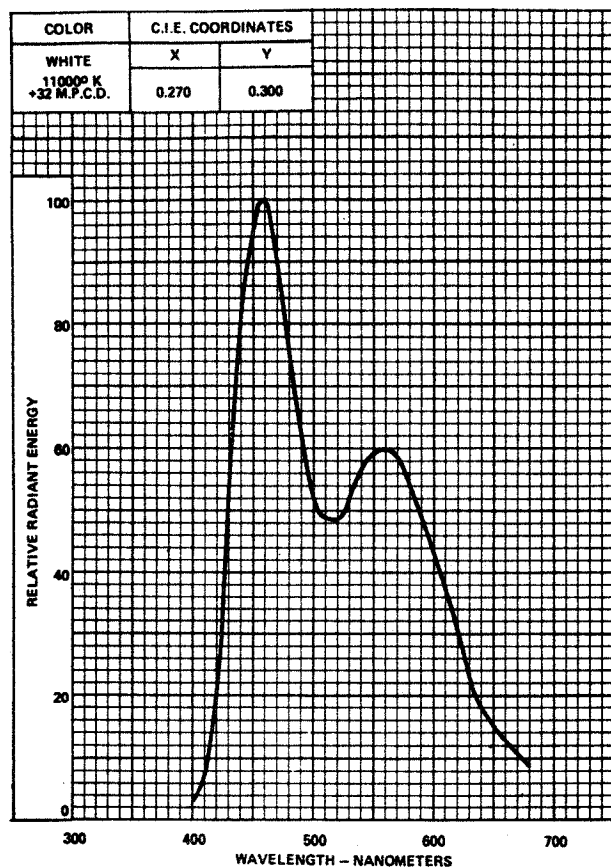


Fig. 10. Black and white SED curve.

contamination—not only to copper, but also to iron and nickel.

The brightness gain possible with the all-sulfide combination was a compelling reason for meeting the challenge of contamination sensitivity. Sources of contamination were tracked down and eliminated and the switch from the sulfide silicate to the all-sulfide was successfully accomplished. After this milestone only minor changes were made in the phosphors. There was of course a gradual increase in brightness, coatings were developed to prevent "ion burn," i.e., brightness loss due to ion bombardment and the silver concentration was reduced in the yellow to lighten the body color [29]. More recently, a copper and aluminum activated ZnCdS yellow emitter was developed for use in the black and white screen [30]. There was a rather lengthy period in the early years of black and white television when the shade of white was constantly being changed. As will be explained later in this paper, shades of white can be described in terms of nearest equivalent color temperature (see Fig. 11). For example, a 100-W incandescent lamp has a color temperature of about 2800 K, a slide projector lamp 3200 K. Fluorescent lamps are available at 3500, 4500, and 6500 K. Sunlight is about 6500 K. Black and white television began at 4500 K, quickly advanced to 6500 K, then 7000, 8500, 10 000 K, and has now leveled off at about 12 000 K in the United States. It will be recognized that all of these shifts are toward bluer and bluer shades of white. No satisfactory scientific explanation has been accepted to explain this trend. The only justification has been to give the customer what he wants. Actually the bluer shades of white are less bright for a given amount of electrical power dissipated in the phosphor screen than are the yellower shades.

SPECIAL APPLICATIONS

A. Radar Tubes

Black and white television had just barely started when World War II came along. As a result, black and white development was halted but the budding technology in phosphors and cathode-ray tube production was quickly applied to the needs of the newly developed radar principle. The most widely used radar system was the plan position indicator (PPI scan) [31]. In this system, the electron beam in a cathode-ray tube scanned radially center to edge while the radial line continuously swept 360° around the tube face in synchronism with the radar antenna rotation. When an echo signal was received the electron beam was turned on and a spot of light appeared on the screen. In order to differentiate between a real echo and noise a phosphor characteristic known as buildup was utilized. Some phosphors such as specially prepared zinc cadmium sulfide:copper have a relatively long persistence ($\frac{1}{2}$ s to the 10-percent level). These same phosphors also take a relatively long time to build up to an equilibrium level once excitation has begun. Under pulsed excitation the brightness increases with the number of pulses until a steady-state level is reached. Thus in a PPI radar system, random noise would only produce random spots of light on the screen which quickly faded away whereas a periodically repeated signal would result in a buildup in brightness for a real target echo. In order to maximize the buildup characteristic, a cascade or two-layer screen was used. The screen on the faceplate seen by the viewer was the long persistence zinc cadmium sulfide:copper phosphor—yellow in color. On the back of this screen was a layer of blue-emitting zinc sulfide:silver phosphor. In operation the electron beam excited the blue layer only. The light from the blue layer then in turn excited the yellow layer. The reason for the cascade structure is that under direct electron bombardment the zinc cadmium sulfide:copper phosphor does not exhibit the buildup and long persistence behavior.

B. Image Tubes and Image Intensifier Tubes

In a simple one-stage image tube light [32] is focused onto a photocathode with a lens. The electrons emitted from the cathode are accelerated and focused on a phosphor viewing screen at the other end of the tube. Originally, a green willemitte screen was used but this was soon replaced by a yellow-green-emitting zinc cadmium sulfide:silver. In intensifier image tube several stages are assembled in series. Between stages a blue-emitting zinc sulfide:silver is backed up to a photocathode and in the final stage the viewing screen is once again a yellow-green silver-activated zinc cadmium sulfide.

C. Voltage-Dependent Color Displays

Perhaps one of the most fascinating developments in phosphor history is the voltage-dependent color phosphors. Called "onionskin" phosphors [33], they consist of a phosphor core of one emission color, and deposited on this core are one or more layers of fine particle phosphors of other colors. A typical example is an "onion" with a blue zinc sulfide:silver core about 25 μm in diameter. On the surface of this is a thin fine-particle layer of green-emitting zinc silicate:manganese. Then on top of the green there is a thin fine-particle layer of a red emitter such as zinc magnesium cadmium silicate. There may even be a barrier layer of nonluminescent material between the phosphor layers. These "onions" can now be applied

to a tube faceplate by conventional techniques described later. In tube operation, the anode voltage is varied to achieve different levels of penetration into the "onion." For example, in the above case, with an applied accelerating voltage of 7000 V only the red layer will emit—at 15 000 V the principal emission will be green and at 20 000 V mostly blue light is obtained. Color separation is quite good—but low brightness and dynamic voltage switching has limited the applications.

Prenner and Kingsley [23] have recently discussed the preparation and characteristics of voltage-controlled multi-color cathode-ray-tube phosphors. They obtained four colors in the red-green system, and two primary color television pictures in the red-cyan phosphor system.

D. Flying-Spot Pickup

Since some phosphors have extremely fast buildup and decay characteristics, of the order of a 100 ns or less, it is possible to use a flying-spot scan technique to generate television signals. One system focuses the scanned raster onto a photographic slide. The light coming through the slide from the cathode-ray tube is received by a multiplier phototube which in turn gives rise to a video signal. This principle can be used for color as well as black and white. It has even been used to scan opaque objects.

E. Beam-Indexing Tube

Blue, green, and red phosphors in an indexing tube are excited consecutively, instead of simultaneously as in the shadow-mask tube. As discussed by Brill *et al.* [34], the screen of a beam-indexing tube can consist of several hundred vertical phosphor strips, which are coated on the gun side with thin aluminum. Electron-beam scanning is carried out in a horizontal line raster, with the beam-indexing signal generated from phosphors on the back of the strips. For this purpose, the special phosphor emission should be fast, and preferably in the ultraviolet, so as not to interfere with the color phosphors. Such phosphors are described by Brill, all with Ce^{+3} as the activator; such as β and γ — $(\text{Y}, \text{Ce})_2\text{Si}_2\text{O}_7$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{+3}$, decay times being 40 and 70 ns, respectively.

F. Projection Systems

This application is fairly obvious. Small diameter tubes, 3 to 7 in, are operated at very high voltage—up to 70 000 V and high current to produce extremely bright displays. These bright images are then projected by a lens or a Schmidt optical system onto a movie-type viewing screen. The phosphors for this application are selected for their ability to sustain very high power input. In some instances it is necessary to force air cool the screen end of the cathode-ray tube.

G. Printing Systems

Many phosphors emit enough energy to permit exposing photographic film in acceptable exposure times. A relatively recent development utilizes a blue-emitting phosphor on the inside of a very thin window cathode-ray tube. The intelligence is displayed on the phosphor screen in the conventional way. The window of the tube is so thin that satisfactory contact printing is achieved simply by placing the photographic film against the window.

H. Infrared Stimulation

Some phosphors such as zinc sulfide:lead:copper have the ability to store the energy received by the writing electron

beam for seconds to minutes. At the instant the electron impinges on such phosphors very little light is emitted. Subsequently, after the electron beam has been shut off, the phosphor screen is irradiated externally with infrared radiation. The infrared stimulation releases the energy stored in the phosphor screen and the phosphor emits its own characteristic light in the areas previously bombarded by the electron beam. One use for this characteristic is in navigation. A ship using this type of radar will scan for a certain time interval and then apply the infrared radiation. The direction and distance covered by all objects in motion during the scan will appear as bright vector traces on the phosphor screen.

COLORIMETRY AND PHOTOMETRY

When a cathode-ray tube is to be offered commercially it is usually registered with the Electronic Industries Association.¹ The registrant supplies pertinent information about the tubes characteristics and a type number is assigned. As part of the type number the letter P appears followed by a number which tells what phosphor is commonly used in the tube. The P numbers start with P1 and are now up to P48. Table IV shows the chemical composition of the P number phosphors [35].

Each phosphor has its characteristic emission as shown by its spectral energy distribution curve. Such curves are now obtained routinely with a recording spectroradiometer. In order to compare the color of one phosphor with another and handle the problems of color addition in black and white and color television it is convenient to use an objective color specification system. A system known as the ICI (International Commission on Illumination) or CIE (Commission Internationale de l'Eclairage) was established in 1931 [36], [37]. This system is based on the principle that an unknown color can be eye matched or duplicated by mixing the correct proportions of three primary colors, for example red, blue, and green. Having achieved a match, the proportions of the primaries used uniquely specify the color. Using real primaries it is not always possible to match an unknown color directly. However, by shining a certain amount of one of the primaries onto the unknown and adjusting the other two primaries a match is achieved. This leads to a color specification in which one of the numbers is a negative quantity.

To avoid this complication and for other benefits theoretical primaries were derived mathematically from real primaries so that the specification numbers are always positive. The tristimulus values X , Y , and Z required to match an unknown color, match not only the quality of the color, i.e., hue and saturation, but also the amount or intensity of the energy present. In fact the Y value represents the luminance or brightness of the unknown sample. In order to specify color only trichromatic coefficients x , y , and z representing relative amounts of X , Y , and Z are used. By definition

$$\begin{aligned} x &= \frac{X}{X + Y + Z} & y &= \frac{Y}{X + Y + Z} \\ z &= \frac{Z}{X + Y + Z} \end{aligned} \quad (7)$$

Since $x + y + z = 1$ the color is specified exactly by any pair of coefficients. By convention x and y are used. The values of x

¹ EIA Engineering Office, 2001 Eye Street N.W., Washington, D. C.

TABLE IV
COMPOSITION OF CATHODE-RAY-TUBE SCREENS

Screen	Composition
P1	Zinc silicate:manganese
P2	Zinc sulfide:copper
P3	Zinc beryllium silicate:manganese
P4	Zinc sulfide:silver and zinc cadmium sulfide:silver
P5	Calcium tungstate
P6	Similar to P4
P7	Zinc sulfide:silver and zinc cadmium sulfide:copper
P8	No information
P9	Calcium pyrophosphate
P10	Potassium chloride (dark trace—nonluminescent—called a Scotophor)
P11	Zinc sulfide:silver
P12	Zinc magnesium fluoride:manganese
P13	Magnesium silicate:manganese
P14	Similar to P7
P15	Zinc oxide
P16	Calcium magnesium silicate:cerium
P17	Zinc oxide and zinc cadmium sulfide:copper
P18	Calcium magnesium silicate:titanium and calcium beryllium silicate:manganese
P19	Potassium magnesium fluoride:manganese
P20	Zinc cadmium sulfide:silver
P21	Magnesium fluoride:manganese
P22	Zinc sulfide:silver, zinc silicate:manganese, zinc phosphates:manganese Zinc sulfide:silver, zinc cadmium sulfide:silver, zinc cadmium sulfide:silver Zinc sulfide:silver, zinc cadmium sulfide:silver, yttrium vanadate:europium Zinc sulfide:silver, zinc cadmium sulfide:silver, yttrium oxysulfide:europium Zinc sulfide:silver, zinc cadmium sulfide:copper, yttrium oxide:europium Zinc sulfide:silver, zinc cadmium sulfide:copper, yttrium oxysulfide:europium
P23	Similar to P4
P24	Zinc oxide
P25	Calcium silicate:lead:manganese
P26	Same as P19
P27	Zinc phosphate:manganese
P28	Zinc cadmium sulfide:copper
P29	Similar to P2 and P25
P30	The reservation for this phosphor has been cancelled
P31	Zinc sulfide:copper
P32	Calcium magnesium silicate:titanium zinc cadmium sulfide:copper
P33	Magnesium fluoride:manganese
P34	Zinc sulfide:lead:copper
P35	Zinc sulfide selenide:silver
P36	Zinc cadmium sulfide:silver:nickel
P37	Zinc sulfide:silver:nickel
P38	Zinc magnesium fluoride:manganese
P39	Zinc silicate:manganese:arsenic
P40	Zinc sulfide:silver zinc cadmium sulfide:copper
P41	Zinc magnesium fluoride:manganese calcium magnesium silicate:cerium
P42	Zinc sulfide:copper, zinc silicate:manganese:arsenic
P43	Gadolinium oxysulfide:terbium
P44	Lanthanum oxysulfide:terbium
P45	Yttrium gadolinium oxysulfide:terbium
P46	Yttrium aluminate:cerium
P47	Yttrium silicate:cerium
P48	70:30 mix P46:P47

and y for the pure spectrum colors when plotted on Cartesian coordinates gives rise to a horseshoe shaped locus. The ends of the horseshoe are then joined with a straight line which represents the nonspectral shades of purple, i.e., mixtures of blue and red. This graph, Fig. 11, is called a color-mixture diagram. The enclosed area represents the domain of all real colors. A straight line between 2 color points plotted on the diagram represent the colors obtained by mixing the two colors. Fig. 12 shows how white is obtained for black and white television by mixing blue and yellow [38]. Fig. 13 shows the CIE mixture diagram divided into named color area. This is known as the Kelly chart. Fig. 14 shows the triangular-shaped color gamut for the present-day color-television primaries. The significance of the triangle is that any color lying in or on the triangle can be reproduced by the picture tube. Fig. 15 shows the location for the color of a number of familiar objects listed in Table V.

One disadvantage of the x, y CIE diagram is that it is non-linear in respect to color differences. For example, if the color at a certain point is changed until the eye just detects the change and this is repeated in all directions, the just detectable color change area turns out to be an ellipse rather than a circle. Furthermore, the size of the ellipses varies within the mixture diagram. Recently there has been a movement toward the use of a uniform chromaticity system (UCS) diagram (Fig. 16) which is more linear than the x, y plot. The UCS uses u and v which are related to x and y as follows:

$$u = \frac{4x}{-2x + 12y + 3} \quad v = \frac{6y}{-2x + 12y + 3} \quad (8)$$

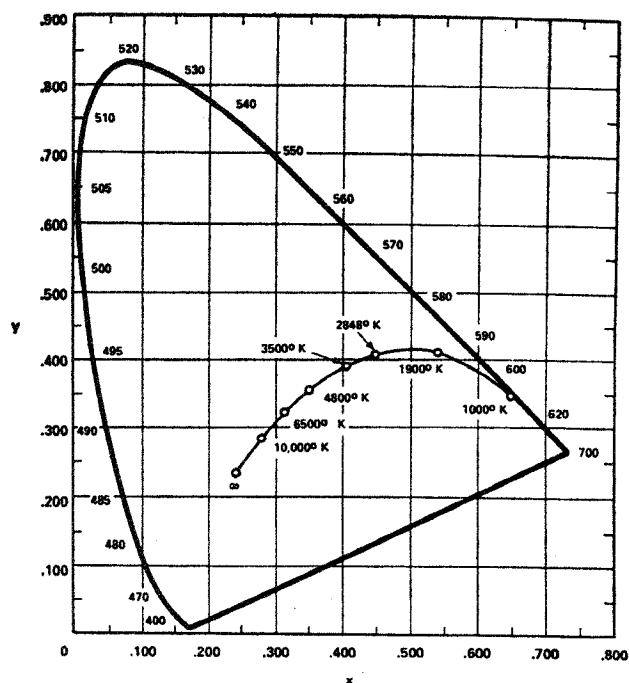


Fig. 11. CIE color mixture diagram with Planckian locus.

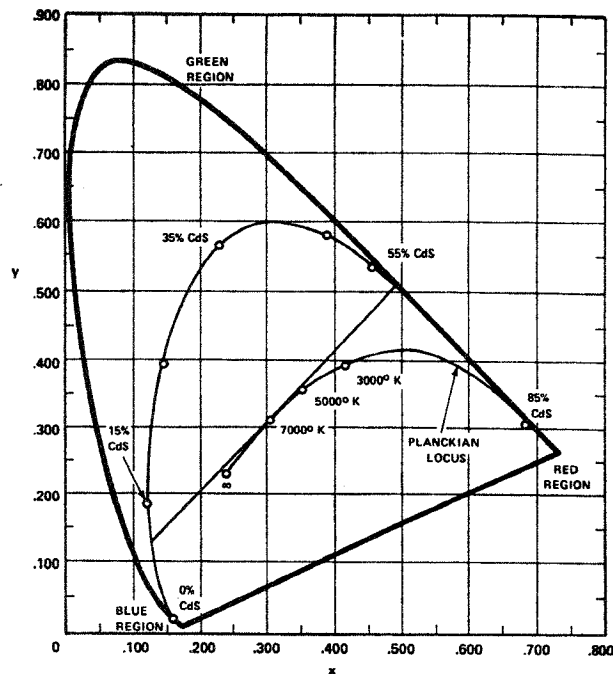


Fig. 12. Blue-yellow mixture locus.

As discussed earlier, in a complete match of an unknown source, the color is given by the values of X , Y , and Z while the visual stimulation or colorimetric weight is equal to the sum of $X + Y + Z$. The colorimetric weight is sometimes called stimability S , and can also be defined by Y/y . This is very convenient since Y is the luminosity of the source and may be expressed in lumens emitted per watt of electrical energy directed to the phosphor screen.

Lumens per watt is the most generally used unit for expressing the efficiency of phosphor screens. The measurements are usually made with an eye-corrected photovoltaic cell. The screens are assumed to be essentially Lambertian emitters

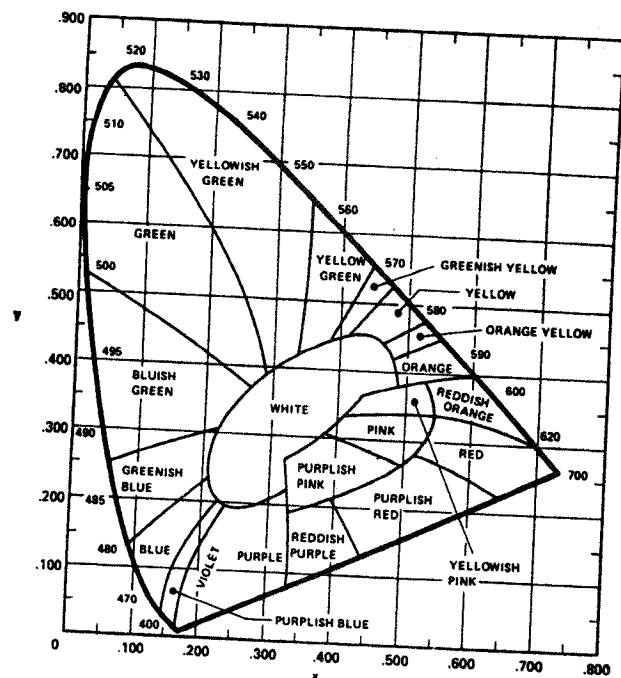


Fig. 13. Kelly color chart.

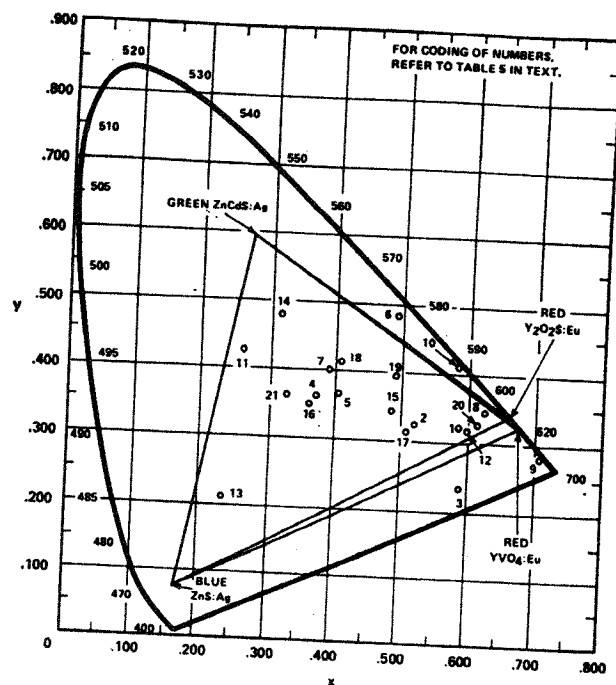


Fig. 15. CIE plot of some familiar colors.

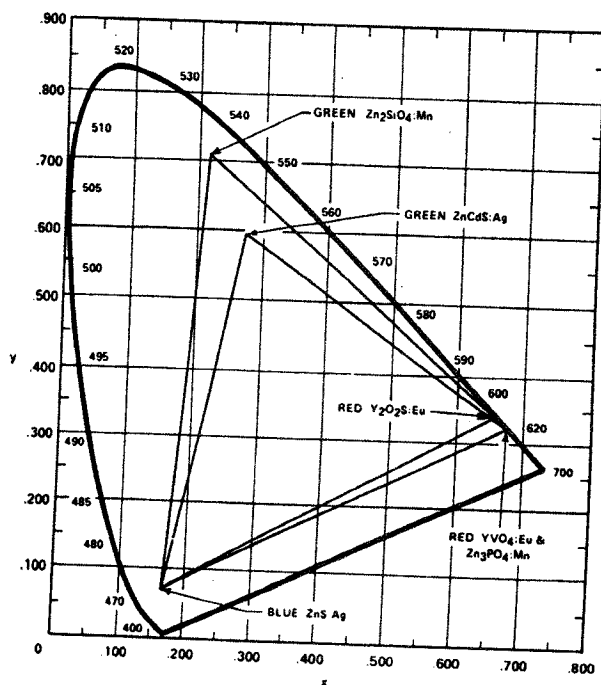


Fig. 14. Color TV primary triangle figure.

TABLE V
CIE x, y , COORDINATES FOR FAMILIAR OBJECTS

Object	x	y
RCA monogram	0.586	0.318
Apple (Stehman)	0.514	0.330
Rose (Best Times)	0.589	0.245
Caucasian	0.372	0.361
Negro	0.400	0.364
Dandelion	0.490	0.482
Banana	0.386	0.397
Tomato Juice	0.626	0.344
Red Traffic Light	0.713	0.287
Amber Traffic Light	0.584	0.410
Green Traffic Light	0.262	0.429
U.S. Flag (Red)	0.600	0.315
U.S. Flag (Blue)	0.239	0.210
Green Grass	0.308	0.475
Hershey Bar	0.485	0.346
Leather Briefcase	0.357	0.351
Lipstick (Clear Red)	0.505	0.318
Lemon	0.404	0.415
Orange	0.490	0.395
Coca Cola	0.613	0.323
Light Source (6000°K)	0.330	0.356

and a screen of one candela intensity emits π lumens normal to the screen. In television displays the subjective term brightness is used to express the objective quantity, luminance. Thus one speaks of a television picture with a brightness of 100 fL. If relative performance of tubes is being compared it might be that tube A has an efficiency of 100 fL/mA of beam current (at constant voltage) while tube B produces 110 fL/mA.

In Europe the nit and the lux are used in place of foot-lamberts.

$$1 \text{ fL} = 3.43 \text{ nit}$$

$$1 \text{ fL} = 10.76 \text{ lux.}$$

Another concept that is useful is luminous equivalent. Simply stated this is the number of lumens contained in one watt of radiant energy of a particular spectral distribution. It is not related to the basic efficiency of the phosphor but is based on the mechanical equivalent of light. The maximum value is 685 lm/W for radiation at 556 nm.

Conversion efficiency is quite a different thing. Expressed as percent it is the watts of radiant energy from the phosphor per watt of electrical energy dissipated in the phosphor. Values range from a low of 3 to 4 percent up to 20 percent for commercially used phosphors. The conversion efficiency tends to be fairly constant within a family of phosphors of similar composition. Silicates for example are usually around 6 per-

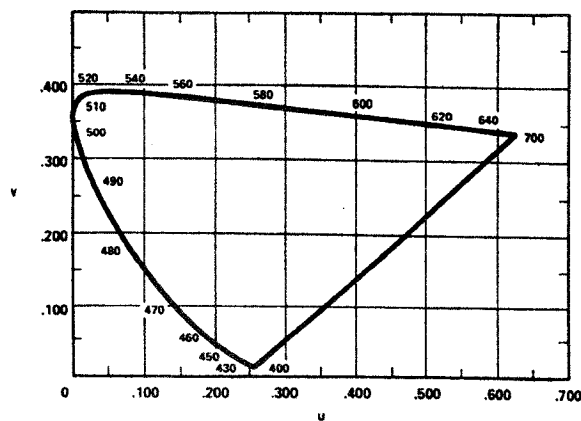


Fig. 16. UCS diagram.

cent and sulfides are about 15 percent. (See Table III.) The conversion efficiency is somewhat dependent on voltage and current density. It tends to rise with increasing voltage and to fall with increasing current density. In actual tubes the radiant output increases linearly with current only up to a certain level. Above this level, the increase is less than linear and is referred to as current or current-density saturation.

Persistence by definition is the emission from a phosphor that continues after excitation has ceased. The intensity of the persistence decreases with time following either as an exponential or a power law function. In some instances it is possible to resolve the decay curve into several exponential functions with different time constants. The actual persistence observed is a function of the excitation conditions. For cathode-ray-tube applications the persistence is stated as the time for the emission to decay to the 10-percent level. The fastest decay in the P number series is P47 at 80 ns. The longest decay is P32 at up to 20 s. Persistence categories have been established as follows [38]:

Time to 10-Percent Level	Description
1 s or longer	very long
100 ms–1 s	long
1 ms–100 ms	medium
10 μ s–1 ms	medium short
1 μ s–10 μ s	short
Less than 1 μ s	very short

Television phosphors are usually in the medium-short range.

PHOSPHOR SCREEN DEPOSITION TECHNIQUES

Down through the years many methods have been developed for depositing a thin layer of phosphor powder in cathode-ray tubes. Without doubt more screens have been prepared by water settling than by any other process. The basic principle is to pour a water suspension of the phosphor powder into a bulb and allow the phosphor particles to settle out due to gravity and in accordance with Stokes law. After a suitable time interval the phosphor will have settled out of suspension and the water can be poured off or otherwise removed. In order to achieve a uniform thickness screen with good adherence to the glass faceplate various binders and electrolytes are used. A typical procedure is as follows.

A certain volume of water containing barium acetate in solution is placed in the bulb to provide a cushion layer of liquid several inches deep. After the turbulence of the cushion

layer has subsided, a small volume of water containing the phosphor particles and potassium silicate is introduced by gravity flow through a multihole spray nozzle. During the following 30 min the phosphor particles settle out onto the glass faceplate and the potassium silicate is partially gelled by the barium acetate thus providing good particle to particle adherence (cohesion) and good particle to glass adherence (adhesion). At the end of this time, the bulb is tilted and the supernatant liquid is poured off. The screen is then dried with warm air. If the screen is to be a multilayer or cascade structure the operation is simply repeated. The water settling technique has developed from the point where settling times of 12 to 24 h have been reduced to less than 30 min today. All black and white picture tube screens, as well as most military and industrial types, are made by water settling.

Some special-purpose high-resolution screens are made by the technique of cataphoresis. Phosphors for this application are much smaller in particle size (0.1 μ m or less) than phosphors for television (10 μ m or larger).

In cataphoresis a suspension of the fine particles is prepared and are caused to migrate to the faceplate under the influence of an electric field.

Cathode-ray tubes designed to operate at an accelerating potential greater than 10 000 V usually are provided with a thin (2000–5000-Å) aluminum film on the back side of the phosphor screen. The aluminum film serves three purposes. It prevents the phosphor screen from changing negatively under electron bombardment by providing good electrical conductivity back to the power supply. The film is sufficiently thick to prevent ions from penetrating to the screen which would suffer a significant loss in brightness known as ion burn. Finally, the aluminum film serves as an optical mirror to reflect forward toward the viewer the light radiating from the back of the screen. This effect alone nearly doubles the brightness of phosphor-screen display.

The aluminum film is deposited on the back of the phosphor screen by vacuum deposition. Before aluminizing, however, an organic lacquer film is deposited in the back of the phosphor screen to act as a temporary substrate to receive the aluminum. In the absence of a temporary substrate, the aluminum deposit would not be a continuous or light-reflecting film. After the aluminum metal deposition the organic film is removed by thermal decomposition by baking at about 425°C.

Most color-television picture tubes operate on the shadow mask principle. Consequently, the phosphor screen consists of small discrete elements arranged in a very precise and orderly geometric array. In order to achieve the high degree of geometric precision required, a photographic technique is used to print the phosphor elements. The principal color-television screening process used is known as the slurry process. Another process used by a few companies is called dusting and one company is known to be using a spraying system. In all of these systems the basic steps are the same. One color phosphor at a time is incorporated into a water soluble photosensitive binder such as polyvinyl alcohol (PVA). The PVA is made photosensitive by the addition of ammonium dichromate. After a film of the PVA containing the first color phosphor has been applied to the inner surface of the faceplate and dried the shadow mask is inserted and the mask-panel assembly is placed on an exposure unit. The exposure unit or lighthouse contains a high-intensity small-diameter ultraviolet light source. The light source is located in the exact geometric position that one of the electron guns in the finished tube will

occupy. The ultraviolet radiation passes through the openings in the shadow mask and falls on discrete areas of the PVA phosphor-containing film. Wherever the ultraviolet radiation impinges the PVA film undergoes cross-linking and becomes insoluble in water. After a suitable exposure time, the mask-panel assembly is removed from the lighthouse, the mask is removed from the panel, and the screen is developed with warm water. The film areas not exposed to the ultraviolet radiation are washed away leaving an array of phosphor dots or lines depending on the tube design. The process is repeated two more times to deposit the other color phosphor elements. Finally the three-color structured phosphor screen is filmed and aluminized as explained earlier.

In the slurry process of color screening, a dispersion of the phosphor in the PVA is made by ball milling and stirring. The slurry is dispensed into the glass panel which is rotated and tilted to produce a uniform film of the phosphor slurry. After drying the exposure and developing are carried out as previously described.

In the dusting process the panel is first coated with clear PVA, i.e., it contains no phosphor at this stage. The coating can be done by spraying or slurring. After a uniform clear PVA film has been applied and while it is still wet, dry phosphor powder is blown or dusted onto the wet film. After drying the dusted screen is handled like a slurried screen.

A third process, used by only one company, involves a dispersion of phosphor in PVA like the slurry method but the dispersion is sprayed onto the panel assembly. Following drying all other process steps are the same as previously described.

Other methods have been used including water settling and tacky dot. In the latter method, the clear PVA film is dried, and exposed before the phosphor is introduced.

Very recently, a tube design has become available commercially using the so-called matrix or black surround principle [39]. In this design, a black material such as graphite surrounds each phosphor element. The graphite absorbs ambient illumination falling on the face of the tube reducing the dilution effect of adding ambient light to the light being emitted by the phosphor screen. The dilution effect was previously minimized by incorporating light absorbers in the faceplate glass itself. For example a common faceplate glass transmission used to be 50 percent. Since ambient illumination has to make a double pass through the glass in order to reach the observer's eye the intensity is reduced to 25 percent of the incident value. The fluorescent light from the phosphor screen makes only one pass through the glass and loses only 50 percent. As a result, there is a net increase in picture contrast, but at the cost of a significant loss in brightness.

In the matrix tube the matrix absorbs a significant portion of the ambient light, thus the faceplate glass transmission can be raised. A typical glass transmission in the matrix tube is 85 percent. Of course, the phosphor efficiency in a matrix tube is no greater than a nonmatrix tube but the picture brightness is increased by the factor of 85 over 50.

CONCLUSIONS

Cathode-ray tubes employing phosphor screens will probably continue to be used indefinitely into the future. The low-cost-per-display element addressed is difficult to match with any other principle.

In the specific case of color television it also appears that the shadow mask picture tube and similar tubes will continue to be used. Consequently, it is expected that considerable effort will continue to be spent throughout the world in the search for brighter and colorimetrically more saturated green phosphors and deeper hue and lower cost red phosphors.

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Color Picture Tubes

I. Luminescent Materials (Phosphors)

Inorganic crystals which emit light when struck by electrons or other forms of energy such as x-rays and ultraviolet radiation.

A. Chemical Composition

1. Blue: Zinc Sulfide + Trace Amount of Silver
2. Green: Zinc Cadmium Sulfide + Trace Amount of Copper
3. Red: Yttrium Oxysulfide + Trace Amount of Europium

II. Colorimetry

A. Color Mixture Diagram (C.I.E.)

1. Primary Colors
2. Mixture Colors
 - a. Red + Green = Yellow
 - b. Red + Blue = Purple (Magenta)
 - c. Blue + Green = Cyan
 - d. Blue + Yellow = White

B. Spectral Energy Distribution (S.E.D.)

- a. Broad Band Emitters
- b. Line Emitters

C. Spectroradiometer

D. Color Temperature

1. $9300^{\circ}\text{K} + 27\text{MPCD's}$
2. $6550^{\circ}\text{K} + 7\text{MPCD's}$ (Illuminant D)

III. Photometry

A. Brightness

1. Units
 - a.) Footlambert (1 Lumen/ft^2)
 - b.) Footlamberts per Milliampere (fL/ma)
 - c.) Nits (Candle/m^2) = $3.43 \times \text{fL}$

B. Equipment - Eye-Response Photocell

GENERAL COMMENTS/PHOSPHOR MFG.

It is not difficult to prepare phosphors -- even the novice may very easily be successful in preparing a new phosphor.

The difficult part is preparing a phosphor which will have a practical application.

The most efficient phosphors are well-crystallized, white, high melting materials which are prepared from highly purified base materials to which no amounts of impurities or activators are added. There are some phosphors to which no known activators are added. They are thought to have an excess of one atom over another (eg. in case of zinc sulfide type -- more zinc atoms than sulfide).

Phosphor preparation takes place at high temperatures in range between 700°C and 1600°C.

These high temperatures are necessary to form well-crystallized materials and to incorporate the impurities (activators) into the crystal lattice.

Must have highly purified materials.

Must have atmosphere free of contamination. Trace amounts of certain impurities can drastically alter phosphor characteristics.

- like 2×10^{-5} % of nickel in a copper activated zinc sulfide phosphor will modify the decay characteristics.
- like in a silver activated zinc sulfide phosphor, 10^{-2} % of nickel almost kills it.

Flux (2 purposes):

- usually a low melting material thought to partially dissolve and reprecipitate the phosphor base material - promotes crystallization.
- appears to facilitate the entry of positive ion (maybe Ag) into the ZnS lattice structure.

Coating:

- gives phosphor good flow characteristics.
- makes phosphor more resistant to ion burn.

Phosphors of the oxide type generally require larger amounts of activator than do the sulfide phosphors. The purity requirements is not as strong as sulfide systems.

All activated phosphors require ultimate mixing of the solid starting materials.

Search for new phosphors may be classified:

- 1) formation and activation of new base materials (base materials previously known)
- 2) activation of established compounds with new activators or with previously tried activators in new ways
- 3) the modification of established phosphors by means of preparation techniques or impurity additions

Compound formation is determined by X-ray diffraction.

Elaborate air filtering.

Things which can affect phosphor properties:

- 1) variation in reaction temperature
- 2) variation in reaction time
- 3) varying atmosphere in which preparation takes place (may use H₂ air)
- 4) varying activator concentration
- 5) changing composition of the base material
- 6) fluxing the mix
- 7) adding impurities
- 8) variations in firing temperature or time
- 9) distribution of the activator
- 10) the crystallization of the phosphor
- 11) crystal structure of the base material

Extremely important to avoid metallic or organic contamination. All reactors, pipes, valves, etc. caused in neutralization must be made of materials impervious to 1.5 - 2.0 N sulfuric acid.

Glass lined reactor vessels, etc.

Safety:

H₂S used - very toxic

Construction materials

glass lined steel
stainless steel
hastelloy C
polyvinyl chloride
porcelain
pyrex
fused silica
graphite

Contaminants

grease
oil

Coating of phosphors:

--coating of particles with magnesium silicate to prevent ion burn

Storage:

--in moisture tight opaque containers

Building environment must have:

- temperature control
- humidity control

Color phosphors:

- blue emitting - silver activated zinc sulfide
- green emitting - manganese activated zinc orthosilicate
- red emitting - manganese activated zinc orthophosphate

Causes of white non-uniformity:

- Mechanical
 - misregistry
 - dented masks
 - small dots
 - overlapping dots
 - missing dots
- Electrical
 - stray emission
- Chemical
 - poisoning
 - contamination
- Physical
 - variation in screen weight

Al. thickness 3000° - 4000° A (about 2X black/white)

- needed to alternate high velocity electrons
- needed to absorb low velocity secondary electrons

GREEN-MARION

Cadmium oxide + sulfuric acid (only new material used) → cadmium sulfate + water



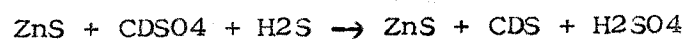
Thru filter press to get rid of undissolved material



Zinc sulfate + hydrogen sulfide → zinc sulfide + sulfuric acid



Zinc sulfide and cadmium sulfate are mixed such that with hydrogen sulfide added the resultant zinc sulfide and cadmium sulfide products are in an approximate 9 to 1 ratio. Sulfuric acid is a by product.



Wash



Add very low quantity of copper aluminum nitrate (CU AL NO3) activator



Bake



Add 4% sulfur and 1% carbon to prevent oxidizing phosphor



Tumble



High temperature fire in quartz boats

--1165°C for 1 hour +



Cool approximately 3 hours

--visual appearance - "yellowish"



UV visual inspection



Add DeI water



Put thru course mesh basket to get out carbon chunks

↓
Add Ludox (colloidal silica) few cc/lb of phosphor
--coats phosphor particles, aids flowability characteristics
↓
Rotary filter to get rid of H₂O
↓
Dry in pyrex discs
--300+°F for 24 hours
↓
Screen thru approximately 320 mesh
↓
Tumble
↓
Dry
↓
Bag

BLUE-MARION

Sulfuric acid + zinc oxide \rightarrow zinc sulfate + water
 (acid resulting from reactions later in process and new acid as needed)



(small amount of ammonium hydroxide added
 to take out iron and other possible contaminants)



Thru filter press to get rid of undissolved material



Zinc sulfate with H₂O added to constant volume ZnSO₄



H₂S feeds into bottom of tank and allowed to bubble up thru zinc sulfate and H₂O



H₂S will be fed in at rate which will take part in reaction. This rate is controlled/observed but allowing small amount to bubble off. This small amount is fed on to fume scrubber.



This reaction is:

Zinc sulfate + hydrogen sulfide \rightarrow zinc sulfide + sulfuric acid
 (this acid goes back
 to storage for later use)



Silver nitrate (AgNO₃) added to ZnS to give about .030% Ag₂S



Wash to specific PH level



Add 1% sulfur to prevent oxidizing of the phosphor



Add $\frac{1}{2}\%$ MgCl₂ + .05% NaCl flux materials to help make phosphor resistant to contamination. Also influences particle size, PH and color.



Bake dry - 350° F to get rid of H₂O

↓
Tumble
↓
Add 1% sulfur (again to prevent oxidizing of phosphor)
↓
High temperature firing (influences particle size and luminescent efficiency)
--quartz boats
--980°C
↓
Cool approximately 3 hours
--visual appearance - "whiteish"
↓
UV visual inspection
↓
Add DeI water (thru slurry)
↓
Add small quantity potassium silicate and zinc silicate
or
zirconyl nitrate + ammonium sulfate
↓
Coats phosphor particles
↓
Centrifuge (to get rid of H₂O and chlorides)
--mixture out of centrifuge is almost dry
↓
Dry in oven at about 310°F
↓
Put phosphor thru 200 mesh
↓
Tumble
↓
Bag

RED-LANCASTER

Yttrium oxide + Europium oxide + Sodium carbonate + Disodium phosphate

Blend for an hour



Fire at 1150°C for 5 $\frac{1}{4}$ hours



Ball mill in water for 1 hour



Filter



Dilute with DM water and stir for 1 hour



Settle for 3 hours



Decant



Add water - stir - check PH



Repeat above 4 steps 6 times



Repeat above until no longer collodial



Decant, dry in oven at 200°C



Screen thru 200 mesh



Pack in drums