GE Electronic TUBES

Final Report on the Development of a Long Persistence Lead-Manganese Activated Calcium Silicate Phosphor

BUREAU OF SHIPS
CONTRACT No. NObsr-63056

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Inspector of Naval Material 1206 Santee Street Los Angeles 15, California	END. NO. **1.** ON BuShips ltr 30-A-439 (816G) Ser 816-1039 dtd 18 May 56.

TO: (Check routing in boxes below)

Vacuum Tube Products Co.
506 S. Cleveland Street, Oceanside, California

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Silicate Phosphor, G. E. Syracuse Contract NObsr 63506 - Forwarding of

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IN REPLY REFER TO
30A-439(816G)
Ser 816-1039

18 MAY 1956

To: Vacuum Tube Products Co.,
       506 S. Cleveland Street
       Oceanside, California

Via: Inspector of Naval Material, Los Angeles

Subj: Request for Report on cathode ray tube phosphors

Ref: (a) Vacuum Tube Products ltr of 6 April 1956 to
          Inspector of Naval Material, Cleveland
     (b) Inspector of Naval Material, Los Angeles, End. 1
          File No. 10C2/VAC:dr Vacum/Misc Ser 10-749
     (c) Inspector of Naval Material, Cleveland, ltr
          L4-3/20/G.E. 5:je of 10 May 1956

Encl: (1) Copy of Final Report on the Development of a
          Long Persistence Lead-Manganese Activated Calcium
          Silicate Phosphor, G.E., Syracuse Contract
          NObsr-63056

1. Enclosure (1) is furnished for information, and retention,
as requested by Reference (a).

F. R. Darne

F. E. Darne
By Direction

FINAL REPORT

ON THE DEVELOPMENT OF

A LONG PERSISTENCE LEAD-MANGANESE

ACTIVATED CALCIUM SILICATE PHOSPHOR

BUREAU of SHIPS
CONTRACT NO. NObsr-63056

Period Covered:
January 1, 1953 to July 1, 1955

A. I. Friedman

F. D. Gordon

T. C. Vincent

GENERAL ELECTRIC COMPANY

Cathode-Ray Tube Sub-Department

ELECTRONICS PARK

SYRACUSE, N. Y.

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I. INTRODUCTION:

At the present time there are two phosphors which are largely used in the manufacture of long persistence radar screens. These are the double-layer zinc cadmium sulfides, and the single-layer zinc magnesium fluorides. In the sulfides, the blue emission of the short persistence component excites the long persistence component in a cascade process. Very often the display is photographed at the same time it is being viewed, and then it is necessary to use beam splitter devices to divert the actinic emission to a photographic system. At other times, when the display is only being observed by the radar operator, the short persistence blue flash is filtered out. In either case, there is a substantial reduction in the brightness of the display that is being viewed. In addition, the use of cascade screens results in heavier screen coatings. This increases the light scattering properties of the screen, and consequently reduces resolution and contrast because of larger spot size and a halation phenomenon which occurs.

The single-layer zinc magnesium fluoride screen obviates the disadvantages of double-layer screens. However, the fluorides are not very stable under electron bombardment, and the phosphor screens deteriorate at fairly low current densities. This seriously limits the operation of cathode-ray tubes using fluoride screens. A major need for cathode-ray tube screens for radar displays has been a single component, long persistence, "red" phosphor having good maintenance characteristics.

This report covers both phases of the Bureau of Ships Contract NObsr - 63056 for the development of a lead-manganese activated calcium silicate phosphor having optical properties, i.e., color, spectral energy

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emission, brightness and persistence similar to the P-19 fluoride phosphor, and having in addition improved maintenance characteristics.

The work plan for the development of this phosphor and its ultimate incorporation into specific tube types was divided into two phases. The first phase covered the evaluation of the physical and optical properties of the phosphor powder and screen. Also, some work was done to develop suitable production methods as a means of obtaining more satisfactory powders with higher phosphor yield. The first phase of the work plan concluded with the building of tubes and evaluation of samples on life test.

The second phase concerned the development of specific tube types using the calcium silicate phosphor. As a result, tubes have been supplied to Buships for evaluation tests, and for direct replacements in equipment now in use.

The properties of lead manganese activated calcium silicate have been studied by many workers in the field. However, the main emphasis has been toward its development as a lamp phosphor. As a consequence, its optical properties when excited with UV radiation (figure 1) have been of primary interest. It was observed, however, that when the phosphor was excited by cathode rays it exhibited the same long-tail phosphorescence as the fluoride, and in addition it was more resistant to electron or raster burn. Since the silicate was not specifically developed for cathode-ray tube application, it was believed that a considerable improvement in the brightness and decay characteristics could be obtained by investigating the effects of activator variation and preparation techniques.

SPECTRAL ENERGY EMISSION OF CaSiO$_3$:Pb:Mn
EXCITED WITH λ2537 RADIATION (H.C. FROELICH)(I)
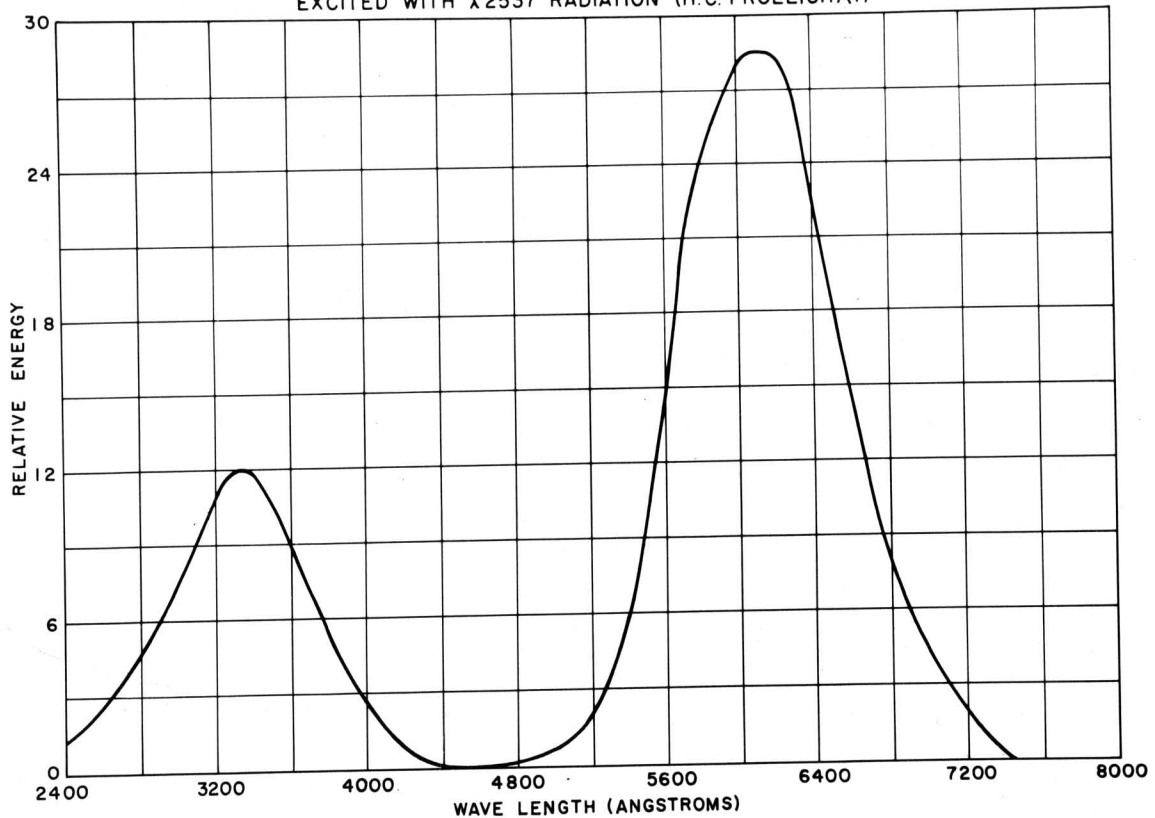
Figure 1

II. CHARACTERISTICS OF CALCIUM SILICATE PHOSPHORS

Preliminary investigations at Chemical Products Works of the General Electric Company indicated that double activated CaSiO$_3$:Pb:Mn phosphor had many characteristics similar to the (Zn:Mg) F$_2$:Mn phosphor. Not only were the spectral distributions and persistences of the two phosphors comparable, but burning tests under cathode rays gave evidence that the CaSiO$_3$:Pb:Mn types did not deteriorate as rapidly as the fluoride type phosphors. One feature of the CaSiO$_3$:Pb:Mn which appeared to be desirable was that a number of colors could be produced from the same host crystal with only slight changes in the manganese concentration. This is not possible in (Zn:Mg)F$_2$:Mn type phosphors.

In general, the fluorescent color of $CaSiO_3$:Mn, and double acti-
vated $CaSiO_3$:Pb:Mn can be described as being "yellow". However, a wide range
of colors varying from light green to deep orange may be obtained if the
phosphors are properly prepared. Previous investigators have found that under
cathode-ray excitation the fluorescent emission of $CaSiO_3$:Mn is composed of
two bands; one peaking in the green-yellow at about 5600A; and the other
peaking in the orange at about 6200A. The green-yellow band is of reasonable
intensity only at very low concentrations of manganese, while the longer
wave-length band is produced only at higher concentrations of manganese. At
intermediate concentrations, the two bands merge into what appears to be a
single band. The relative preponderance of the two bands, however, can also
be associated with the particular crystal structure of the phosphors. Phos-
phors with low manganese concentrations give the α form of wollastonite,
while phosphors with higher concentrations of manganese give the β or low
temperature form.

The inability of $CaSiO_3$:Mn to emit under 2537A radiation is due to
the absence of an absorption band at this wave-length. However, the addition
of a lead sensitizer introduces the needed absorption band, and good fluo-
rescence occurs both under cathode-ray and 2537A radiation. Some of the
excitation energy absorbed by the lead atoms is transferred to the manganese
activator atoms and re-appears as the emission band of the latter. The
fluorescence of the phosphor, however, is a composite one and includes the
emission bands of both lead and manganese at relative intensities which de-
pend upon their concentration. The emission band due to the lead occurs at
approximately 3400A, and that of the manganese from 5600 to 6200A.

Although a considerable amount of information has been written on calcium silicate-lead and manganese activated phosphors, very little data has been published about the factors affecting the decay rates of these types. About all that has been revealed is that both the $CaSiO_3$:Mn, and $CaSiO_3$:Pb:Mn have strong phosphorescence under excitation with short wave-length radiation. The long persistence has been attributed to the second stage of a bi-molecular decay.

It was the purpose of this project to determine if a suitable substitute for $(Zn:Mg)F_2$:Mn could be obtained from calcium silicate type phosphors, and also, to determine what factors influence the decay rates of these silicate types.

III. PREPARATION OF SAMPLES

A - Method of preparation

In contrast to zinc oxide and silica, calcium oxide and silica can form true metasilicates of mol ratio 1:1, as well as orthosilicates of mol ratio 2:1. However, the thermal synthesis of calcium silicates is not so easily accomplished as the synthesis of zinc silicates. The reaction is very sluggish, and abnormally long firing times are required to bring about the formation of the material. The same undesirable feature is true in the formation of lead-and manganese-activated calcium silicate type phosphors. Various methods, such as firing in an atmosphere of steam, have been em-ployed by investigators in order to minimize the long firing times required. However, this technique does not lend itself to inexpensive large-scale pro-duction even though efficient powders can be obtained when fired from 2-4 hours in a temperature range of 1000°- $1200^{\circ}C$. The most feasible means of producing efficient and inexpensive calcium silicate phosphors is by

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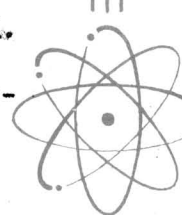
firing the reacting ingredients in the presence of flux or mineralizing agent. In general, fluorides, such as calcium fluoride and ammonium bifluoride, are the most potent fluxes in accelerating the reaction rate of silicates. Efficient phosphors can be made by firing 3 hours at 1160°C by this method. All the phosphors prepared in Phase I of the contract were synthesized by the halide-flux technique.

The preliminary and exploratory work conducted at the Chemical Products Works of the General Electric Company involved the preparation and synthesis of a number of calcium silicate samples with various chemical compositions. The variations in chemical composition of the samples were centered about a base formulation typed CS-6-62. This base formulation was as follows:

<div align="center">CS-6-62</div>

		Grams		Mols
$CaCO_3$	-	284	-	2.84
SiO_2	-	232	-	3.86
$MnCO_3$	-	20.32 (44.2% Mn)	-	.177
$PbSO_4$	-	15.20	-	.500
$NH_4F \cdot HF$	-	2.88	-	.050

The following is a list of the samples specifically prepared for the G-E Electronics Division for analysis of their color, efficiency, and decay characteristics under electron bombardment. Included in the list are the sample numbers, and their basic differences from type CS-6-62.

Group 1 - Variation in manganese concentration.

Expected Results: Variation in color and possibly afterglow.

Sample #	Variation
CS-67-62	10% of Mn as in CS-6-62
CS-66-62	25% " " " " "
CS-65-62	50% " " " " "
CS-5-62	75% " " " " "
CS-6-62	100% " " " " "
CS-8-62	125% " " " " "
CS-11-62	150% " " " " "
CS-9-62	200% " " " " "

Conditions of test: Fixed Ca, SiO_2, Pb-variation in Mn.
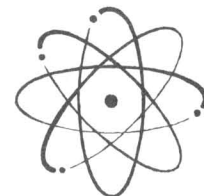
Group 1A - Variation in manganese concentration - no Pb.

Expected Results: Variation in color and afterglow.

Sample #	Variation
CS-5-62A	75% of Mn as in CS-6-62
CS-6-62A	100% " " " " "
CS-8-62A	125% " " " " "
CS-11-62A	150% " " " " "
CS-9-62A	200% " " " " "

Conditions of test: Fixed Ca and SiO_2- no Pb.

Variation in Mn.

Group 2 - Variation in lead concentration.

    Expected Results: Variation in efficiency and possibly afterglow.

Sample #	Variation
CS-14-62	50% of Pb as in CS-6-62
CS-6-62	100% " " " " "
CS-15-62	150% " " " " "
CS-16-62	200% " " " " "

    Conditions of test: Fixed Ca, SiO_2, Mn - variation in Pb.

Group 3 - Variation in calcium concentration.

    Expected Results: Variation in color and possibly afterglow.

Sample #	Variation
CS-23-62	67% of CaO as in CS-6-62
CS-28-62	85% " " " " "
CS-29-62	95% " " " " "
CS-6-62	100% " " " " "
CS-39-62	105% " " " " "

    Conditions of test: Fixed SiO_2, Pb, Mn - variation in Ca.

Group 3A - Variation in SiO_2 content.

    Expected Results: Variation in decay and possibly color.

Sample #	Variation
CS-43-62	150% of SiO_2 as in CS-6-62
CS-41-62	125% " " " " "
CS-6-62	100% " " " " "

    Conditions of test: Fixed Pb, Mn, CaO - variation in SiO_2.

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<u>Group 3B</u> - Partial substitutions for SiO_2.

   Expected Results: Variation in decay and possibly color.

<u>Sample #</u>	<u>Substitution</u>
CS-32-62	WO_3
CS-33-62	TiO_2
CS-34-62	SnO_2
CS-35-62	Bi_2O_3
CS-36-62	P_2O_5
CS-36-62A	GeO_2
CS-37-62	As_2O_3
CS-37-62A	Sb_2O_3
CS-37-62B	80 mol percent SiO_2 of CS-6-62) control
CS-37-62C	100 " " " " ") samples

   Conditions of test: Fixed Mn, Pb, and Ca - substitution of

   20 mol percent anions for SiO_2.

<u>Group 3C</u> - Partial substitutions for Ca.

   Results: Variation in decay and possibly color.

<u>Sample #</u>	<u>Substitution</u>
CS-42-62A	MgO
CS-42-62B	SrO
CS-42-62C	CdO
CS-42-62D	CeO_2
CS-42-62E	80 mol percent Ca of type CS-6-62) control
CS-37-62C	100 " " " " ") samples

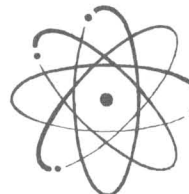   Conditions of test: Fixed Mn, Pb, and SiO_2 - substitution of

   20 mol percent cations for Ca.

Group 3D - Partial substitutions for Ca.

Expected Results: Variations in decay and possibly color.

Sample #	Substitution
48-62A	La_2O_3
48-62B	Na_2O
CS-42-62E	80 mol percent Ca of type CS-6-62) control
CS-37-62C	100 " " " " " ") samples

Conditions of test: Fixed Mn, Pb, and SiO_2 - substitution of

5 mol percent cations for Ca.

Group 5 - Mn concentration similar to those samples prepared in Group 1.

Expected Results: Variation in color and possibly decay.

Sample #	Variation
51-62	75% Mn - 50% less Pb than in type CS-6-62
14-62	100% " " " " " " " "
51-62A	125% " " " " " " " "
53-62	150% " " " " " " " "
63-62A	200% " " " " " " " "

Conditions of test: Fixed Ca, and SiO_2 - variation in Mn, 50%

less Pb than in type CS-6-62.

Group 6 - Addition of decay "killer".

Expected Results: Reduction of decay time.

Sample #	Variation
CS-90-62A	0.01% Indium added
CS-90-62B	0.001% " "
CS-90-62C	- control

Conditions of test: All samples similar to CS-9-62, variation

in Indium content.

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All phosphors were prepared by ball milling the batch ingredients
in a one gallon ball mill until the caking point of the mixture was attained.
The powders were fired in deep (3" x 3" x 4"), open silica-quartz trays in
an oxidizing atmosphere. After firing for 3 hours at 1160°C in a Hevi-Duty
type furnace, the phosphors were crushed and sifted through a #325 mesh
screen. The amount of useable phosphor recovered after sifting was in most
cases only 50% of the initial fired batch. Although this low yield was an
undesirable feature, the sifting operation was required in order to obtain
phosphors with good screening characteristics.

IV. EVALUATION OF SAMPLES AT G-E's CHEMICAL PRODUCTS WORKS

All samples were visually inspected for color and brightness under
cathode-ray and 2537A radiation. Their relative fluorescent intensities,
under 2537A radiation, and spectral distributions were determined with a
General Electric Recording Spectroradiometer. Inspections under cathode-
ray excitation were only qualitative.

Average particle diameters were determined by an air permeation
method.

After samples were tested by the Chemical Products Works they
were submitted to the G-E Cathode-Ray Tube Sub-Department for analysis in
cathode-ray tubes.

V. RESULTS

Group 1 phosphors, prepared to determine effects of Mn concentra-
tion, showed that the manganese concentration alters the phosphor color.
As activator concentration increased, the emission band shifted to longer
wave-lengths. There appeared to be an optimum manganese concentration for

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maximum energy in the manganese emission band. This optimum occurs approximately in sample CS-11-62 which contains 150% of the manganese in the base formula. It is also apparent that as manganese concentration is increased, there is a depression of the lead emission band at 3400A and of the manganese band at 5600A. The above results are tabulated in Table I and in Figures 2, 3 and 4.

Table I

Sample #	Mn conc. [1]	Peak λ (A) of Mn band	Height of MN [2] band at peak	Height of Pb band at 3400A	Average Particle Diameter (μ) (thru #325 mesh)
67-62	10%	-	-	-	-
CS-66-62	25%	5905	55	127	5.8
65-62	50%	6105	81	86	6.0
5-62	75%	6165	92	54	6.0
6-62	100%	6185	97	34	5.8
8-62	125%	6225	99	24	5.9
11-62	150%	6235	100	22	6.3
9-62	200%	6240	86	12	6.2

G. E. $(Zn:Mg)F_2:Mn$ - No activation under 2537A radiation.

(1) - Refers to the Mn concentration in CS-6-62 as 100 percent.

(2) - Refers to 11-62 as 100 percent.

In the preparation of phosphors one cannot always depend on the composition of the finished phosphor being the same as the composition of the mix before thermal synthesis. This is particularly true if there are volatile components present whose volatilization depend on the time-temperature relationship used for firing. Table II presents a comparison of theoretical and actual composition of various phosphors from Group 1 derived from calculation of theoretical composition and from quantitative analyses of the completed phosphors.

VARIATION OF Mn BAND PEAK INTENSITY vs MOL % Mn

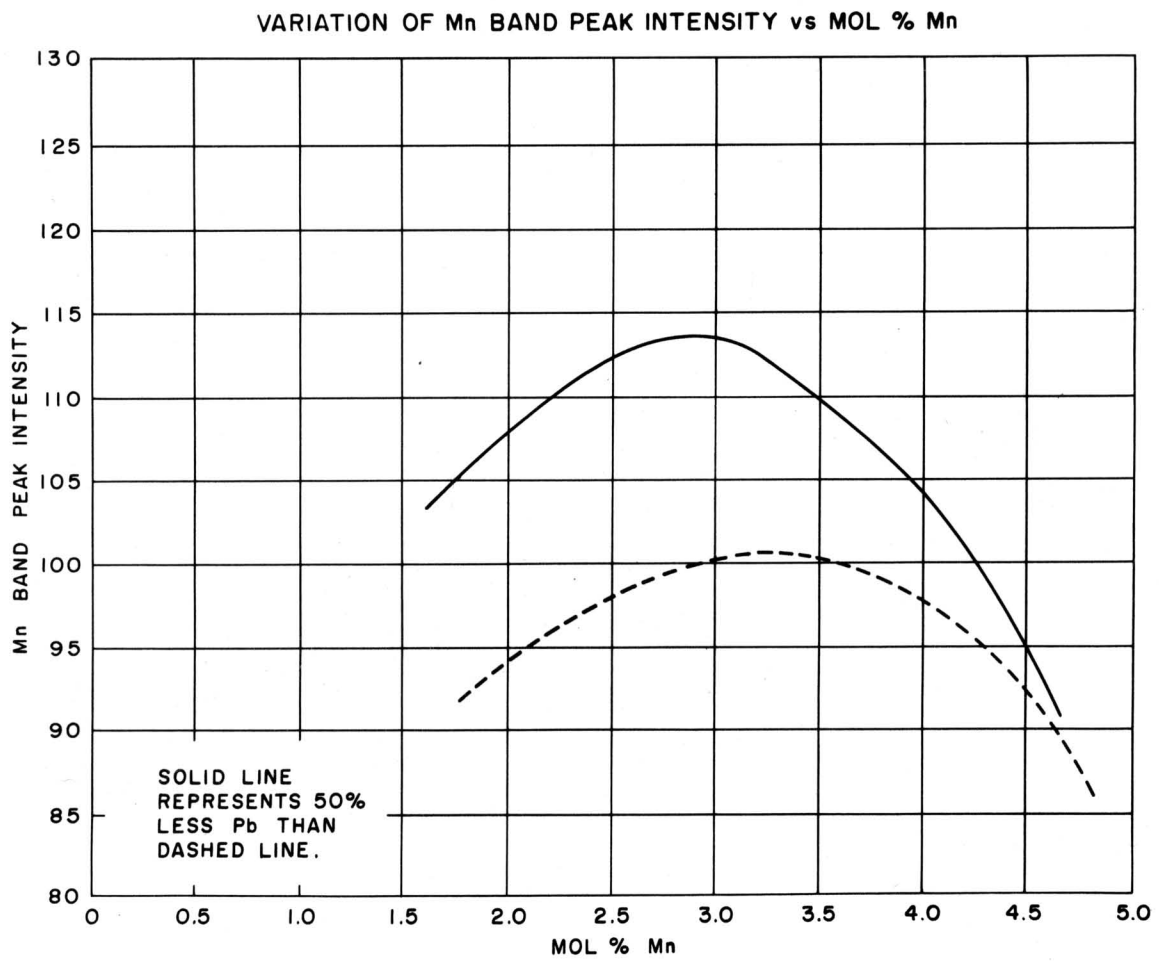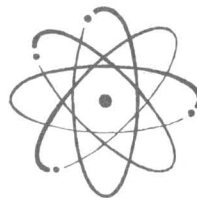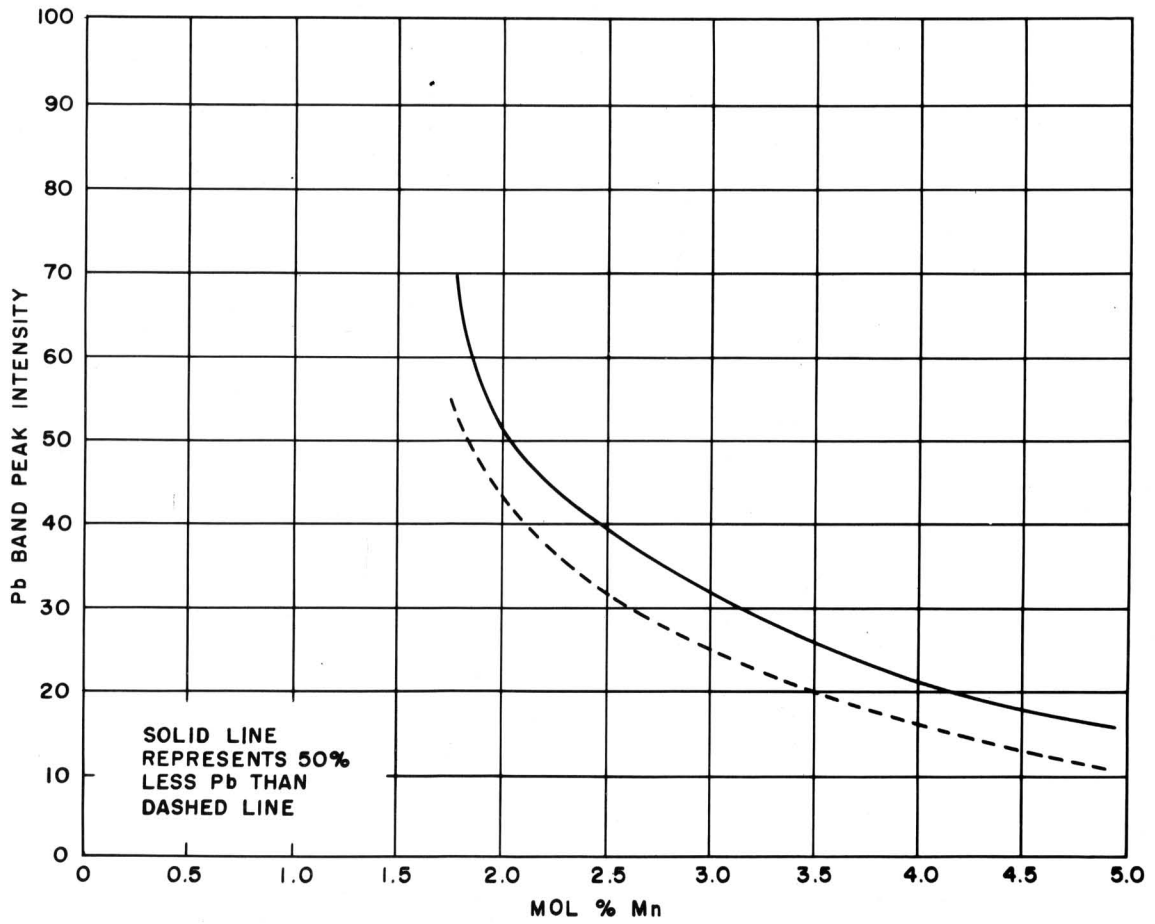SOLID LINE REPRESENTS 50% LESS Pb THAN DASHED LINE.

Figure 2

VARIATION OF Pb BAND PEAK INTENSITY vs MOL % Mn

Figure 3

A PEAK λ (Mn BAND) vs MOL % Mn
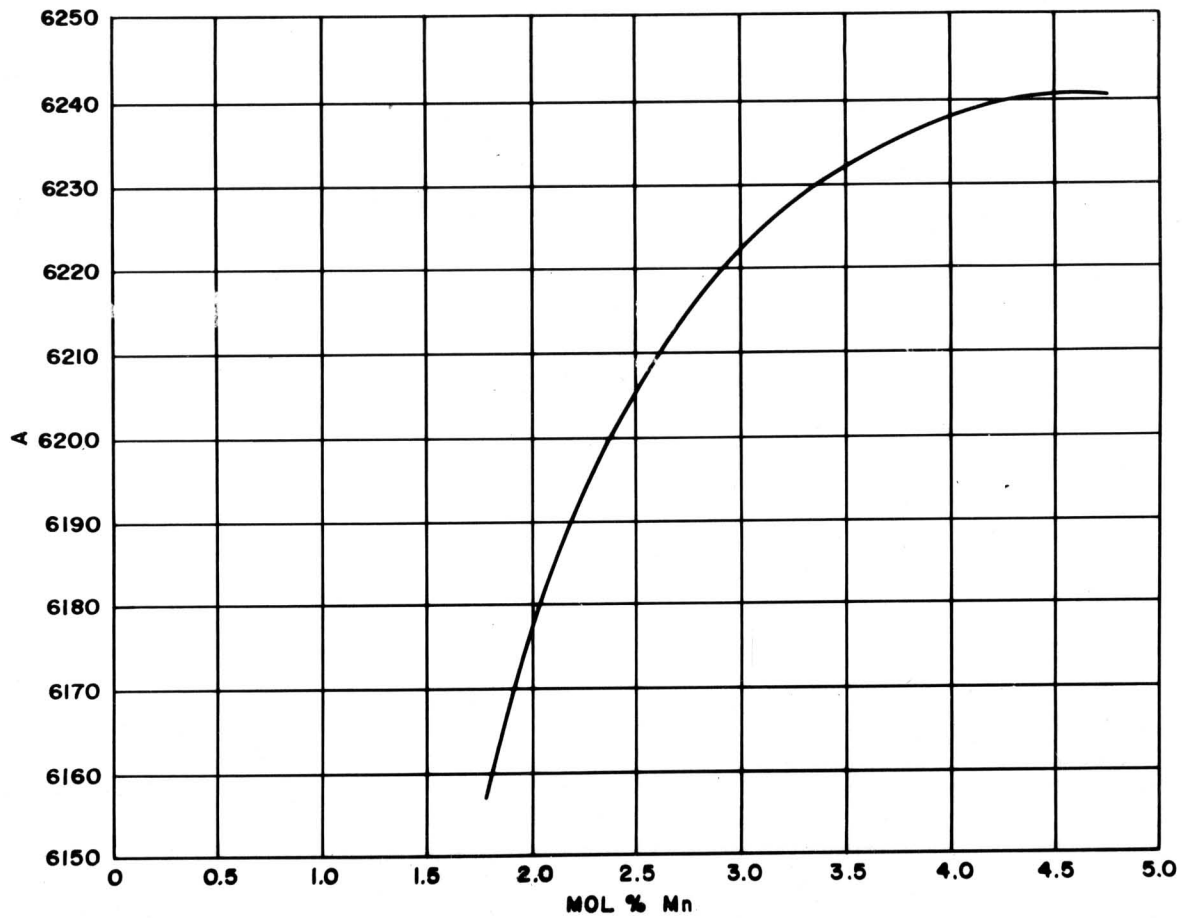
Figure 4

Table II
(all values are weight per cent)

Sample No.	MnO*	MnO Found	PbO*	PbO Found	CaO*	CaO Found	SiO$_2$*	SiO$_2$ Found
5-62	2.12	2.22	2.69	2.35	38.5	38.3	56.0	-
6-62	2.28	2.92	"	2.45	"	39.9	"	56.2
smaller than #325 mesh								
6-62	2.82	2.95	"	2.60	"	39.0	"	53.8
larger than #325 mesh								
8-62	3.53	3.58	"	2.49	"	-	"	-
11-62	4.23	4.26	"	2.34	"	-	"	-
9-62	5.64	5.62	"	2.45	"	-	"	-

*Theoretical

An inspection of Table II reveals the following: There is little or no MnO lost during firing. Some of the Pb is volatilized, and the amount lost varies slightly from sample to sample.

Sample CS-6-62 was split in two fractions for this test: that fraction retained on a 325 mesh screen; and the fraction thru 325 mesh. (The other samples in Table II, and all other samples noted in this report are the portion of the batch thru 325 mesh.) There was a considerable difference in fluorescent intensity between the two fractions, as well as the obvious difference in crystal size.

The chemical analysis of these fractions did not point out any chemical difference between the two. The MnO contents were the same. This was substantiated by both fractions having the same fluorescent color. There was slightly more lead in the oversize, but the 6% difference does not appear significant. Also, the CaO and SiO_2 contents are not substantially different. The difference in efficiency and particle size are undoubtedly due to poorer crystallinity of the oversize fraction.

The analysis of the oversize material only totals to 99.25%. The reason for this departure from theoretical (0.75%) is not known, but it is believed to be in the analysis of one of the major constituents. Fluorine was not determined, since it was assumed to be volatilized during the firing process.

Sample #CS-67-62 was prepared with a composition similar to #6-62, but containing only 10% the amount of manganese. It was thought that by enhancing the emission of the 5600A band (low Mn), the decay characteristics of the phosphor would be altered. After firing this material at 1160°C for 3 hours in a silica-quartz container, an interesting phenomenon was observed.

There was a sharp line of demarcation between the top and bottom halves of the fired cake. The top half fired white, and the bottom half fired brown to visible light. An inspection of these segments under 2537A radiation revealed that the white layer fluoresced slightly pink, and the brown layer was "dead". Under cathode-ray excitation, the white layer exhibited a bright yellow fluorescence, whereas the brown layer fluoresced green. Visually, the decays of these two layers appeared to be identical.

A possible explanation for this phenomenon is that the brown layer on the bottom of the cake formed the high temperature α structure, and the white layer the low temperature β structure. The shorter wave-length emission under cathode-ray excitation is characteristic of the α structure, and the longer wave-length emission is characteristic of the low temperature β form.

These two structures probably formed because there was a difference in the amount of Pb retained between the top and bottom layers. Since Pb is rather volatile, it is believed that more of it was lost from the top of the fired cake.

To test this hypothesis, two samples of the same composition were fired. One sample was fired uncovered and the other covered with the expectation of retaining more Pb in the covered tray. An inspection of the fired samples confirmed the above. The uncovered sample fired white, exhibited fluorescence (pink) under 2537A radiation, and was yellow under cathode-ray excitation. The covered sample fired brown, a characteristic of oxidized manganese and was "dead" under 2537A radiation, and green under cathode-rays.

Previous investigators report that $CaSiO_3$ occurs in a high tem-

perature form, α wollastonite, which is formed from the β, or low tempera-
ture form when the latter is heated above an inversion temperature of 1150°C.
Powders with PbO have also been found to give the α structure when prepared
at 1150°C or greater, but with increasing amounts of MnO, or MnO and PbO in
combination and added as activators, the low temperature β structure pre-
dominates even when heated considerably above its normal inversion tempera-
ture of 1150°C. To our knowledge, no information is available concerning the
mode or action which the PbO contributes in developing the α, or β structure
in low manganese phosphors. In our preliminary investigation it appears
that at low manganese concentrations, and at the particular temperature we
employed (1160°C), high PbO concentrations favor the formation of the α
structure, and low PbO concentrations favor the β form. An investigation
of the effect which PbO contributes in forming these crystal structures
would be interesting.

Group 1A samples could not be evaluated under 2537A radiation since
they contained no lead. A qualitative examination of the phosphors under
cathode-ray showed the decay rates to be similar within the group, but that
this rate was faster than Group 1 phosphors which contained lead.

The properties of Group 2 samples are tabulated in Tables III and
IV below. Table III is an evaluation of fluorescent characteristics; Table
IV lists chemical and particle size data.

Table III

Sample #	Pb Concentration [1]	Height of Mn[2] band	Height of Pb[2] band
CS-14-62	50%	111	42
CS-6-62	100%	97	34
CS-15-62	150%	84	29
CS-16-62	200%	77	25

(1) Percentage of Pb as in base formula CS-6-62.

(2) Based on Mn band of sample CS-11-62 = 100% (see Table I).

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Table IV

Sample #	Theoretical PbO Content	Actual PbO Content	% Found	Average Particle Diameter
CS-14-62	1.35	1.21	89.6	5.5
CS-6-62	2.69	2.45	91.1	5.8
CS-15-62	4.04	3.63	89.9	6.3
CS-16-62	5.38	4.63	86.1	6.3

As lead content was increased both the manganese and lead bands were suppressed. This data is also presented in Figures 5 and 6.

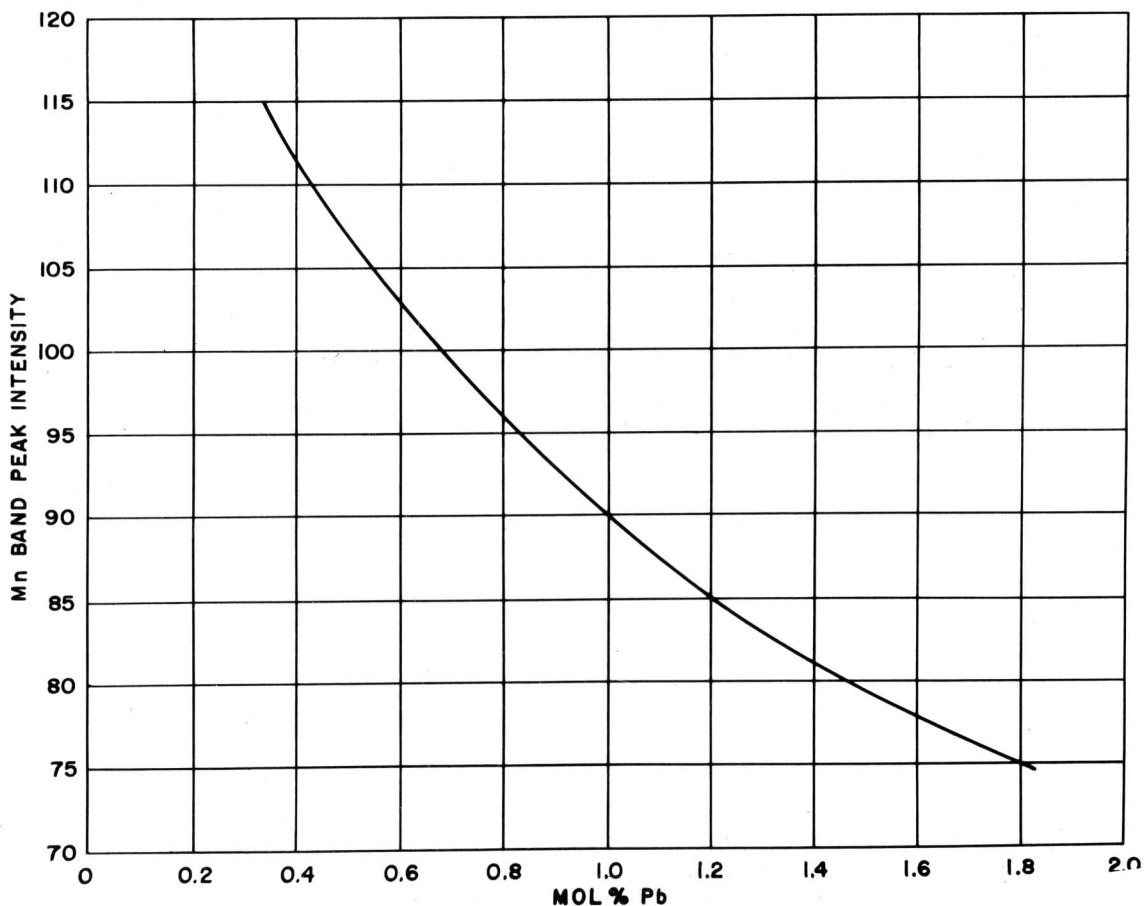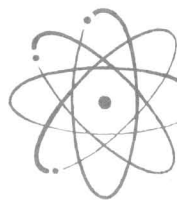**VARIATION OF Mn BAND PEAK INTENSITY vs MOL % Pb**

Figure 5

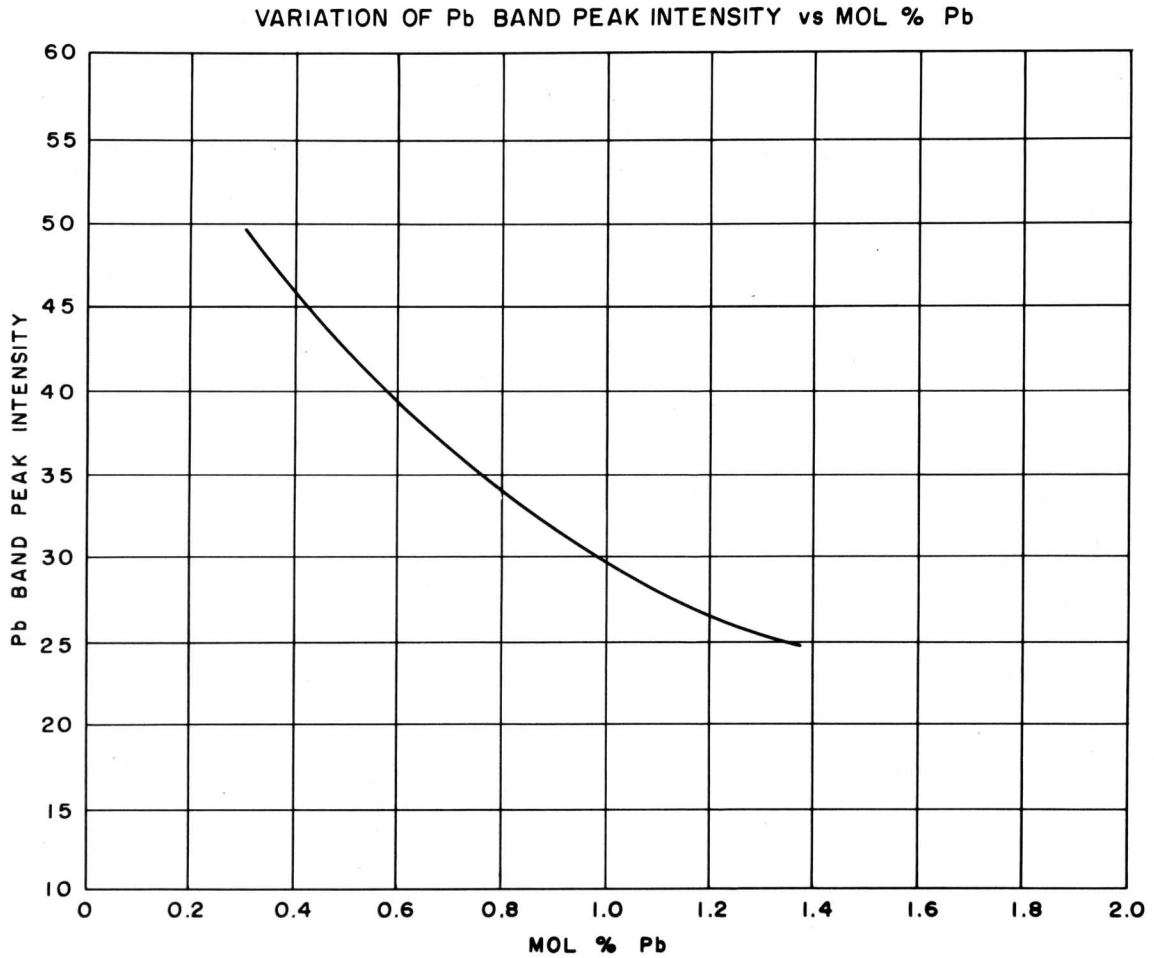## VARIATION OF Pb BAND PEAK INTENSITY vs MOL % Pb

Figure 6

Table IV shows that the amount of lead retained during the firing is reasonably constant independent of the amount of Pb originally present. Finally, the average particle diameter increases slightly with increasing Pb concentration.

Group 3 samples were concerned with the effect of variations of the host crystal lattice on the color efficiency and decay characteristics of the phosphor. In Group 3 and 3A only simple variations in the CaO/SiO_2

ratio were made. In Group 3B, 3C, 3D various partial substitutions were made for either the CaO or SiO_2.

<div align="center">Table V</div>

Sample #	CaO (1) Concentration	Peak λ (A) of Mn Band	(2) Height of Mn Band	(2) Height of Pb Band	Average Particle Diameter
CS-23-62	67%	6242	80	14	5.8
CS-28-62	85%	6190	92	25	5.35
CS-29-62	95%	6185	94	30	5.25
CS-6-62	100%	6185	97	34	5.80
CS-39-62	105%	6185	96	36	5.50

(1) Refers to CaO content in base formula CS-6-62.

(2) Based on Mn band of sample CS-11-62 = 100% (see Table I).

Table V lists the results obtained under 2537A excitation of Group 3 samples. This data is also presented in Figure 7.
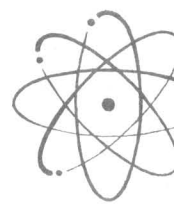
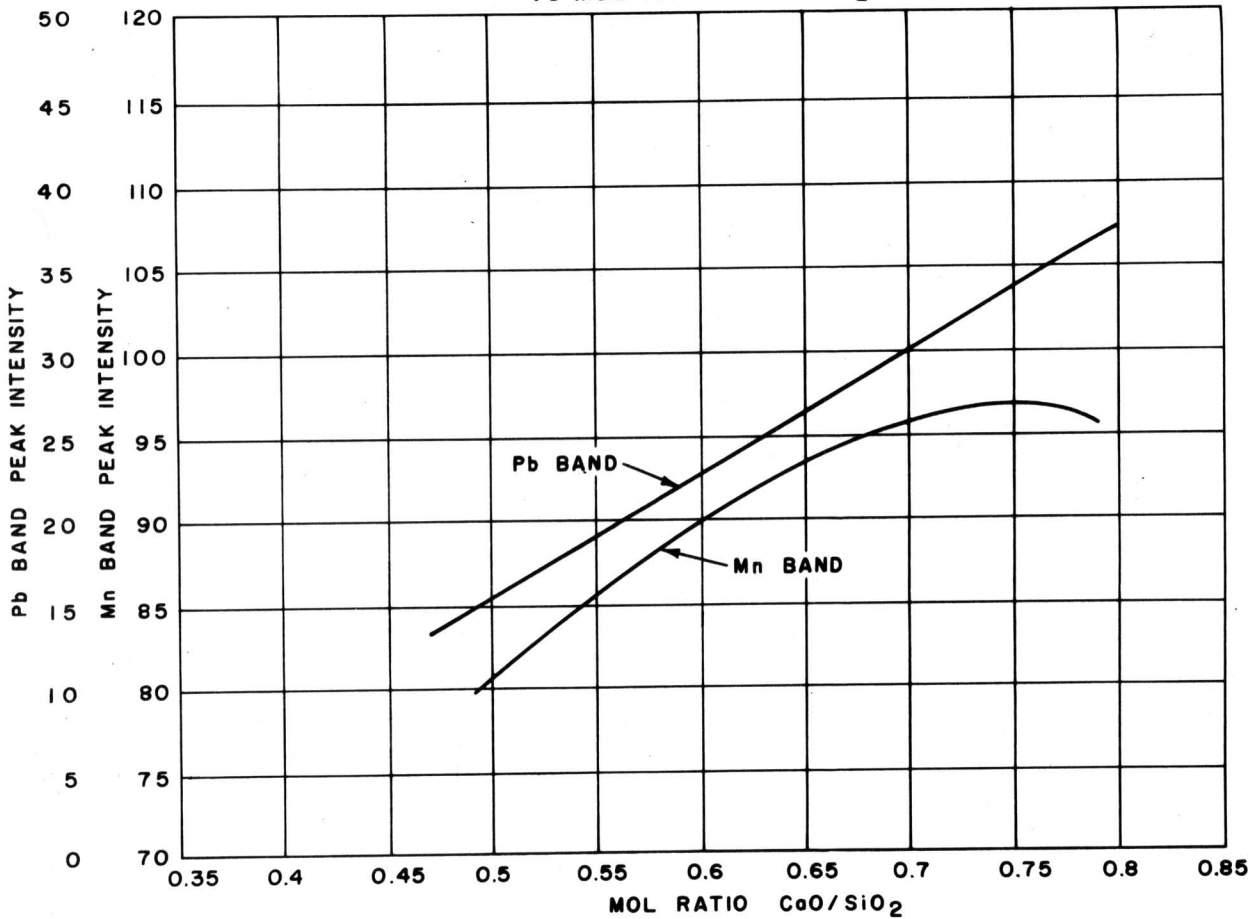VARIATION OF Mn & Pb BAND PEAK INTENSITIES VS MOL RATIO CaO/SiO$_2$

Figure 7

Table VI lists the results obtained from Group 3A samples.

Table VI

Sample #	SiO$_2$ [1] Concentration	Peak λ (A) of Mn Band	Height of Mn [2] Band	Height of Pb [2] Band
CS-43-62	150%	6185	94	34
CS-41-62	125%	6185	95	34
CS-6-62	100%	6185	97	34

(1) Refers to SiO$_2$ content in base formula CS-6-62.

(2) Based on Mn band of sample CS-11-62 = 100% (see Table I).

Some interesting differences may be noted from Tables V and VI. First, the color shifts to longer wave-length with decrease in CaO content at fixed SiO_2 content, but color is not affected by increase of silica with a fixed CaO content. Hence, the color of the phosphor is dependent on the Mn to CaO ratio, and not just the Mn concentration itself.

Whereas increasing the SiO_2 content has little or no effect on the efficiency of the Pb and Mn emission, decreasing the CaO content has a pronounced effect on the same properties.

The average particle diameter did not vary consistently with CaO content in Group 3 samples. It was noted, however, that the yield of phosphor thru 325 mesh increased as CaO content decreased.

Sixteen samples were prepared for Groups 3B, 3C and 3D. Group 3B concerned substitutions for 20 mol percent of the SiO_2. In Group 3C substitutions were made for 20 mol percent of the CaO, and in Group 3D, substitutions were made for 5 mol percent of the cation.

The sample numbers, substituting cations and anions, and brief comments are listed in Tables VII, VIII and IX.

Table VII

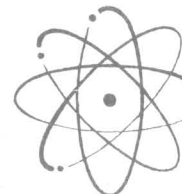| Sample #	Substituting Anion	Comments
32-62	WO_3	Fired white, blue band formed which was probably due to $CaWO_4$. Lavender under cathode-rays.
33-62	TiO_2	Fired brown, no brightness.
34-62	SnO_2	Fired brown, very poor brightness.
35-62	Bi_2O_3	Fired hard and black, green emission under cathode rays.
36-62	$(PO_4)^{\equiv}$	Fired very soft and white, slight shift in emission band to longer wave-lengths, fairly good efficiency.

Table VII (cont'd)

Sample #	Substituting Anion	Comments
36-62A	GeO_2	Fired white and hard, slight shift in emission band to longer wave-lengths, low brightness.
37-62	As_2O_3	No definite compound formation. Fired uneven.
37-62A	Sb_2O_3	No definite compound formation. Fired uneven.
37-62B	80 mol percent SiO_2 of CS-6-62	Control sample.

Table VIII

Sample #	Substituting Compound	Comments
CS-42-62A	MgO	Fired uneven. Appeared red and orange under cathode-rays. Red emission was probably due to the formation of $MgSiO_3$ or Mg_2SiO_5.
CS-42-62B	SrO	Fired brown, good green under cathode-rays, not excited under 2537A radiation.
CS-42-62C	CdO	Phosphor body color very white. Brightness increased. Decreased decay time.
CS-42-62D	CeO_2	Reduced Brightness - phosphor appeared to show reduced "flash" in decay.
CS-42-62E	80 mol % Ca of CS-6-62	Control sample.
CS-37-62C	100 mol % SiO_2 of CS-6-62	Control sample.

Table IX

Sample #	Substituting Compound	Comments
CS-48-62A	La_2O_3	Fired white, fair brightness and decay.
CS-48-62B	Na_2O	Phosphor body color purple. Very hard cake. Brightness decreased, killed decay.

Group 5 samples were prepared to fill in the gap of Pb content between samples in Groups 1 and 1A. They were prepared to determine if the optimum manganese concentration (for maximum fluorescent intensity) was a function of the Pb, sensitizer concentration. A lead concentration of 50% of that used in CS-6-62 was used in all the samples.

<div align="center">Table X</div>

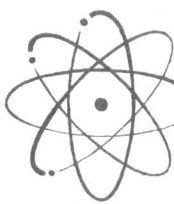| Sample #	Mn [1] Concentration	Peak λ (A) of Mn Band	Height of Mn [2] Band	Height of Pb [2] Band
51-62	75%	6165	105	65
14-62	100%	6185	111	42
51-62A	125%	6225	112	32
53-62	150%	6235	105	27
63-62A	200%	6240	92	18

(1) Refers to Mn concentration in base formula CS-6-62.

(2) Based on Mn band of sample CS-11-62 = 100% (see Table I).

A comparison of Table X with Table I reveals that Pb concentration has no effect on peak wave-length for a given CaO and Mn concentration. Also, within the accuracy of our measurements it appears that the optimum manganese is not affected by Pb concentration. (See Figure 2)

A short persistence calcium silicate phosphor may be necessary for some radar display applications. The samples in Group 6 were prepared with small additions of indium to kill the long decay tail.

A qualitative inspection of the samples indicated that 0.01% indium was sufficient to also reduce the fluorescent intensity. Both samples, CS-90-62A and CS-90-62B, had very short decays.

VI. ADDITIONAL SPECIAL TESTS

The data presented so far have been concerned with the effects of alteration of the chemical composition of the phosphor. A few additional tests, worthy of description, were performed in connection with physical changes in the method of preparation.

It has previously been shown that some lead was lost during the firing process. It has also been shown that this loss of lead was not uniform over the depth of the tray. It was obvious that if the phosphor charge could be rolled or stirred during the thermal synthesis then the volatilization of lead would be more uniform.

A rotating tube-type furnace was assembled and tried. The results were not very encouraging. The phosphor tended to form into small pellets, and the fired phosphor was very inefficient. Since satisfactory phosphors could be made using the standard crucible firing technique, this project was not actively followed. Most probably, a more elaborately designed furnace would have yielded satisfactory phosphors.

The second special test was concerned with the raw materials used to prepare the phosphor. All the phosphors that have been described were prepared from Silicic Acid - Special Bulky manufactured by the Mallinckrodt Chemical Company and from calcium carbonate manufactured at The Chemical Products Works, General Electric Company. Both of these ingredients are chemicals of extremely fine particle size.

One often finds that phosphors prepared from relatively coarse raw materials show less aggregation of the finished phosphor crystals. This effect would have been beneficial in the calcium silicate phosphor since only the fraction of a batch that passed 325 mesh was useable in screening cathode-ray tubes.

A phosphor was prepared from "coarse" calcium carbonate specially precipitated at The Chemical Products Works, and from a C.P. Silicic Acid manufactured by the J. T. Baker Chemical Co. This grade of silicic acid is many-fold times as coarse as the Special Bulky.

As was expected, the phosphor prepared with these new starting materials gave a greater yield of useable (through 325 mesh) phosphor. However, the phosphor was not as efficient as the control sample prepared with the bulkier chemicals. Since there was little, if any, difference in chemical purity, the difference in efficiency must have been caused by the physical differences. Most probably a different time-temperature cycle was required for the coarser starting materials.

The final test was concerned with a special double firing technique. Lead and lead fluoride are excellent fluxes or mineralizers for the calcium oxide-silica reaction. High lead concentrations in the batch are useful in promoting the reaction, but lower lead concentrations may be necessary in the finished phosphor to achieve sufficient visible fluorescence and to give proper decay characteristics. It is possible to achieve both these ends by firing first with lead fluoride which has little volatility, and then re-firing with ammonium chloride which will form volatile lead chloride with the residual lead. The problem is then to control the lead content left in the phosphor.

A sample (CS-60-62) was prepared similar to CS-6-62, but with twice the lead content of the latter sample. After firing at $1160^{\circ}C$ for three hours, the sample was milled with the theoretical amount of ammonium chloride necessary to bring the residual lead down to the concentration found in CS-6-62. However, on second firing, the powder formed a fused cake.
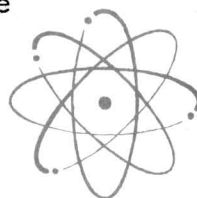
Additional samples were prepared similar to CS-60-62 and re-fired at 1160°C with 1% (per cent by weight of once fired batch), and 2% NH₄Cl. See Table XII.

Table XI

Sample #	% NH₄ Cl Added	Pb Retained
CS-60-62	1.0	2.75
CS-64-62	2.0	1.49
CS-6-62	0 (single fire)	2.28

From the above data a value of 1.5% ammonium chloride was selected. Since it was known that phosphors re-fired with only 1% or 1-1/2% ammonium chloride would fuse, a series of phosphors were prepared in which the second firing temperature was varied. See Table XII.

Table XII

Sample #	% NH₄Cl	Second Firing Temp.	PbO Retained	Average Particle Diameter
CS-79-62A	1.5%	1160°C	2.80	6.20
CS-79-62B	1.5%	1100°C	3.06	6.15
CS-79-62C	1.5%	1050°C	3.15	6.01
CS-79-62D	1.5%	1000°C	3.12	5.60

As was expected, the amount of lead retained increased as firing temperature was decreased. Under 2537A excitation the phosphors fired at 1160°C, 1100°C, and 1050°C were all brighter than the standard phosphor, CS-6-62. Under cathode-ray excitation, however, the single fired phosphor was superior to any of the double fired material. No reason for this reversal can be given.

VII. EVALUATION OF SAMPLES - CR EXCITATION

The emission properties of calcium silicate phosphor under electron excitation were investigated next. Of primary interest were the effects of variation of activator content, host crystal composition, flux and firing conditions. In order to evaluate these samples under actual operating conditions, the phosphors were screened in seven-inch (Type 7U) bulbs and aluminized.

Aluminizing is not necessary for the satisfactory operation of these phosphors, but there are many advantages to be gained. An aluminum coating inhibits burning of the screen due to ions and electrons and results in a longer operating lifetime. Further, the mirror-like surface which is formed reflects much of the light that is normally lost to the gun side of the tube. Resolution will be improved as a result of being able to obtain a given brightness using smaller beam currents. For radar applications in which scanning is used, the contrast will be measurably improved since the aluminum coating also prevents "slow" electrons (which are emitted from portions of the neck of the tube during overscanning) from penetrating and exciting the phosphor screen.

The spectral energy emission of each sample in the visible range (400-700 millimicrons) was determined with a prism-type spectroradiometer, and the C.I.E. color coordinates were calculated using the weighted-ordinate method. Brightness measurements were made with a Weston Foot-Lambert meter with an "eye-correction" filter to adjust spectral sensitivity so that it matched the standard C.I.E. luminosity curve. All color and brightness measurements were made with constant power input to the screen. (6) The measuring conditions are given at the end of Table XIII.
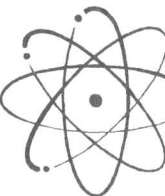
The fluorescent color of lead-manganese activated calcium silicate when excited by electrons can also be described quite generally as being "yellow". The spectral energy emission curves disclose, just as for UV excitation, the existence of several bands - a lead band at 3350A, and the manganese double-band, whose separation and peak values depend on the manganese activator concentration. Thus it is possible to obtain phosphors having a wide range of color and brightness.

VIII. RESULTS

In group #1, as the manganese content is increased for a fixed amount of lead, the color shifts from yellow to red (figures 8 and 9). Likewise, the two manganese bands merge, and the peak wave-lengths shift to longer wave-lengths. The brightness, peak and quantum efficiencies maximize at some activator concentration. It is interesting to note that the maximum efficiency occurs for different activator concentration when other methods of excitation are used. In Table XIV the quantum efficiency of a number of calcium silicate samples were calculated for 2537A UV excitation by Dr. G. R. Fonda.[2] The comparison of efficiencies in this report considers only radiation in the visible region (i.e. the manganese band), because of instrument limitations which restricted spectral emission measurements to the 400-700 millimicron range. Likewise, no measurements could be made of the variation of the lead band with activator variation. For CR excitation, the maximum quantum efficiency is obtained from CS-5-62, whereas for UV excitation sample CS-11-62, which has a higher Mn concentration, is the most efficient of this group.
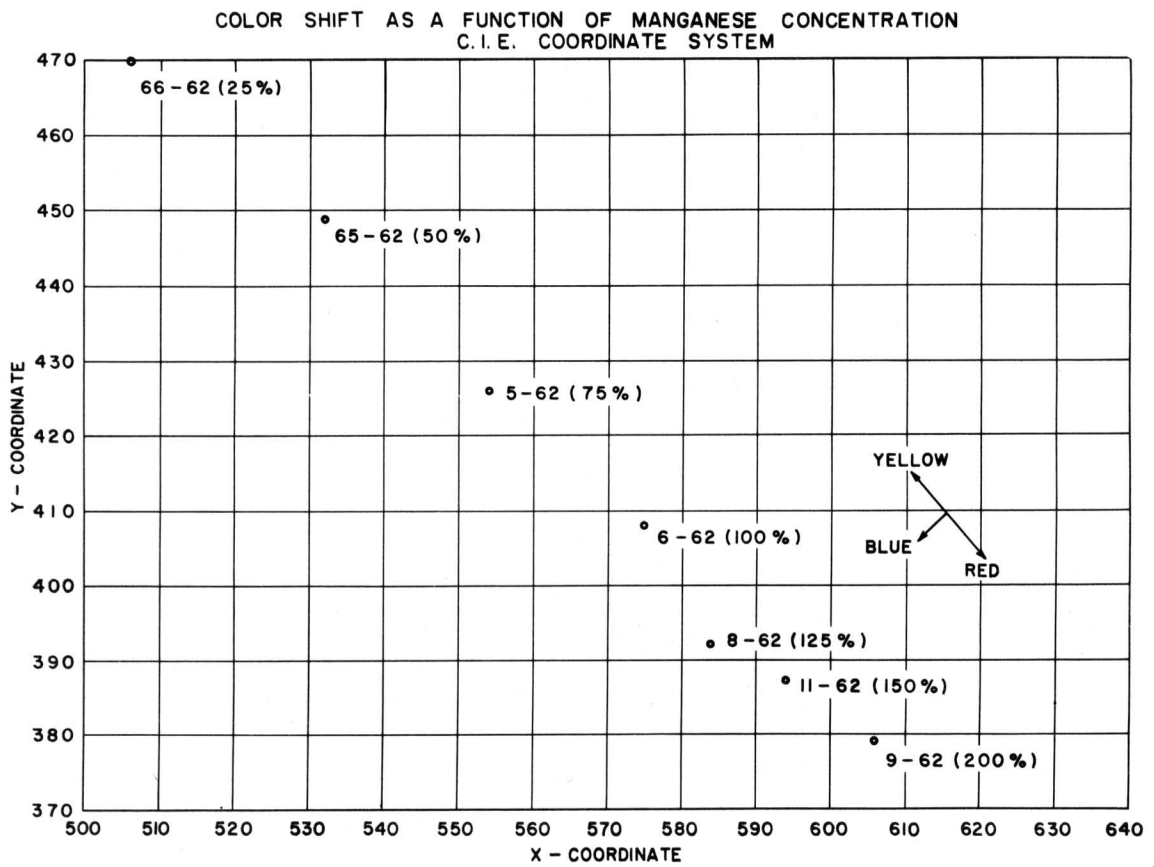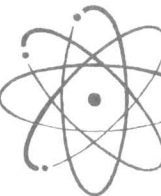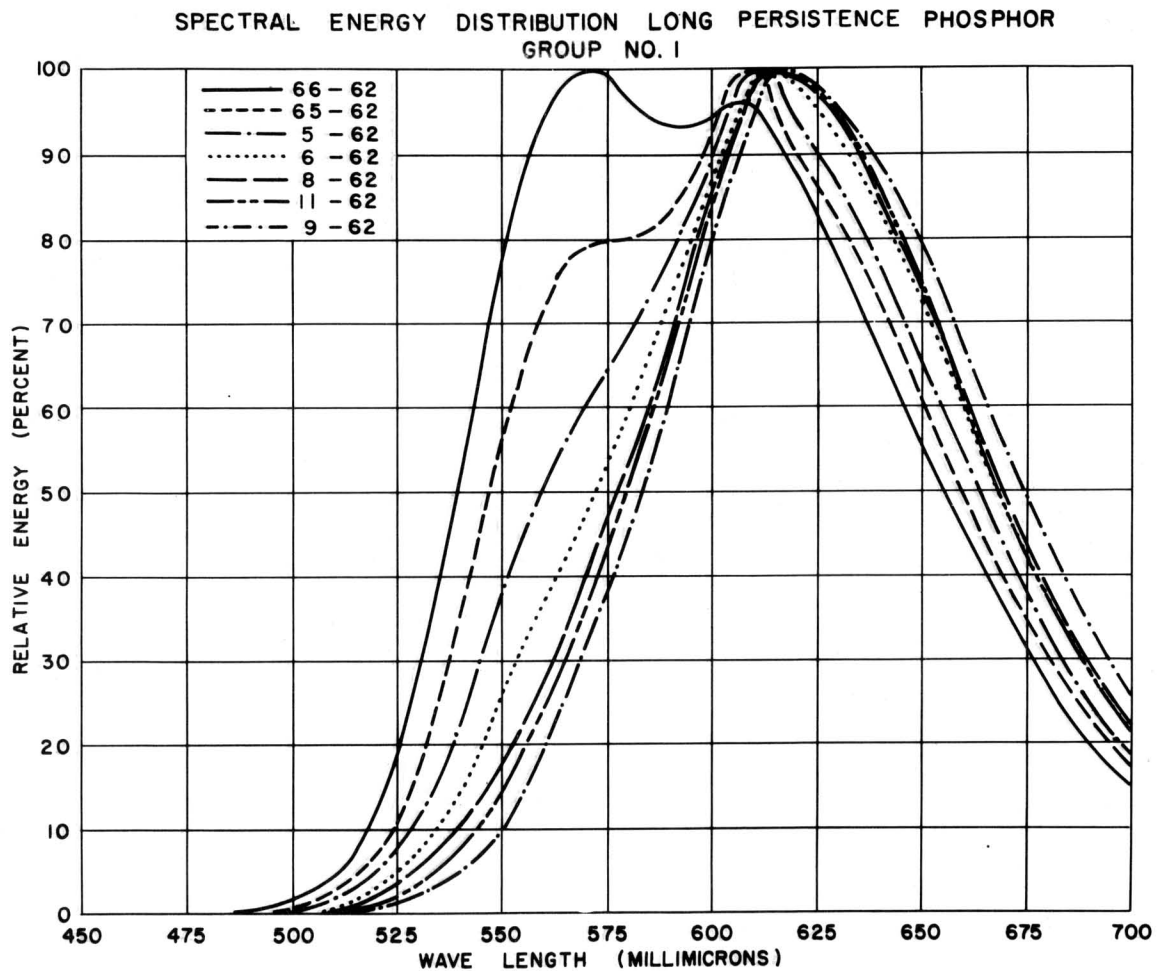
COLOR SHIFT AS A FUNCTION OF MANGANESE CONCENTRATION
C.I.E. COORDINATE SYSTEM

Figure 8

SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
GROUP NO. I

Legend:
- ——— 66 – 62
- - - - - 65 – 62
- —·— 5 – 62
- ········· 6 – 62
- ——— 8 – 62
- —··— 11 – 62
- —·—·— 9 – 62

RELATIVE ENERGY (PERCENT)

WAVE LENGTH (MILLIMICRONS)

Figure 9

　　　　Group #5 (figure 10) and group #1A (figure 11) which have fifty
percent and zero lead content, respectively, show similar spectral charac-
teristics under CR excitation.　UV excitation produces little or no visible
luminescence in samples of group #1A.

SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
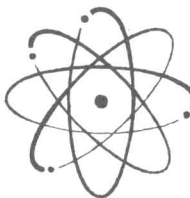GROUP NO. 5
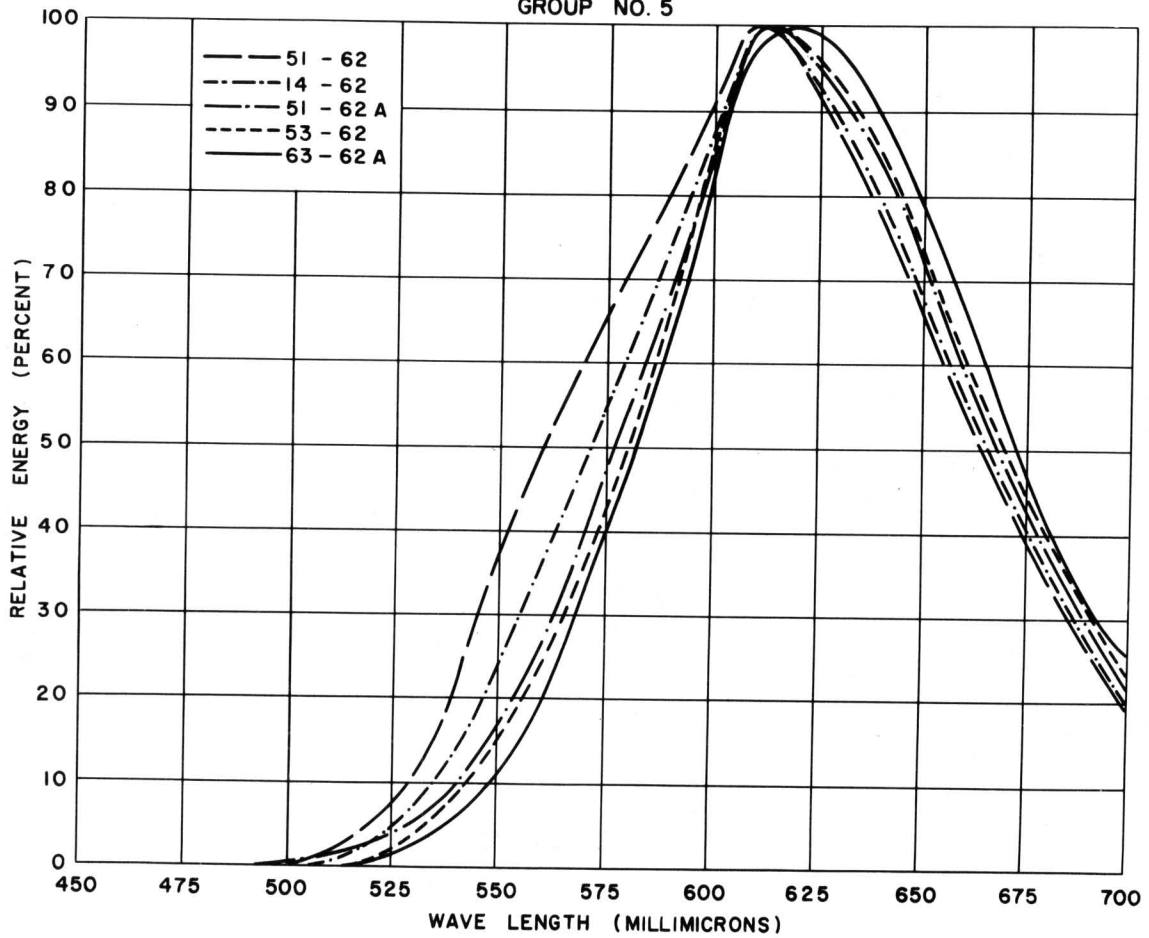
Figure 10

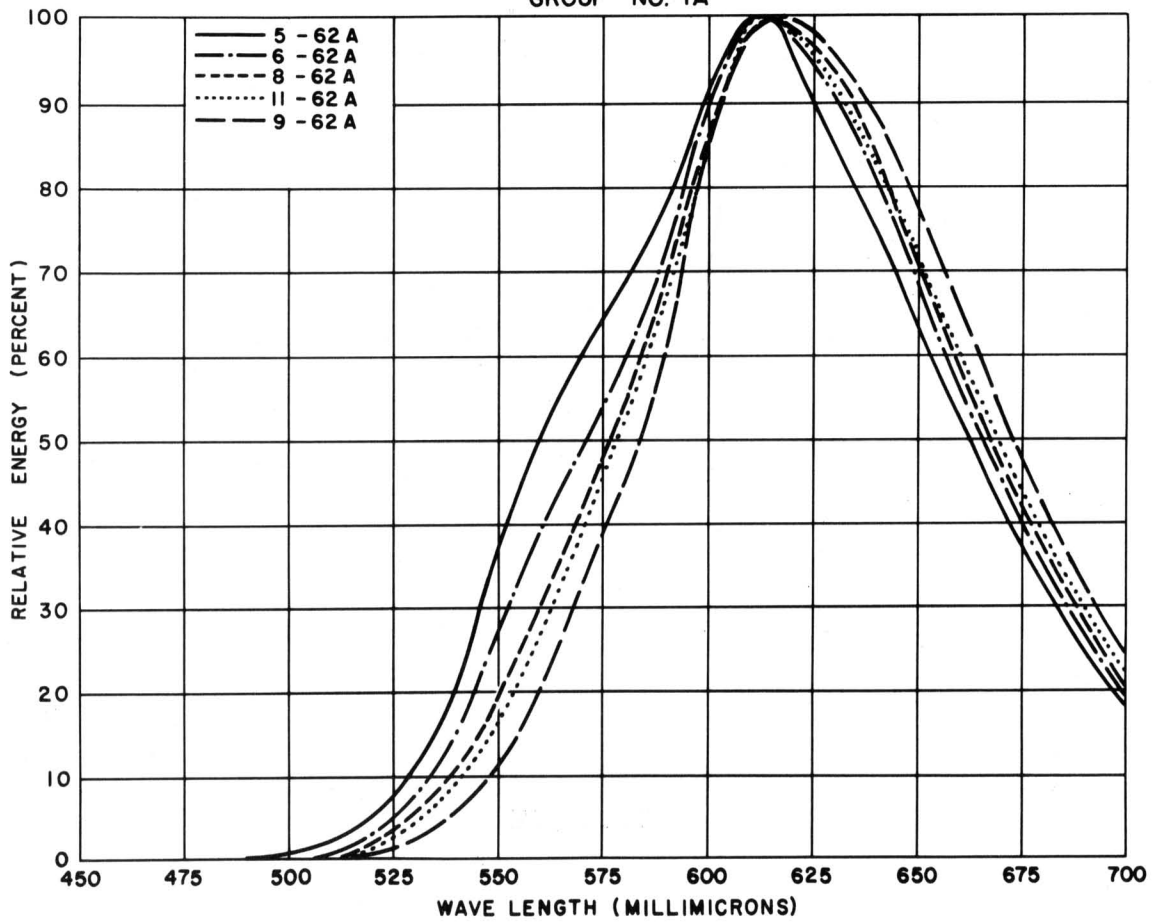SPECTRAL   ENERGY   DISTRIBUTION   LONG   PERSISTENCE   PHOSPHOR
GROUP   NO.   1A

Figure 11

Group #2, (figure 12) in which the lead activator content is varied, shows no spectral changes, or significant changes in brightness or quantum efficiency.
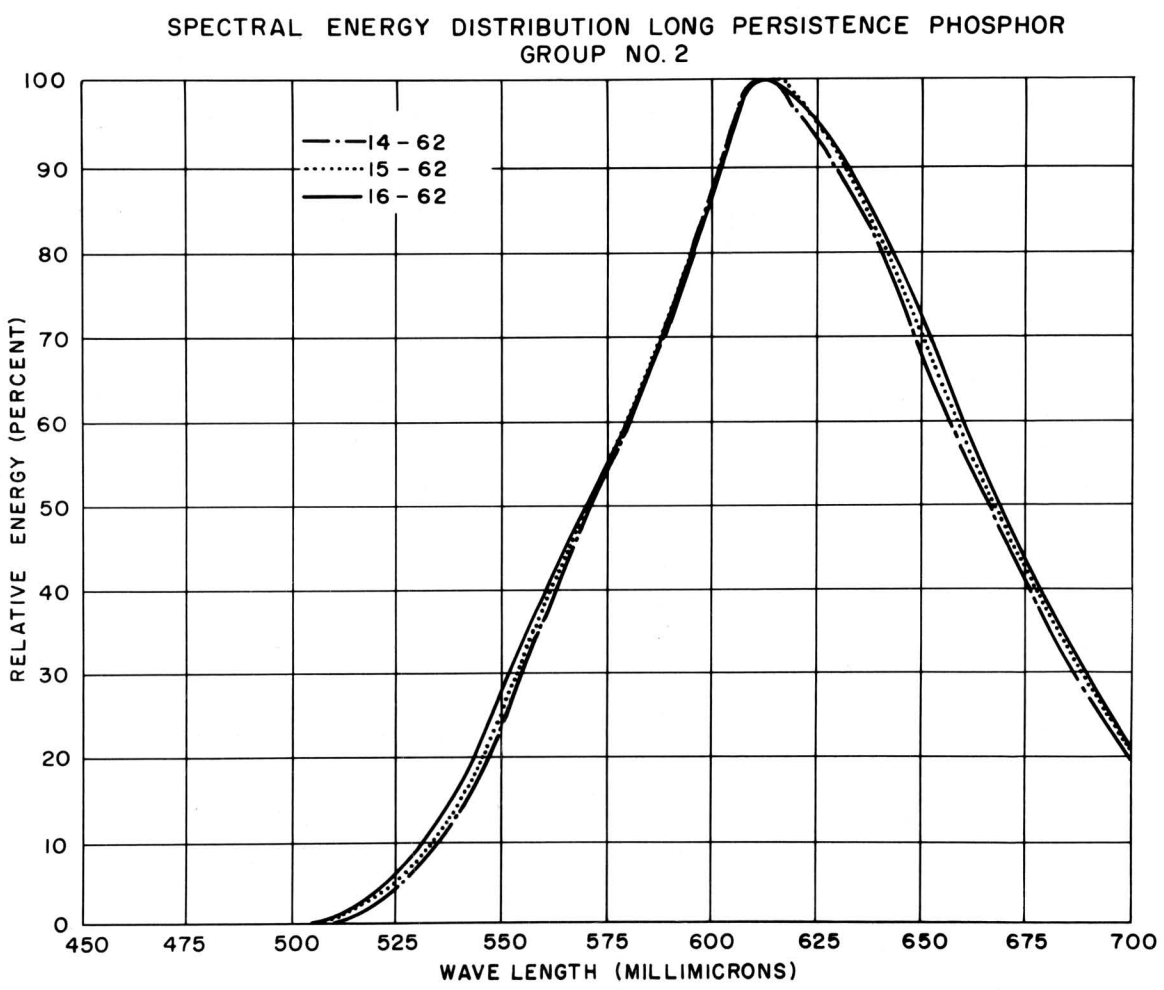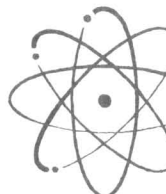
SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
GROUP NO. 2

Figure 12

From the data one can summarize the following activator properties:

(a) Above a certain concentration, increasing one of the activators while keeping the other constant decreases the brightness, peak efficiency and quantum efficiency.

(b) Those samples having the same amounts of manganese show an increase in the efficiency and brightness for a fifty percent increase in lead.

(c) Those samples having the same ratio of manganese to lead show higher brightness and efficiency for decreased amounts of lead.

When the stoichiometric ratios of the matrix components are varied, some slight changes are produced in the color and brightness of the silicate samples. Increasing the CaO content (group #3, figure 13) shifts the color to shorter wave-lengths. The efficiency and brightness, both for CR and UV excitation, increase with increasing CaO content and maximize for sample CS-6-62. Varying the silicon content (group #3A, figure 14) has no effect on the spectral emission characteristics. The brightness and efficiency seem to show somewhat more variation under CR excitation than under UV excitation.

SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
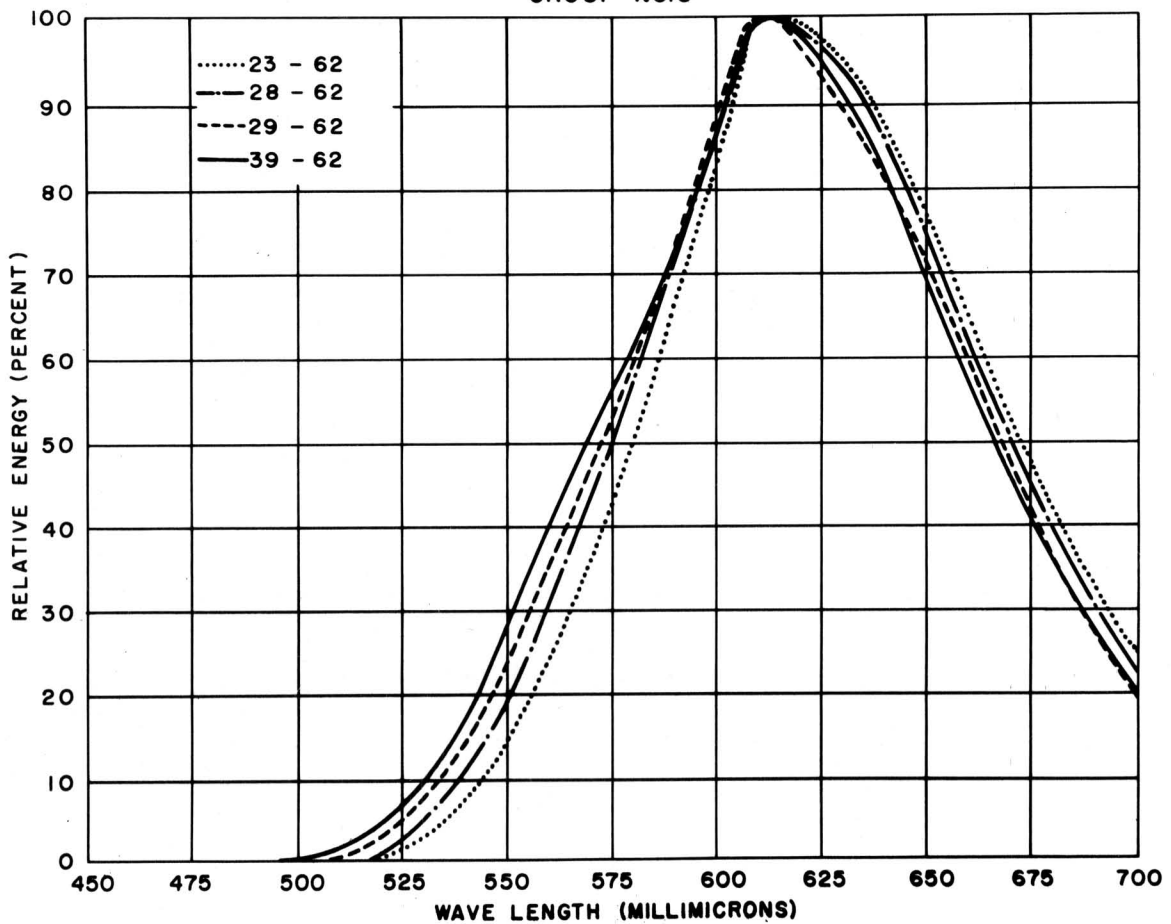GROUP NO.3

Figure 13

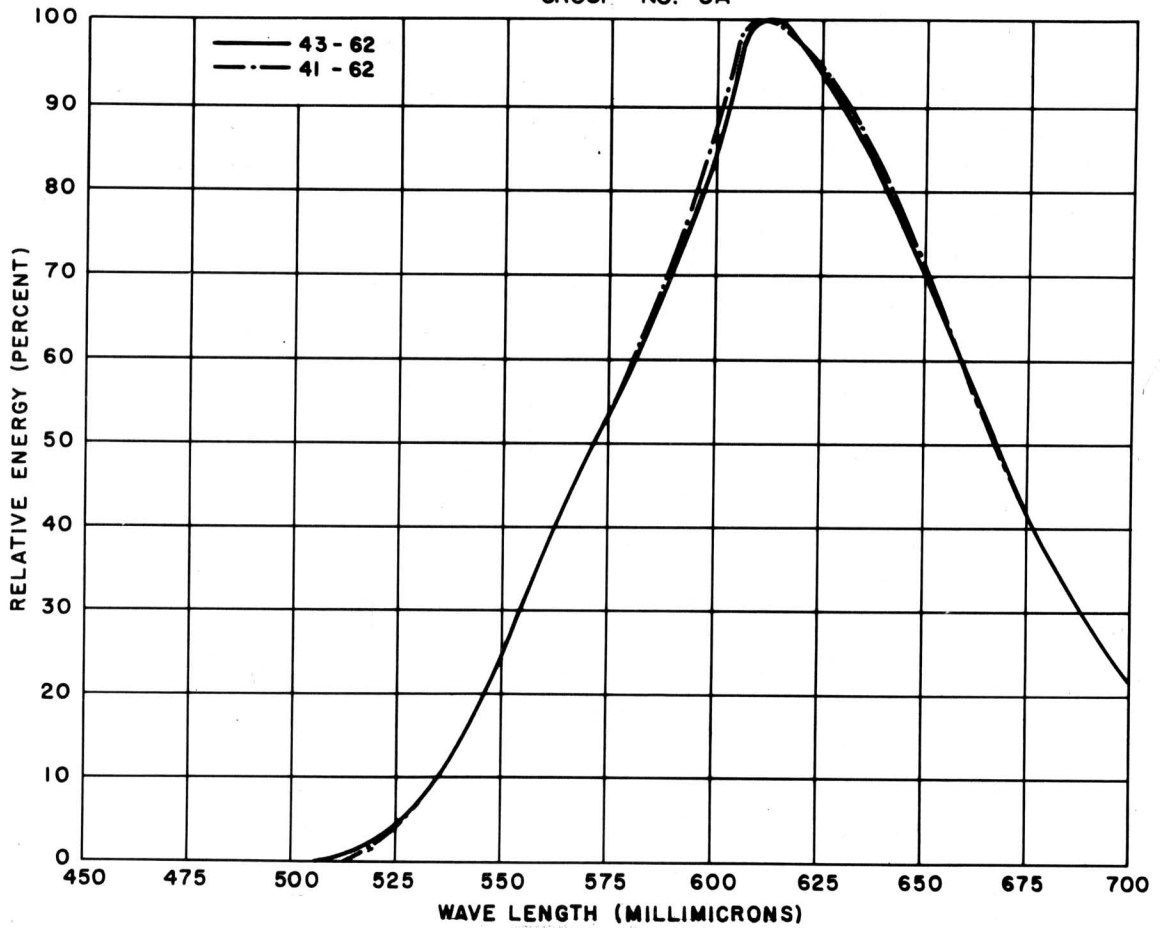SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
GROUP NO. 3A

Figure 14

One sample, CS-49-62, (group #4, figure 15) was synthesized using "coarse" calcium carbonate and silicic acid in its preparation. This was then identical in almost all respects to CS-6-62. There was no change in the spectral emission, however, the brightness, peak and quantum efficiencies decreased twenty-five percent in each case.
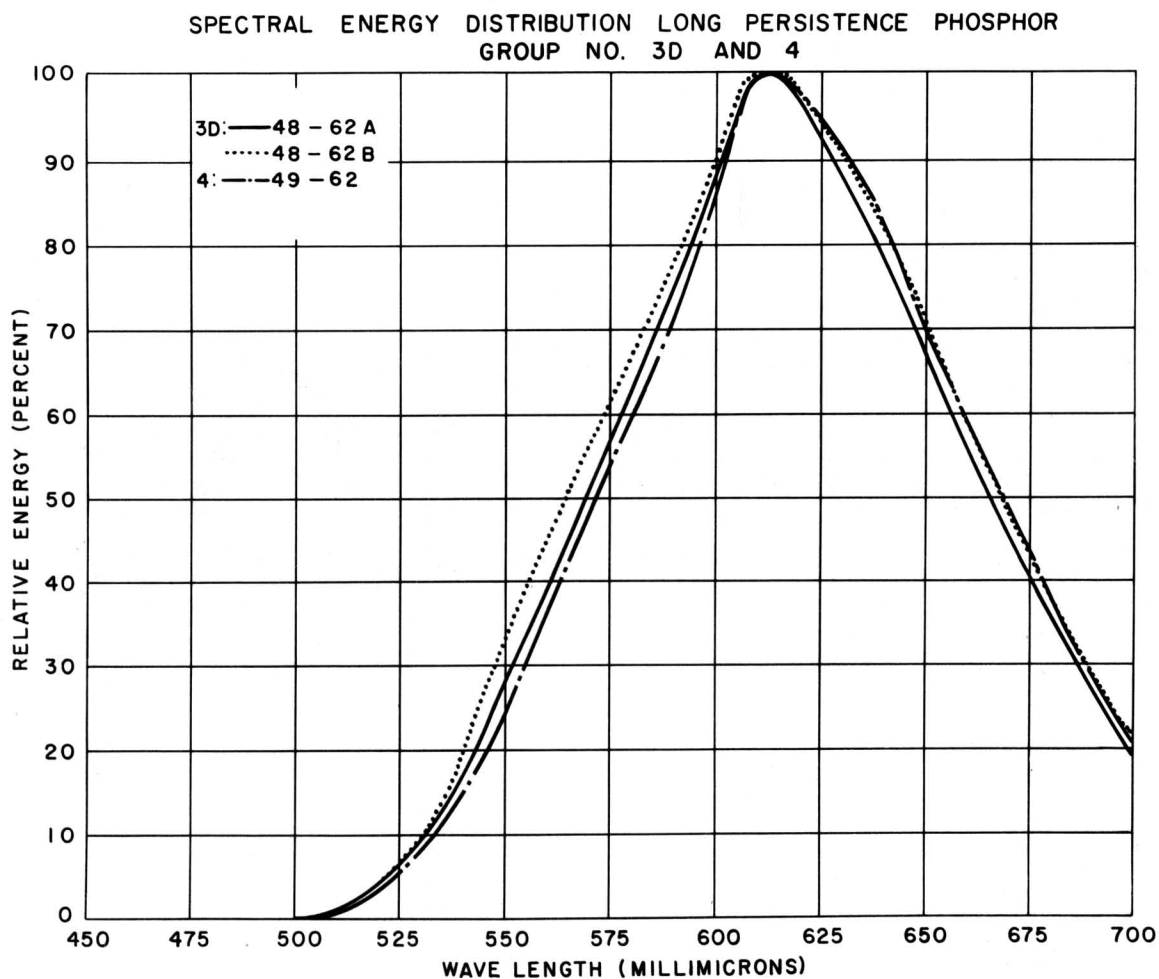
SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
GROUP NO. 3D AND 4

3D: ———— 48 – 62 A
.... 48 – 62 B
4: —·—·— 49 – 62

RELATIVE ENERGY (PERCENT)

WAVE LENGTH (MILLIMICRONS)

Figure 15

Also examined were several samples prepared by a special double-firing technique (group #6) and in which the amount of NH_4Cl flux was varied slightly to control the amount of residual lead. The G-E Chemical Products Works chose the sample containing 1.5% NH_4Cl as that concentration producing the optimum residual lead content. However, this produced a sample having lower brightness and efficiency than the single-fired CS-6-62 under electron excitation. The remaining groups consist of samples in which various compounds were partially substituted for one of the matrix elements (figures 16 and 17). The result is a series of phosphors having high variations in color, brightness and efficiency.
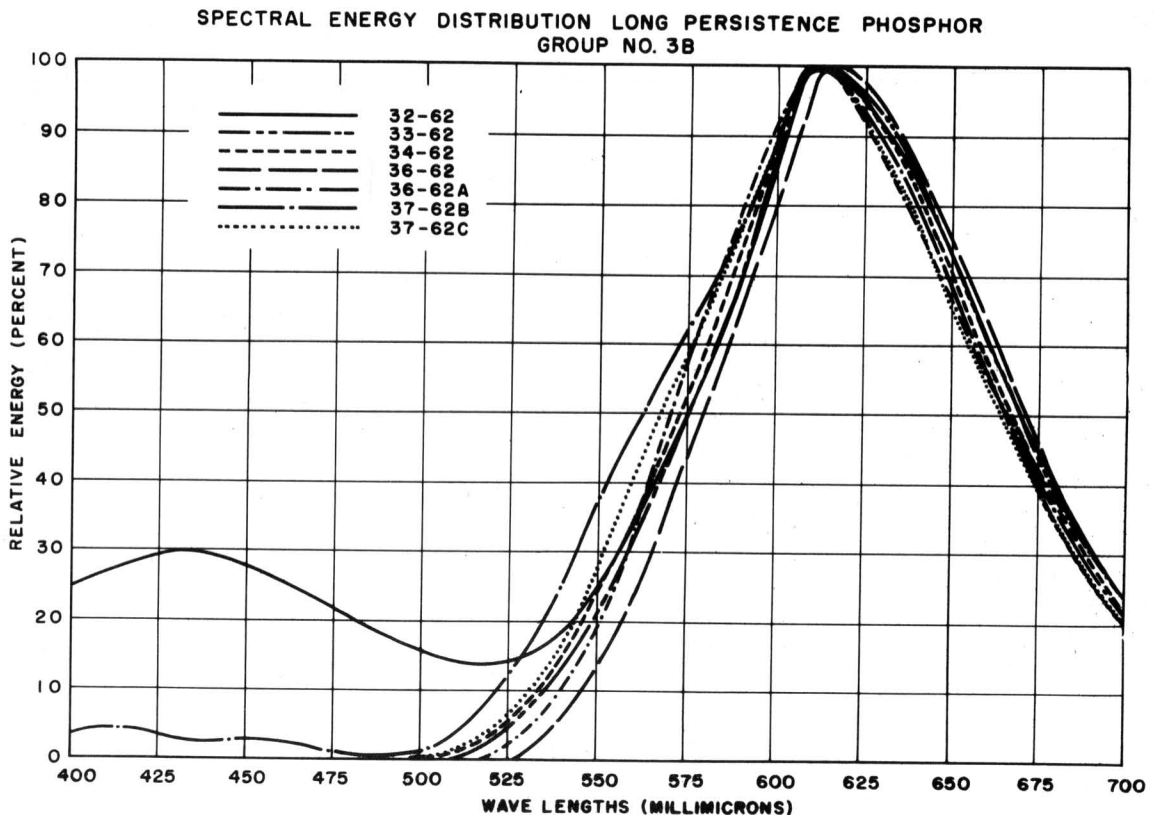

Figure 16

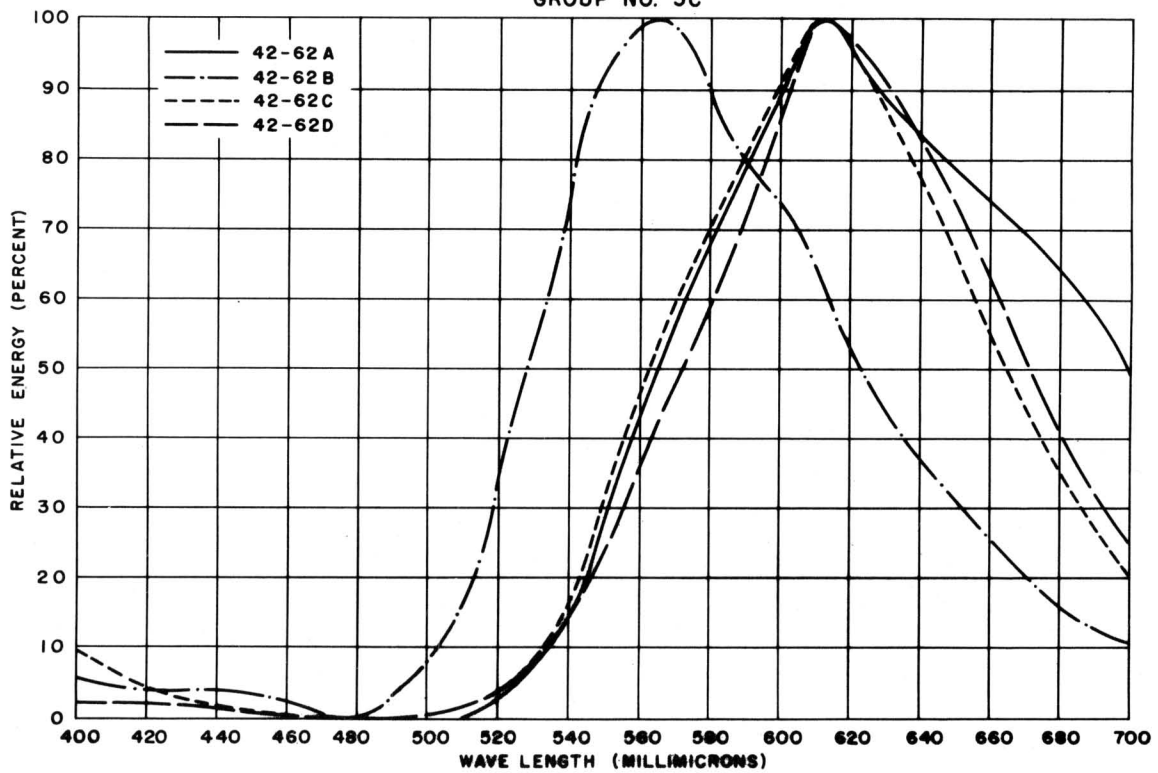SPECTRAL ENERGY DISTRIBUTION LONG PERSISTENCE PHOSPHOR
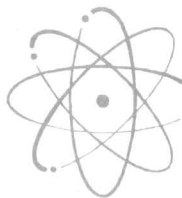GROUP NO. 3C

Figure 17

TABLE XIII

CR Excitation

GROUP NO.	SAMPLE NO.	DESCRIPTION	CIE COLOR COORDINATES x	y	BRIGHTNESS (Ft.L)	PEAK WAVELENGTH (mu)	PEAK EFFICIENCY* 1%	RELATIVE QUANTUM EFFICIENCY
1		Manganese variation - constant lead*						
	CS-66-62	25%	.506	.470	12.8	571,607	81,78	3.17
	CS-65-62	50	.532	.449	13.8	575,609	84,104	3.76
	CS-5-62	75	.554	.426	12.9	611	115	3.90
	CS-6-62	100	.575	.408	9.8	614	100	3.26
	CS-8-62	125	.584	.392	8.9	614	99	3.15
	CS-11-62	150	.594	.387	6.2	615	74	2.26
	CS-9-62	200	.606	.379	4.1	618	52	1.61
1A		Manganese Variation - No lead*						
	CS-5-62A	75%	.555	.425	10.4	612	93	3.15
	CS-6-62A	100	.573	.410	9.0	613	91	2.93
	CS-8-62A	125	.588	.400	8.3	614	92	2.86
	CS-11-62A	150	.588	.392	7.1	614	81	2.54
	CS-9-62A	200	.600	.379	5.0	618	61	1.92
2		Lead Variation - Constant Manganese*						
	CS-14-62	50%	.577	.408	9.5	613	98	3.13
	CS-6-62	100	.575	.408	9.8	614	100	3.26
	CS-15-62	150	.575	.407	9.8	613	102	3.22
	CS-16-62	200	.573	.408	8.2	614	84	2.79

3 CaO Variation*

CS-23-62	67%	.595	.385	5.1	615	60	1.91
CS-28-62	85	.589	.398	6.8	614	75	2.39
CS-29-62	95	.576	.404	8.8	613	92	2.95
CS-6-62	100	.575	.408	9.8	614	100	3.26
CS-39-62	105	.570	.413	9.1	613	90	2.95

3A SiO2 Variation*

CS-43-62	150%	.576	.406	7.2	613	74	2.40
CS-41-62	125	.577	.407	8.0	614	81	2.67
CS-6-62	100	.575	.408	9.8	614	100	3.26

3B Substitution 20 mol% of SiO2

CS-32-62	WO_3	.462	.330	6.0	432,614	17,58	2.39
CS-33-62	TiO_2	.733	.255	1.2	614	13	0.41
CS-34-62	SnO_2	.613	.364	4.0	611	40	1.32
CS-36-62	$(PO_4)\equiv$	.600	.387	2.0	618	24	0.61
CS-36-62A	GeO_2	.581	.406	2.7	612	28	0.90
CS-37-62B	80 mol % SiO_2 of						
CS-6-62 (control)		.545	.419	6.7	613	59	2.10

3C Substitution of 20 mol % of CaO

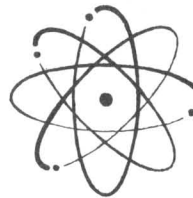|							
CS-42-62A	MgO	.567	.410	5.0	611	50	1.81
CS-42-62B	SrO	.448	.511	2.0	564	13	0.44
CS-42-62C	CdO	.560	.417	10.8	612	100	3.38
CS-42-62D	CeO_2	.569	.403	4.2	614	43	1.44
CS-37-62C	100 mol % SiO_2 of						
CS-6-62 (control)		.518	.382	8.9	612	87	2.84

TABLE XIII (Contd)

CR Excitation

GROUP No.	SAMPLE NO.	DESCRIPTION		CIE COLOR COORDINATES x	y	BRIGHTNESS (Ft.L)	PEAK WAVELENGTH (mu)	PEAK EFFICIENCY* %	RELATIVE QUANTUM EFFICIENCY
		Substitution 5 mol % of CaO							
3D	CS-48-62A	La$_2$O$_3$		.569	.412	4.9	614	48	1.60
	CS-48-62B	Na$_2$O		.562	.421	8.9	612	82	2.77
		Same as CS-6-62 but with coarse CaCO$_3$ and SiO$_2$							
4	CS-49-62			.578	.403	7.1	614	75	2.41
		Manganese Variation - 50% lead*							
5	CS-51-62	75%		.558	.425	9.8	612	87	2.99
	CS-14-62	100		.577	.408	9.5	613	98	3.13
	CS-51-62A	125		.597	.385	8.7	614	100	3.08
	CS-53-62	150		.597	.387	7.0	614	84	2.58
	CS-63-62A	200		.606	.380	4.8	619	59	1.88
		Same as CS-6-62 except double fired, 100% more Pb and variation of percent NH$_4$Cl used in firing							
6	CS-60-62	1.0%		.576	.406	9.0	614	92	3.04
	CS-79-62A	1.5		.578	.406	8.1	614	84	2.72
	CS-64-62	2.0		.580	.405	10.1	614	104	3.36

Same as CS-9-62 and
percent addition of indium

7							
CS-88-62	0.05%	.587	.399	9.1	618	97	3.16
CS-90-62A	0.01	.510	.473	12.0	569,602	74,73	2.94
CS-89-62A	0.001	.511	.471	11.1	569,605	69,68	2.78

Misc.							
CS-1-3		.572	.408	9.8	616	96	3.23
CS-8-62 plus red filter		.677	.311	2.1	638	50	1.49
P-19 $(ZnMg)F_2:Mn$		.579	.402	14.6	605	166	3.95

Conditions of measurement: E_b = 12KV

I_b = 8 ua

$Eg2$ = 250V

Raster 7.1 cm x 71.cm (focused)

* percentages relative to sample CS-6-62
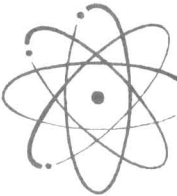
TABLE XIV

Quantum Output of Silicate Samples (2537 A UV Excitation)

Sample No.	Relative Pb	Quantum Mn	Output Pb + Mn
CS-66-62	49	56	105
CS-65-62	34	83	117
CS-5-62	21	98	119
CS-6-62	14	99	113
CS-8-62	9	99	108
CS-11-62	9	100	109
CS-9-62	5	85	90
CS-51-62	26	108	134
CS-14-62	16	115	131
CS-51-62A	11	116	127
CS-53-62	7	106	113
CS-63-62A	3	92	95
CS-14-62	16	115	131
CS-6-62	14	99	113
CS-15-62	13	87	100
CS-16-62	10	80	90
CS-64-62	12	100	112
CS-79-62A	10	86	96
CS-60-60	9	78	97

IX. DISCUSSION

In the case of UV excitation, the luminescence is adequately de-scribed by a sensitizer process.[9] For electron excitation there is no sensitizer process. Instead, both the lead and manganese act as independent luminescent centers. The former has an emission band at 3350A, and the manganese center produces a single, or double band depending upon the manganese concentration.
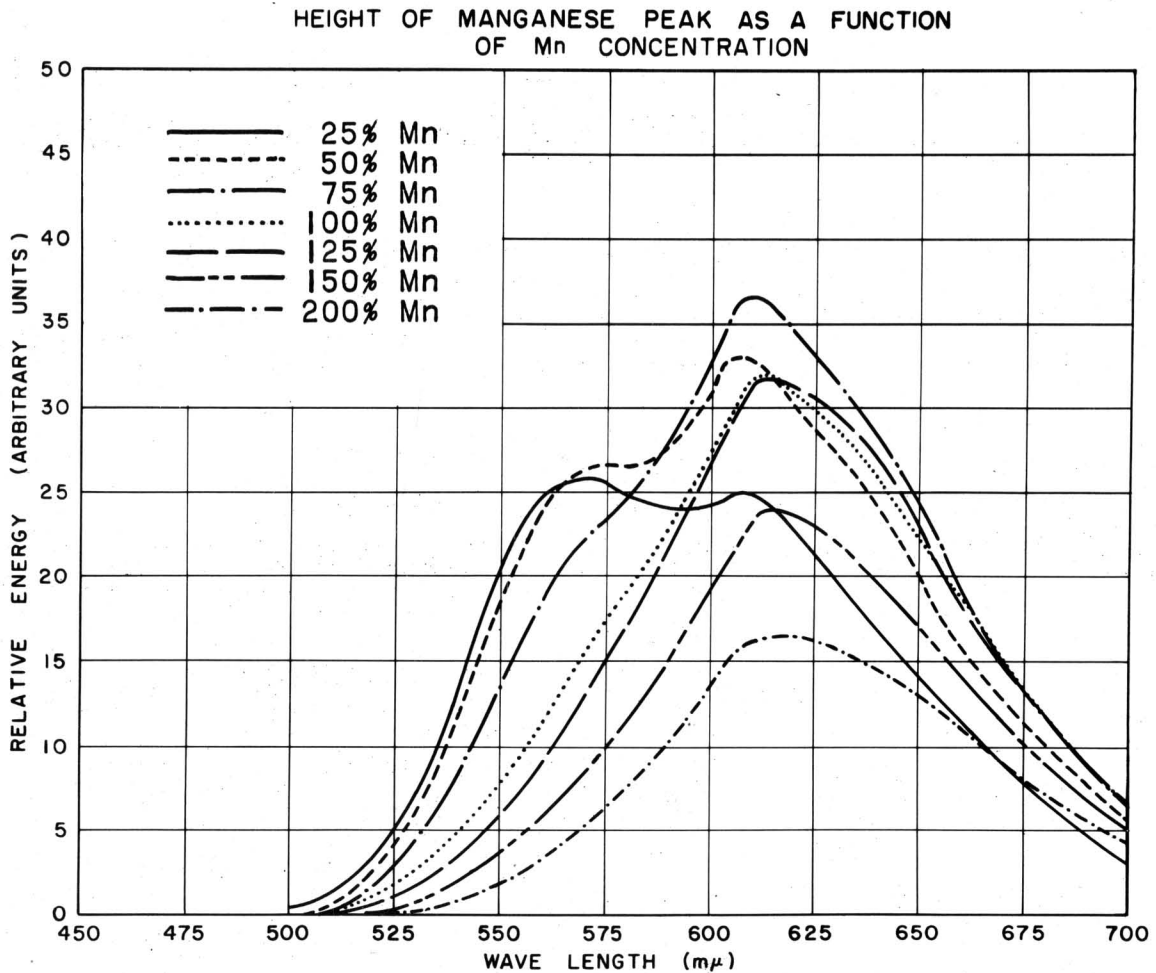

HEIGHT OF MANGANESE PEAK AS A FUNCTION OF Mn CONCENTRATION

Figure 18

A number of phosphors have been found for which two emission bands exist for a single activator. In the case of the mangnaese activator, several explanations have been proposed. R. V. Maurer[11] explains the double band (due to manganese) on the basis of single activator ion centers and activator pairs. The long wave-length band being due to the presence of pairs, and the short wave-length band the result of single activator ions. An increase in activator concentration will therefore favor the formation of pairs.

Another proposal which has had greater acceptance is that of Linwood and Weyl.[8] They have related the emission characteristics of manganese in silicates and similar oxy-anion systems to the coordination of oxygen to manganese. Four-fold coordination produces the short wave-length emission, while six-fold coordination produces the longer emission.

If there are two independent activator systems in cathode-ray excitation it would seem that these centers compete for the energy imparted to the crystal matrix by the incident electrons. The possibility that such a simple competitive process operates in this phosphor would preclude the use of a double activator system. From the data, however, it appears that despite the competitive process involved, some perturbative action creates conditions for improving the phosphor efficiency when both activators are present. In general, maximum phosphor efficiency is obtained with some optimum amount of added activator (figure 19) and any additional activator acts as a "poison" to introduce overlapping energy levels and produce radiationless electron transitions. Not only is the amount of the activator important, but also the relative proportions of the two activators incorporated in the matrix.[7][8]

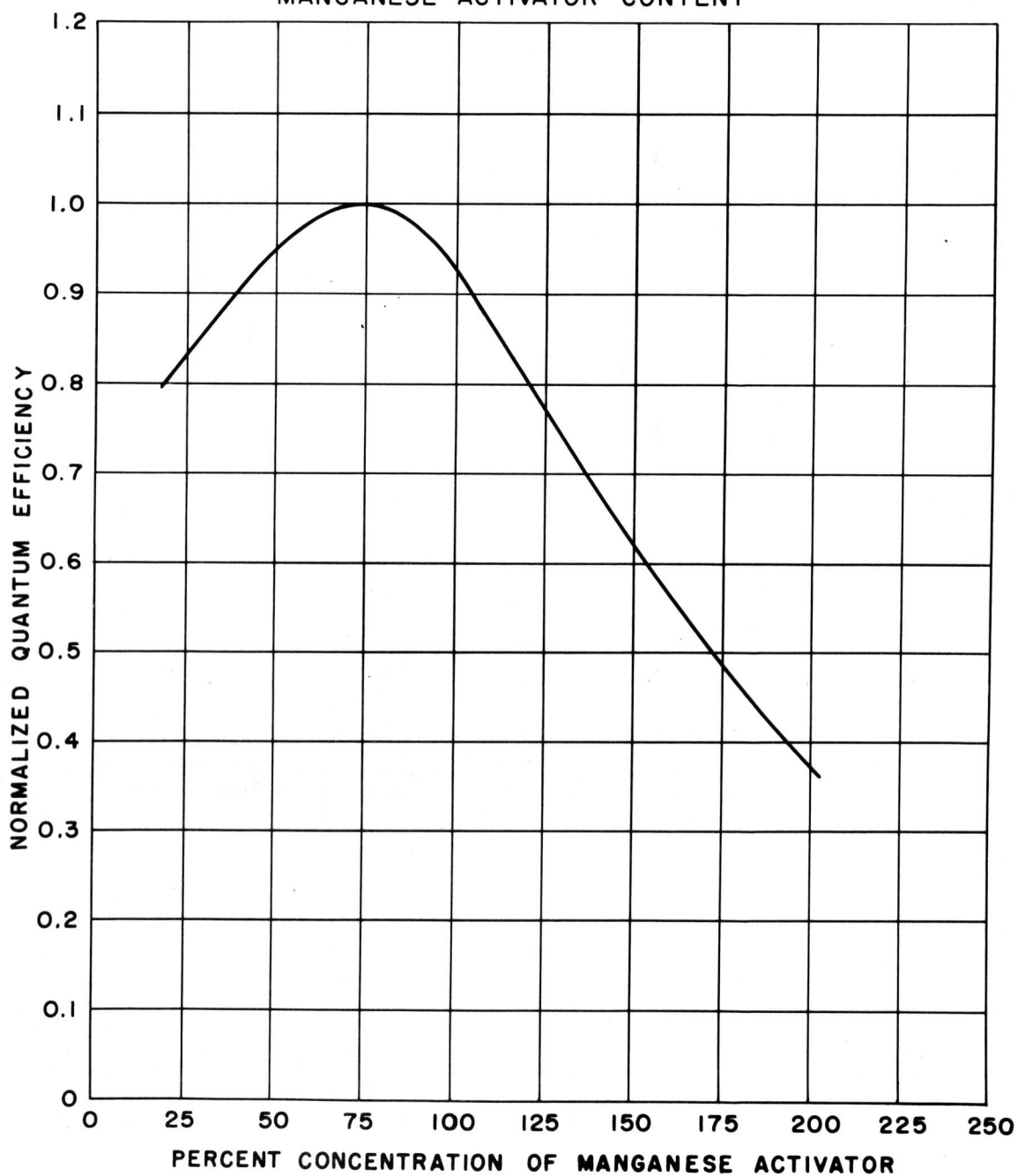QUANTUM EFFICIENCY AS A FUNCTION OF
MANGANESE ACTIVATOR CONTENT

Figure 19

X. DECAY MEASUREMENTS

Two methods of measuring decay were used. In one (figure 20) the light output of a pulsed, de-focused spot is detected with a IP21 photo-multiplier tube.[5] The output of the latter is fed to a logarithmic response amplifier and the resulting signal is presented on an oscilloscope and photographed. This method of measurement was abandoned because of the critical requirements for adjusting the phototube and balancing the log amplifier. In addition, decays of 1.5 seconds duration could only be studied and these are far short of our requirements.

DECAY EQUIPMENT
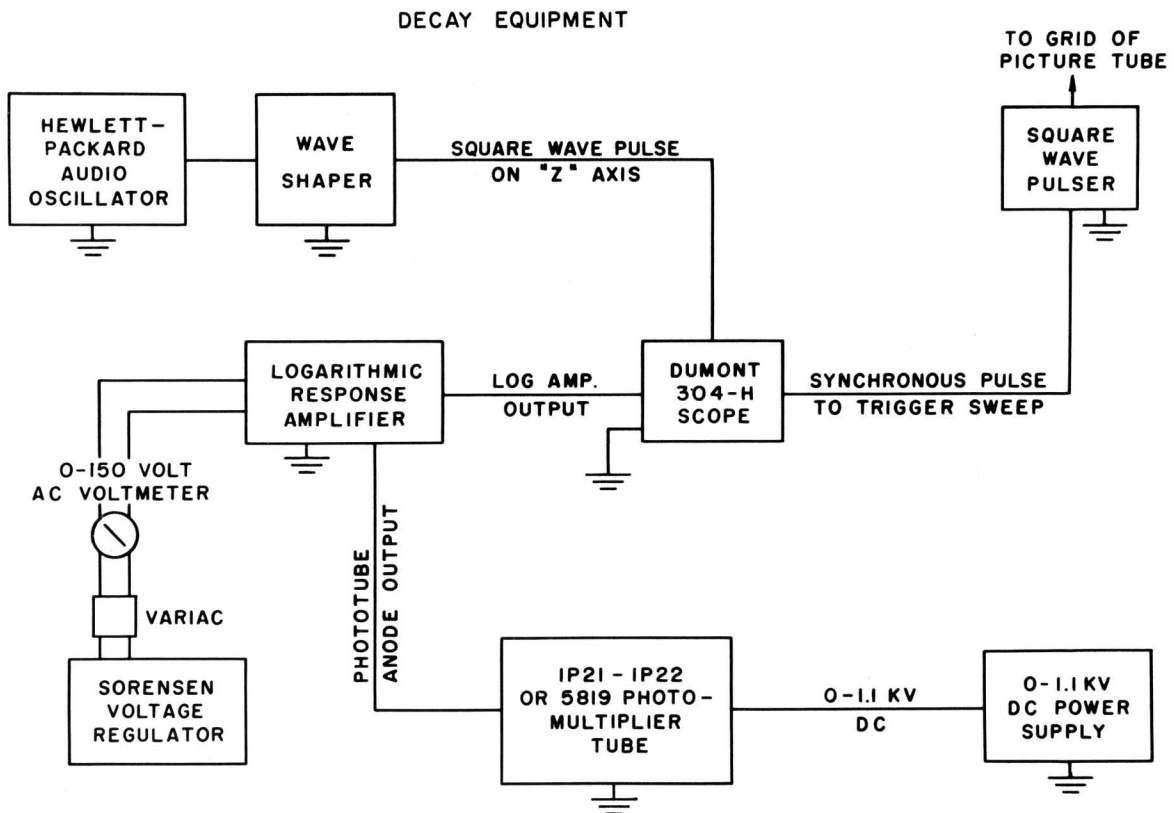
Figure 20

A second method was adopted in which the light output of a pulsed raster is picked up by a photomultiplier tube, amplified and presented on an oscilloscope.[4] Here the problems of stability, alignment and calibration were somewhat reduced. This method permits a much more accurate determination of points on the decay curve in the range from zero to ten seconds, upwards to thirty-five seconds if necessary.

$CaSiO_3$:Pb:Mn is a phosphor in which the two activators produce emission bands which decay independently of one another. The short wave-length band exhibits a rapid exponential type decay, and the long wave-length emission a slower power-law decay. Initially, the decay consists of the exponential decay of the lead band and the power-law decay of the manganese. In the later stages of the decay, the latter type predominates. An exponential decay can be represented by a relationship of the form $L = L_o e^{-\alpha t}$ where, L = light intensity at any time

Lo = initial light intensity at t = o

t = time

α = decay constant

Studer and Rosenbaum[10] conducted some measurements of the manganese emission using 2537A UV to excite the phosphor, and determined the value of alpha in the above relationship. Using a filter to eliminate the lead emission they obtained a value of $\alpha_{Mn} = sec^{-1}$. Measurements of α Mn for samples of group #1 and group #1A were made using the equipment first described in the preceding paragraphs. Plotting light output (a logarithmic-function) as a function of time on a linear scale, the resulting curve of the exponential decay is a straight line. The slope of this determines the value of alpha. The average value of a series of α_{Mn} measurements ob-

tained from samples of groups #1A, which do not contain any lead activator, was 78 sec^{-1}. Group #1 gave a somewhat higher value, $\propto_{Mn} = 85$ sec^{-1}, as expected, since this includes the effect of the more rapid lead band decay.

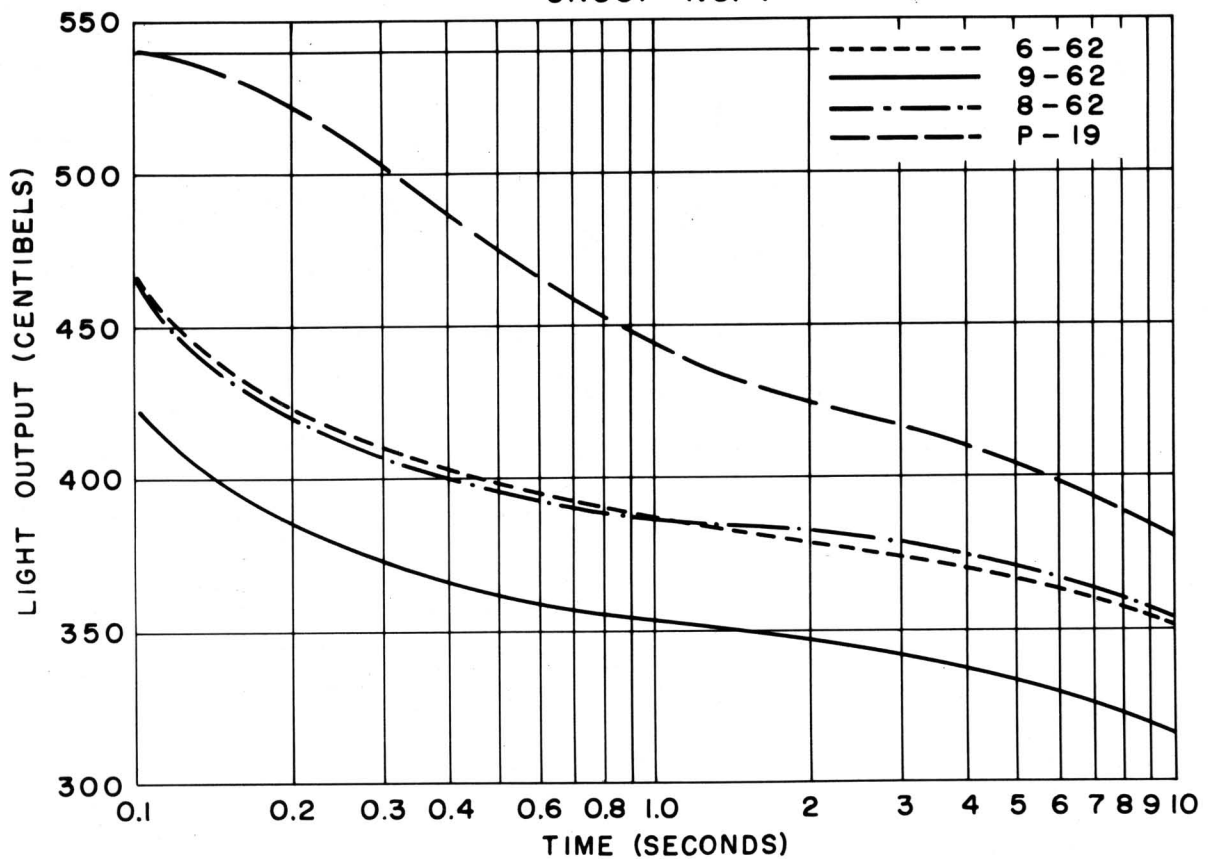DECAY CURVES OF LONG PERSISTANCE PHOSPHORS
GROUP NO. I

Figure 21

The effect of variations in the activator concentration, or the matrix composition on the decay characteristics was investigated next. In group #1 (figure 21) in which the manganese activator concentration was

varied there was no difference in the decay among the samples.

DECAY CURVES OF LONG PERSISTENCE PHOSPHORS
### GROUP NO.2
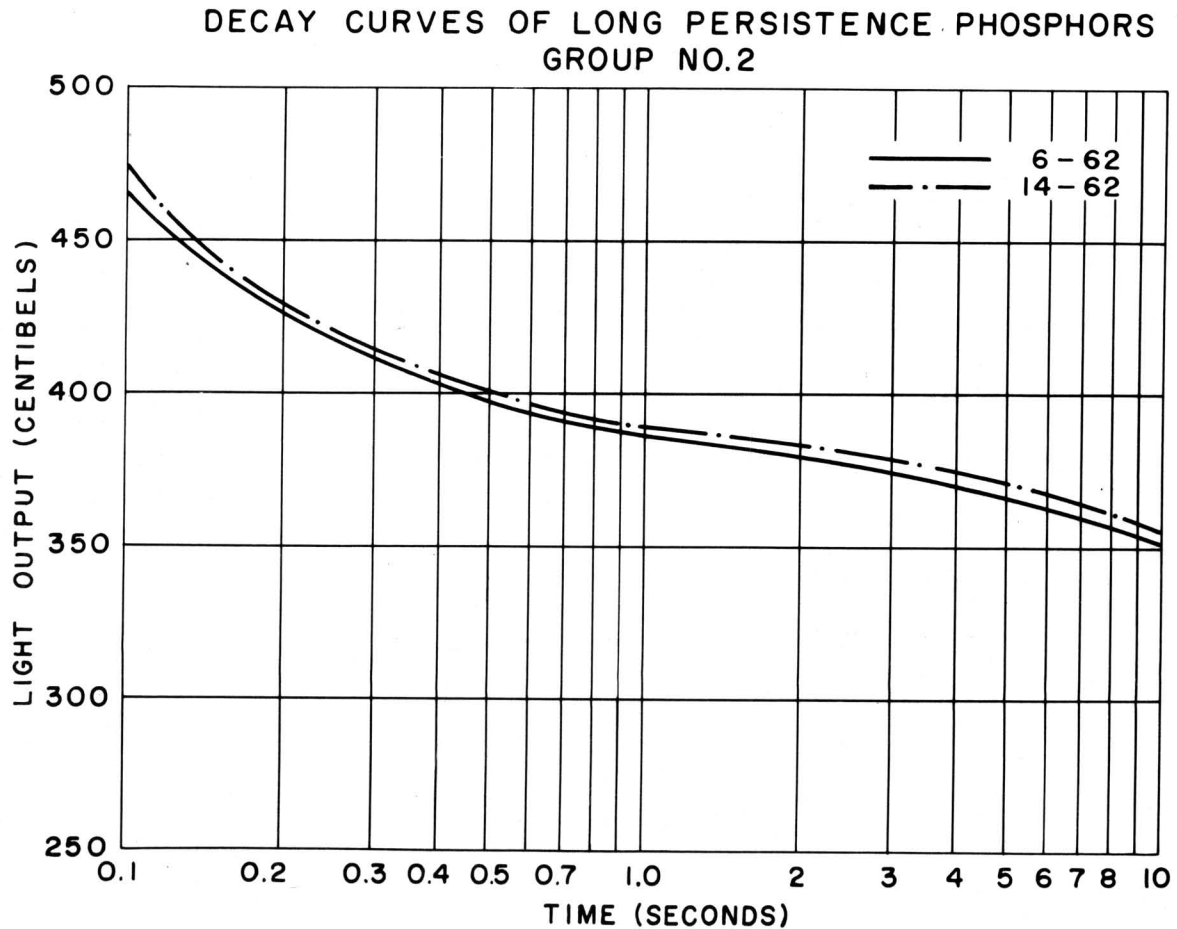
Figure 22

Likewise, in group #2, (figure 22) in which the lead content was varied, no
difference in the decay characteristic of the various samples could be de-
termined. Group #1A, in which the samples have no lead activator, does not
show any decay differences among the samples of the group but does have a
considerably shorter decay than either of the other two groups. Though the
lead band decay is "rapid" and the manganese band "slow", the addition of
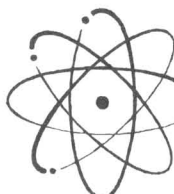
lead to calcium silicate manganese (activated) provides a phosphor with even longer decays. This is illustrated by a comparison of the decay rates of the three groups #1, #5 and #1A in which there is 100%, 50% and zero lead content respectively. The decay of the samples of group #1A is much more rapid than that of the other two groups which have identical decay rates. This would seem to indicate, other than some optimum lead concentration for longer decay, the introduction of traps as a result of the lead activator.

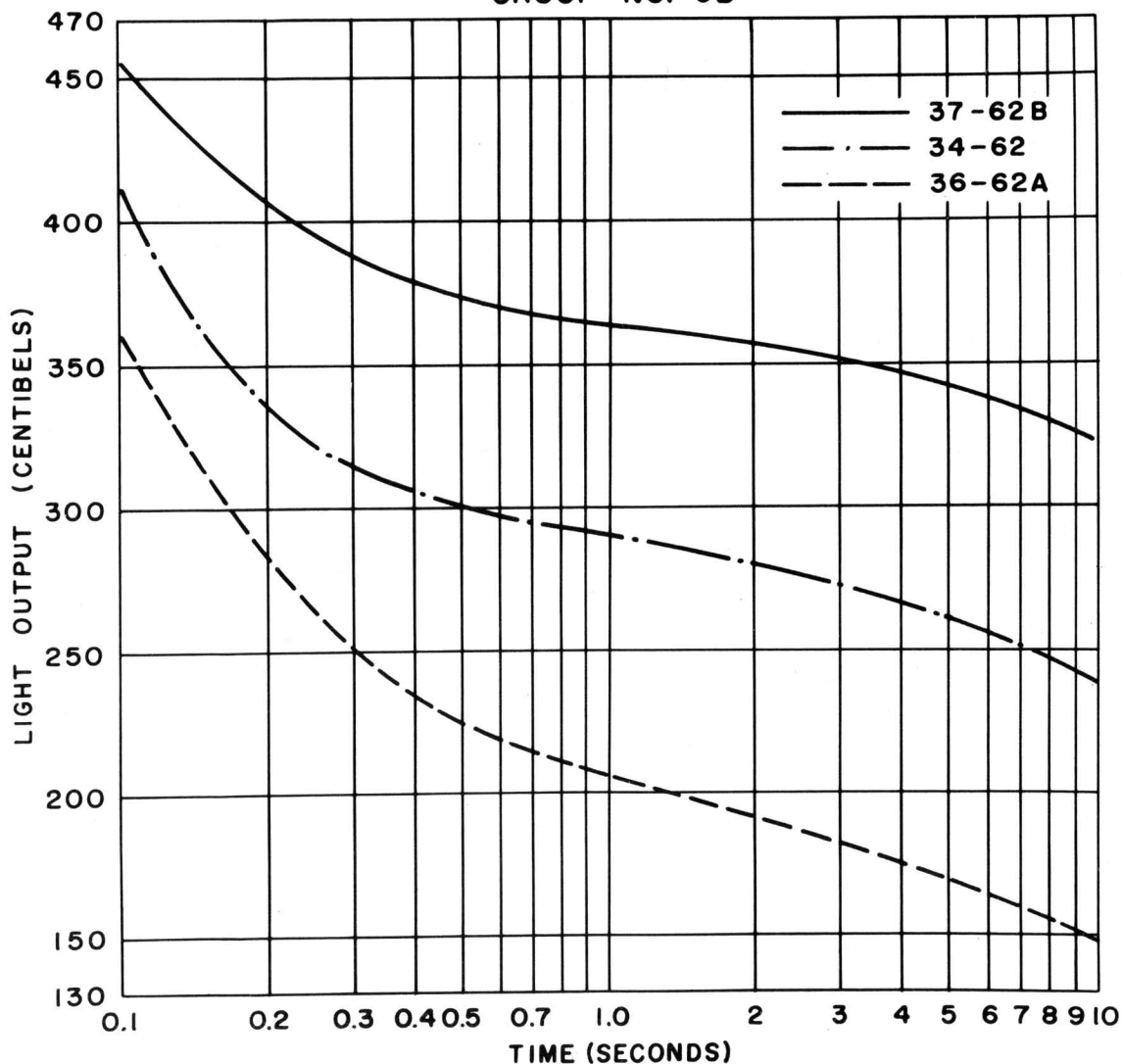DECAY CURVES OF LONG PERSISTENCE PHOSPHORS
GROUP NO. 3B

Figure 23

In the samples in which various compounds were partially substituted for one
of the matrix components, a wide variation in the decay characteristic is
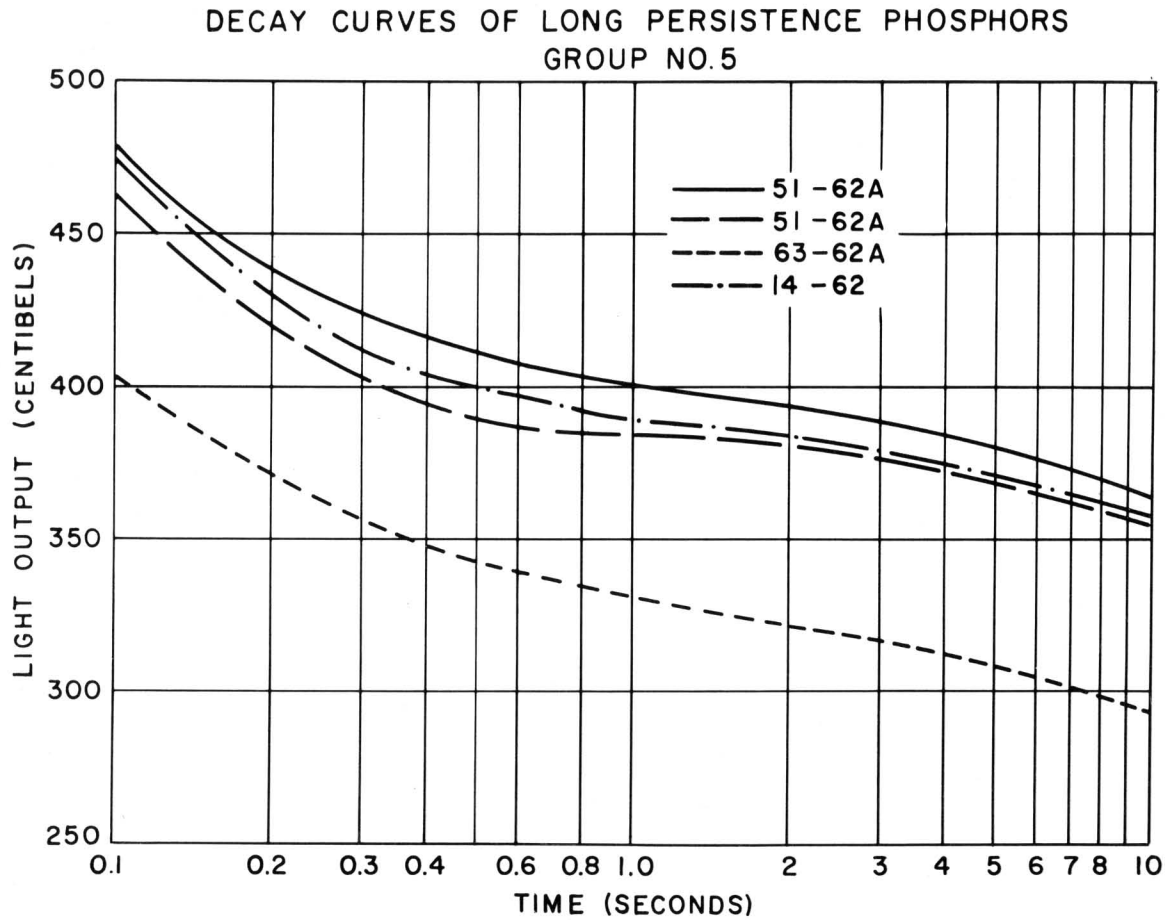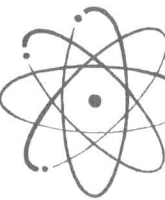obtained (figures 23, 24 and 25).

DECAY CURVES OF LONG PERSISTENCE PHOSPHORS
GROUP NO. 5

Figure 24

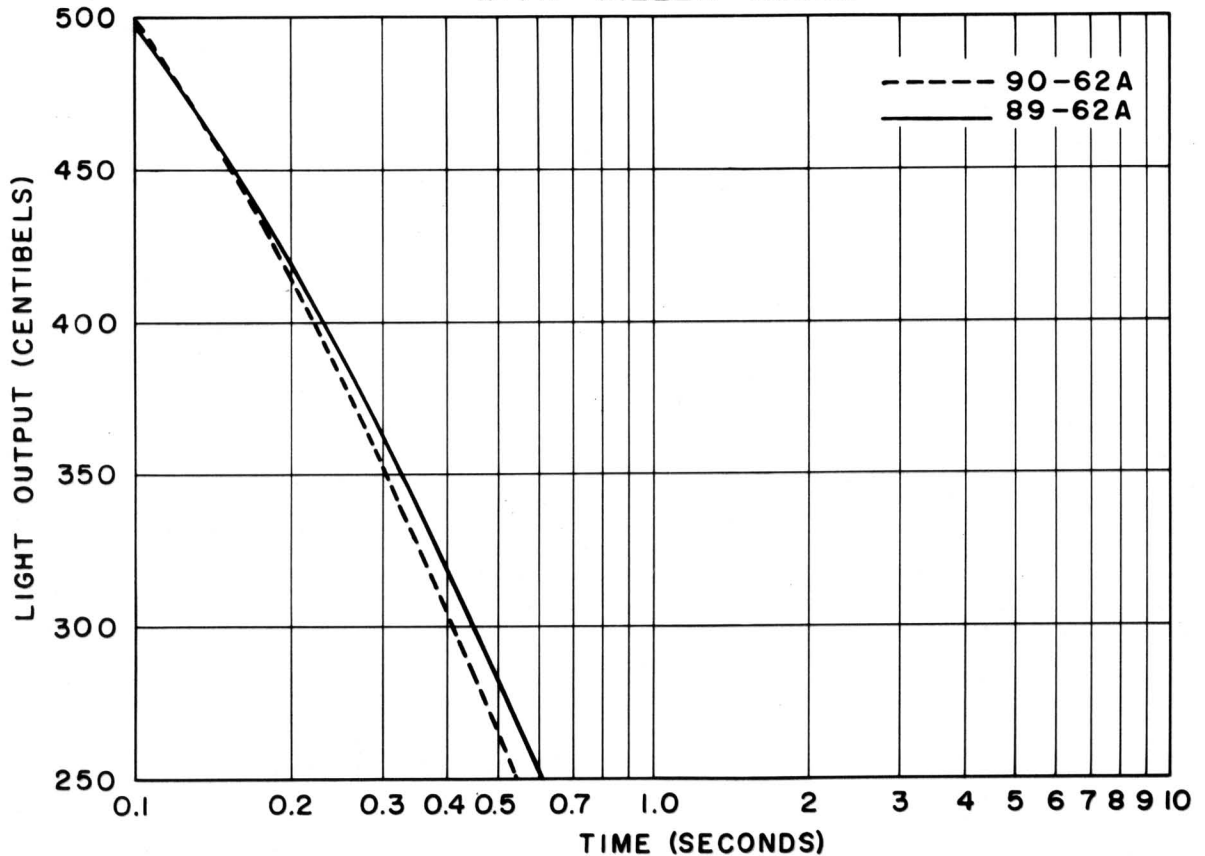## DECAY CURVES OF LONG PERSISTENCE PHOSPHORS
WITH "KILLER" ADDED

Figure 25

XI. LINE WIDTH MEASUREMENTS

In measuring line width, two determinations are made - one at the center of the screen - line width "A" - and the second at a point three-eighths of the maximum tube diameter from the center of the screen along the direction of high frequency scanning - line width "C". These measurements are made with a raster using a 60 cps. sawtooth for the vertical sweep, and 4.5 kc. sawtooth for the horizontal sweep. The combination gives approximately 75 horizontal lines, and the width of the scanning pattern is set equal to about

90 percent of the maximum tube diameter. The low frequency scanning ampli-
tude is expanded until the line structure becomes visible, and is adjusted
for best focus in the center of the pattern. The raster is then narrowed
until the lines just merge. The height of the compressed raster divided by
the number of lines in the raster then gives line width "A". Line width "C"
is determined in a similar manner.

TABLE XV

Line Width Measurements

| | P-19 | | Silicate | | | |
Beam Current (ua)	Line Width "A" (mm)	Line Width "C" (mm)	Line Width "A"	Line Width "C"	A	C
5	0.22	0.24	0.23	0.27	.01	.03
10	.22	.24	.25	.28	.03	.04
15	.23	.25	.26	.29	.03	.04
20	.23	.25	.28	.29	.05	.04
25	.23	.26	.29	.30	.06	.04
30	.25	.27	.30	.31	.05	.04

The results of line width measurements of both the developmental
silicate and the P-19 fluoride are shown above in Table XV. The fluoride has
a somewhat better line width, but the differences are extremely small. On
the average, the line width obtained with the two screens differs by 0.04 mm.

XII. PRELIMINARY LIFE TEST RESULTS

Several tubes were operated for an extended period to determine
the relative rates of screen and brightness deterioration for the two phos-
phors. The tubes were operated at standard life test conditions for 500
hours. At various intervals during this time they were tested and examined
for changes in electrical characteristics, as well as to note the con-
ditions of the screen, and to measure the change in brightness.

Table XVI shows the changes in brightness, efficiency, peak height, peak wave-length and color at zero hours and at the end of the 500 hour test. From this preliminary test data it can be seen that the brightness deterioration of the fluoride is considerably greater than for the silicates. A visual examination of the screens shows screen burning due to electron ("raster burn") in all cases. No instrumental contrast measurements were made, but visually it was possible to observe that the P-19 screens were much more darkened than the silicate screens.

The results of screen burning tests are given in Table XVII, and it is obvious from these data that the fluoride burns at extremely low screen power densities as compared to the silicates.

TABLE XVI

500 Hour Life Test

Sample	Brightness(B)		% ΔB	Efficiency(E)		% ΔE	Peak Height(hp)		% Δ hp	Color				Peak Wavelength(λ p)	
	0 hrs.	500 hrs.		0 hrs.	500 hrs.		0 hrs.	500 hrs.		0 hrs.		500 hrs.		0 hrs.	500 hrs.
										x	y	x	y		
51-62	9.8	7.8	20	2.99	2.37	21	27.66	21.20	23	.558	.425	.554	.428	612.0	611.8
64-62	10.1	7.2	29	3.36	2.15	36	33.12	20.55	38	.580	.405	.577	.409	613.7	614.2
6-62A	9.0	5.9	34	2.93	1.89	36	28.81	18.15	37	.573	.410	.566	.419	612.8	614.7
5-62	11.2	9.6	14	3.39	3.06	10	32.00	27.50	14	.558	.426	.556	.425	612.5	612.1
P-19	12.3	2.8	77	3.95	0.68	83	52.57	8.38	84	-	-	.582	.401	-	601.6

TABLE XVII

Screen Burning Tests

Current Density (milliwatts/cm^2)	Screen Condition after one minute	
	Calcium Silicate	P-19
0.6	no burn	burn
1.2	no burn	
5.8	no burn	
11.6	no burn	
17.4	no burn	
23.2	burn	

E_b = 12 KV

E_{g2} = 300 V

Raster: 10.16 cm. x 10.16 cm.

XIII. SUMMARY

The double-activated calcium silicate phosphor appears to be a very satisfactory replacement for the P-19 zinc magnesium fluoride. A comparison of the optical properties of these two phosphors, i.e., color, spectral emission, brightness, decay and efficiency lead to these conclusions:

a. Color: The color of the fluoride is somewhat "redder" than that of the silicate, however, equivalent color can be obtained with a small sacrifice in brightness and efficiency. (The calcium silicate sample CS-5-62 was selected because of its higher quantum efficiency and peak wave-length. There were samples available with greater luminous efficiency or redder color, but CS-5-62 provided the best compromise.)

b. Spectral Emission: Though the spectral emission bands of the two phosphors lie in the same region of the spectrum they differ in several respects. The fluoride peaks at a shorter wave-length

(λ_p = 605 mu) than the silicate (λ_p = 611 mu). The dominant wave-lengths (λ_d) are 593 mu and 589 mu respectively. Both have a color purity of 95%. The emission band of the fluoride has a broader peak and narrower base than the silicate, except in the case where the two manganese peaks of the silicate can be resolved, and then the peak is much broader (figures 26 and 27).
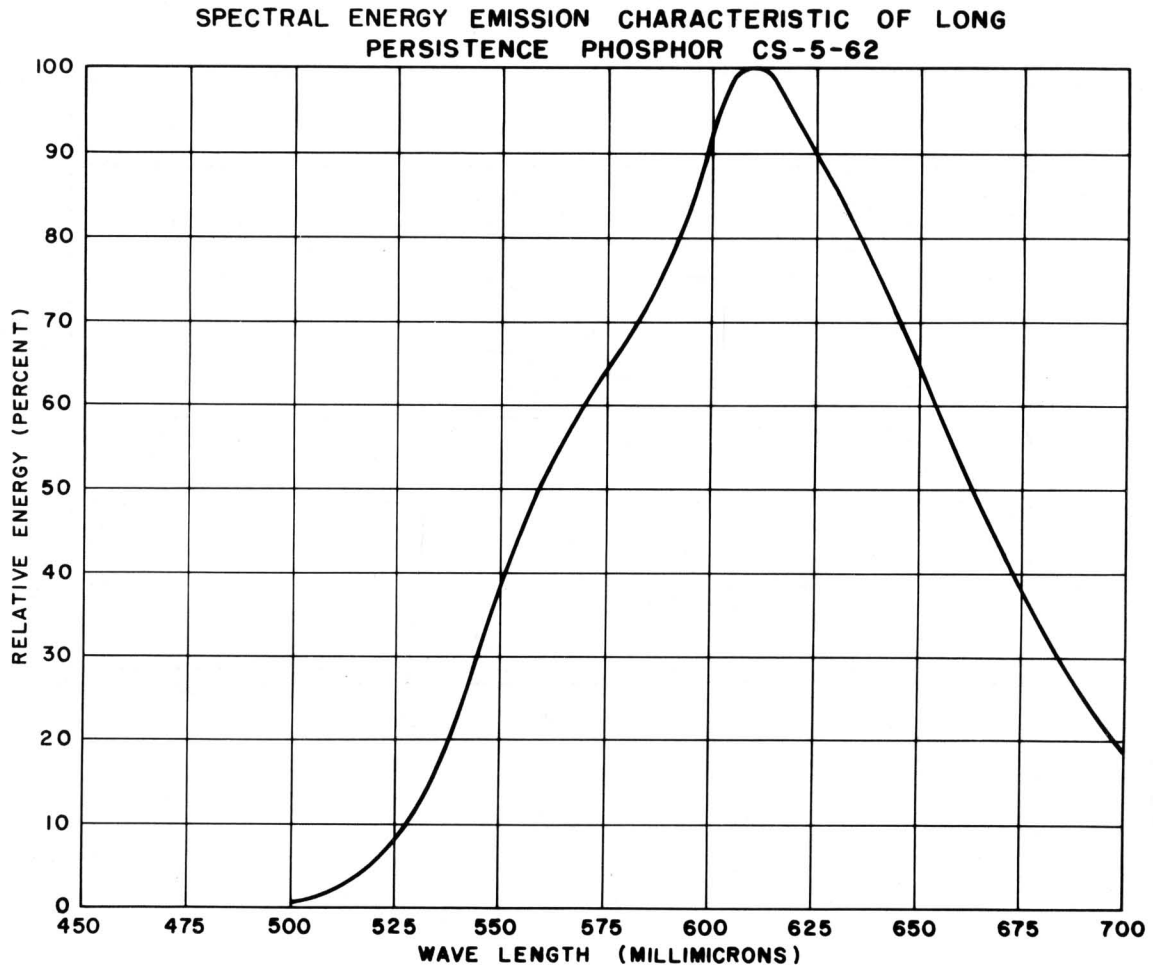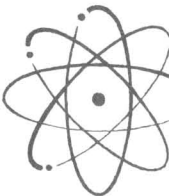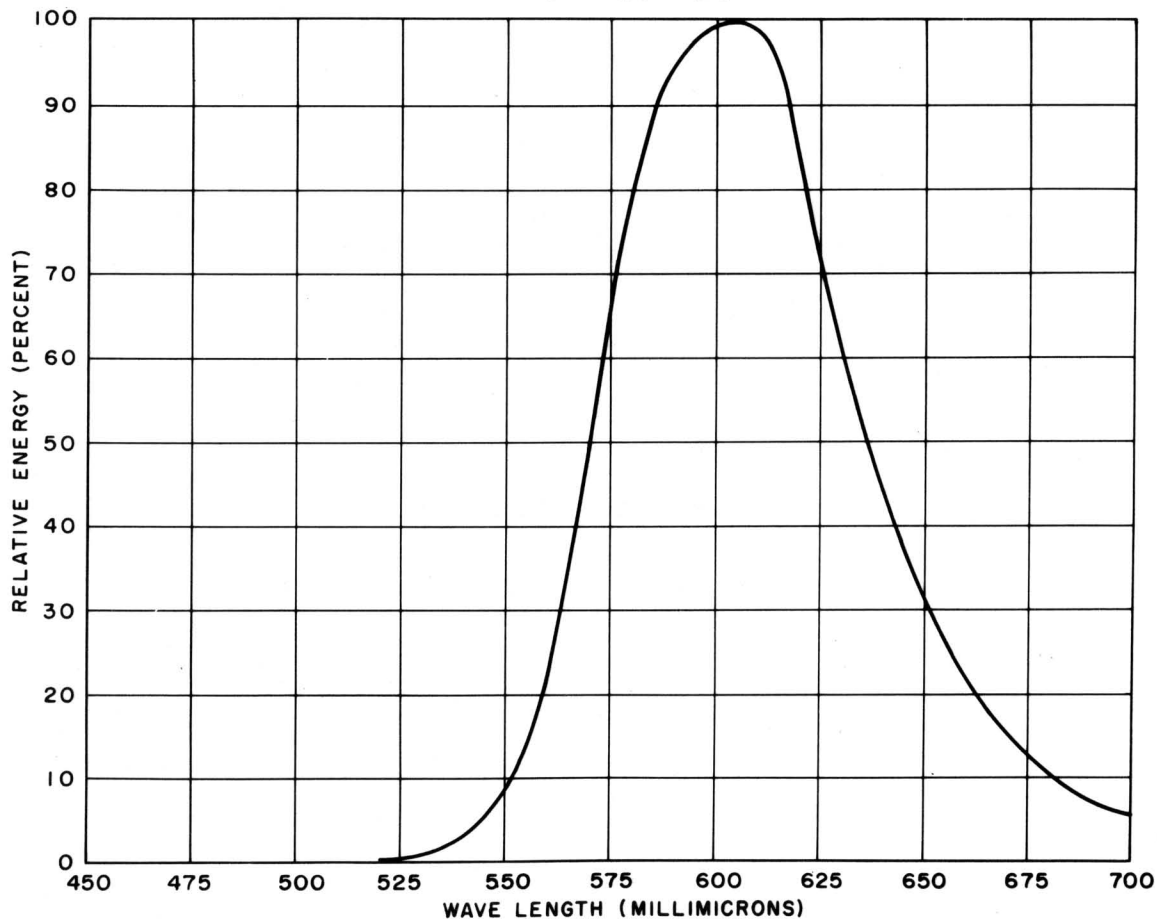
SPECTRAL ENERGY EMISSION CHARACTERISTIC OF LONG
PERSISTENCE PHOSPHOR CS-5-62

Figure 26

SPECTRAL ENERGY DISTRIBUTION
P-19 PHOSPHOR

Figure 27

c. Decay: Figure 28 illustrates the decay characteristic of the
CaSiO$_3$:Pb:Mn phosphor. In the initial stage of the decay, the
decay of the silicate is somewhat faster, and then "levels" off
displaying a long-tail decay in the later stages.

d. Brightness: For an equivalent beam power input to the screen, the
fluoride is somewhat brighter than the silicate. However, because
of the silicate's greater resistance to electron burn, the difference
in brightness can be more than amply reduced by operating at higher
screen current densities. In figure 29 is shown brightness as a
function of power input to the screen for the two phosphors. From
these curves and Table XVIII, it would appear that the fluoride
saturates (this may be due to screen deterioration) much more
rapidly than does the silicate.
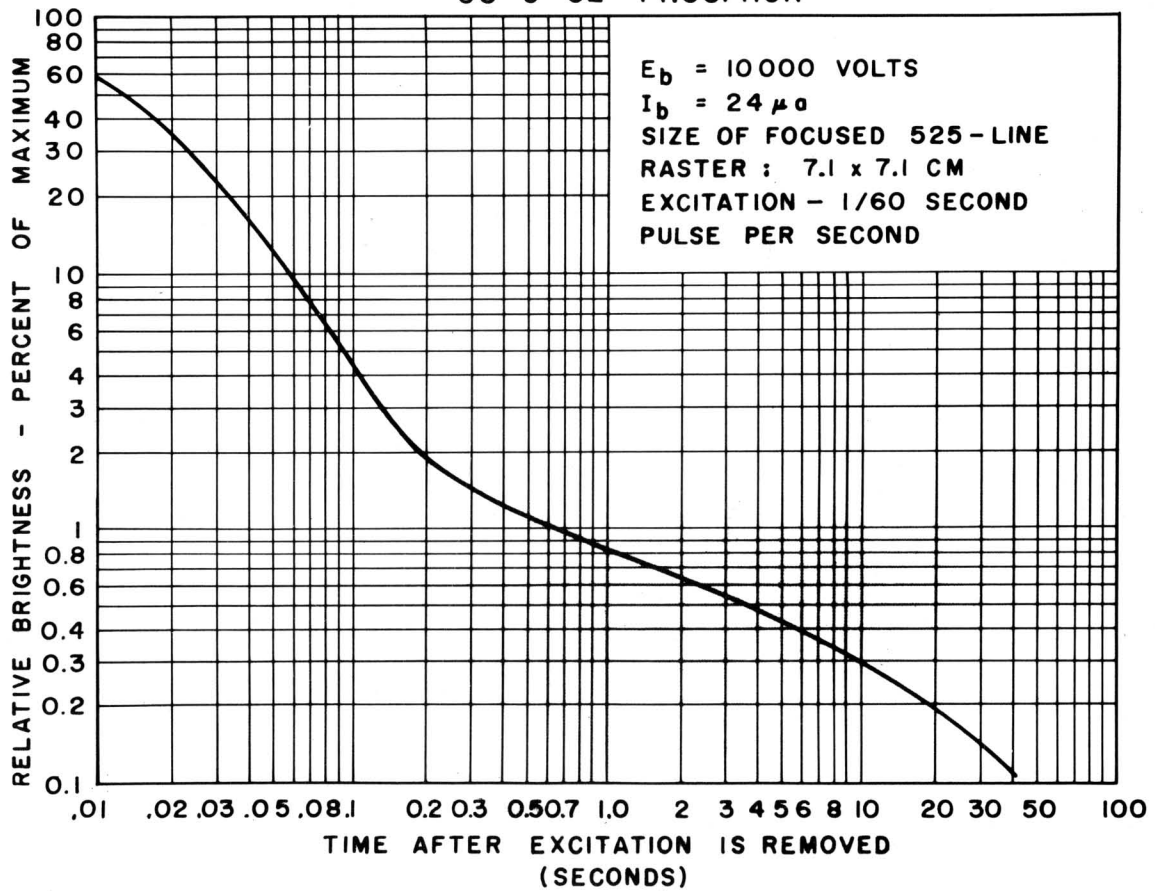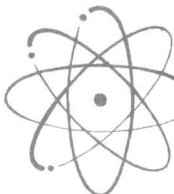
PERSISTENCE CHARACTERISTIC OF
CS-5-62 PHOSPHOR

E_b = 10000 VOLTS
I_b = 24 μa
SIZE OF FOCUSED 525-LINE
RASTER : 7.1 x 7.1 CM
EXCITATION — 1/60 SECOND
PULSE PER SECOND

RELATIVE BRIGHTNESS — PERCENT OF MAXIMUM

TIME AFTER EXCITATION IS REMOVED
(SECONDS)

Figure 28

BRIGHTNESS AS A FUNCTION OF POWER
INPUT TO SCREEN

$E_b = 12\,KV$
$E_{q2} = 250\,V$
15 CM x 15 CM
FOCUSED RASTER

P-19

SILICATE
(5-62)

BRIGHTNESS (FT-L)

CURRENT DENSITY (MILLIWATTS/CM^2)
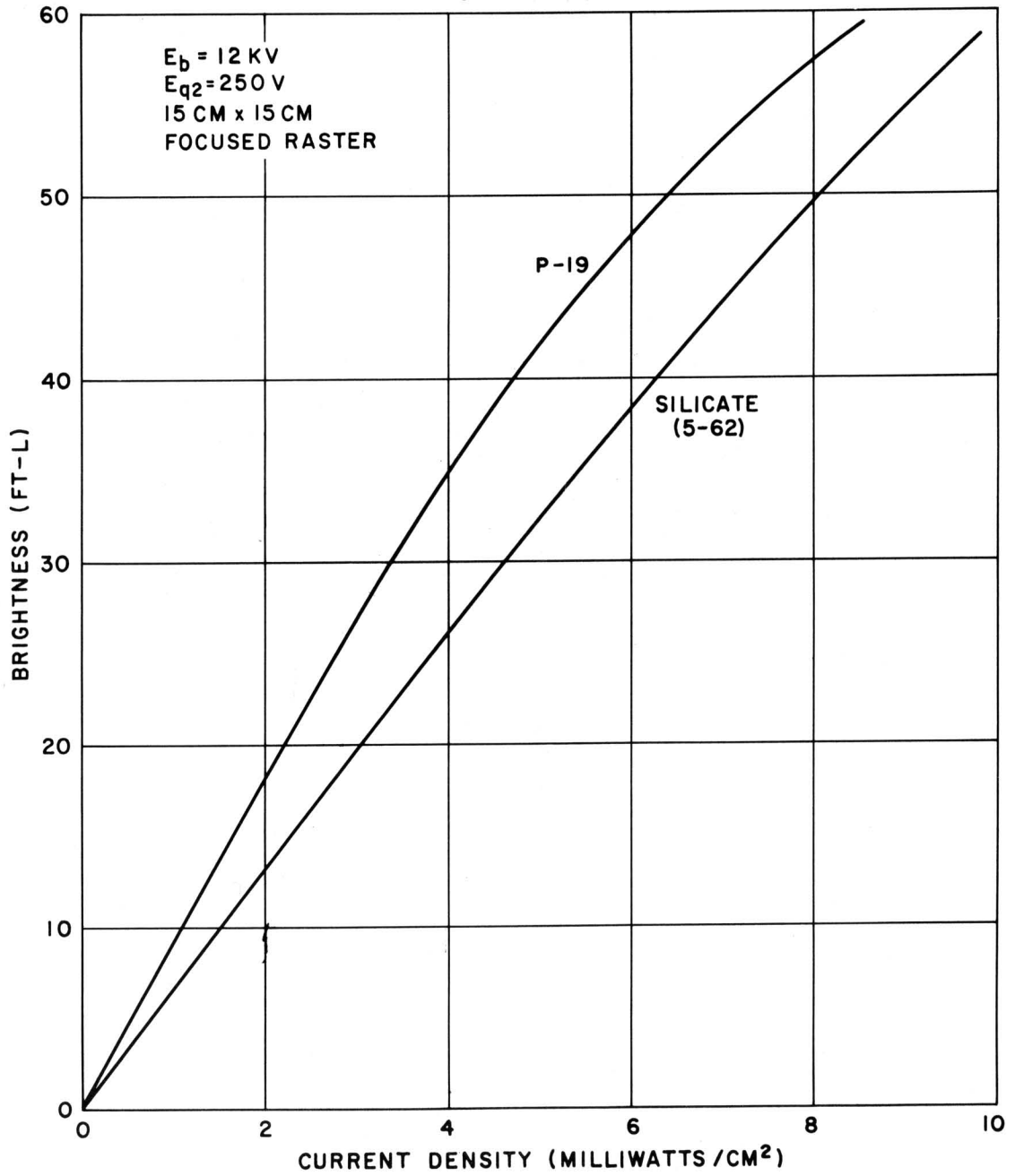
Figure 29

TABLE XVIII

| Current Density milliwatts/cm^2	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Brightness Difference(%)	28.8	27.5	27.5	26.4	24.7	22.5	19.5	16.5	13.2	10.0

The results of the burning tests clearly indicate the superiority of the silicate in this regard since its increased burn resistance permits far greater light output than can be obtained from the fluoride.

XIV. ADDENDUM

One of the requirements of the contract was that the phosphors be tested in a tube whose face plate had the spectral characteristics of a Corning C-273 filter.

The G-E Chemical Products Works supplied the Cathode-Ray Tube Sub-Department a spray-cure lacquer which approximated the transmission characteristics of the above filter. When properly applied, this lacquer (G.E. - No. 3674) formed a uniform, tough, abrasion-resistant coating. Several tubes were made using this lacquer.

The spectral characteristics are shown in figure 30, and the spectral emission characteristic of the calcium silicate phosphor used with the filter is shown in figure 31.
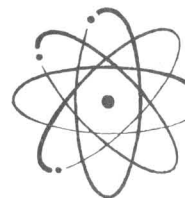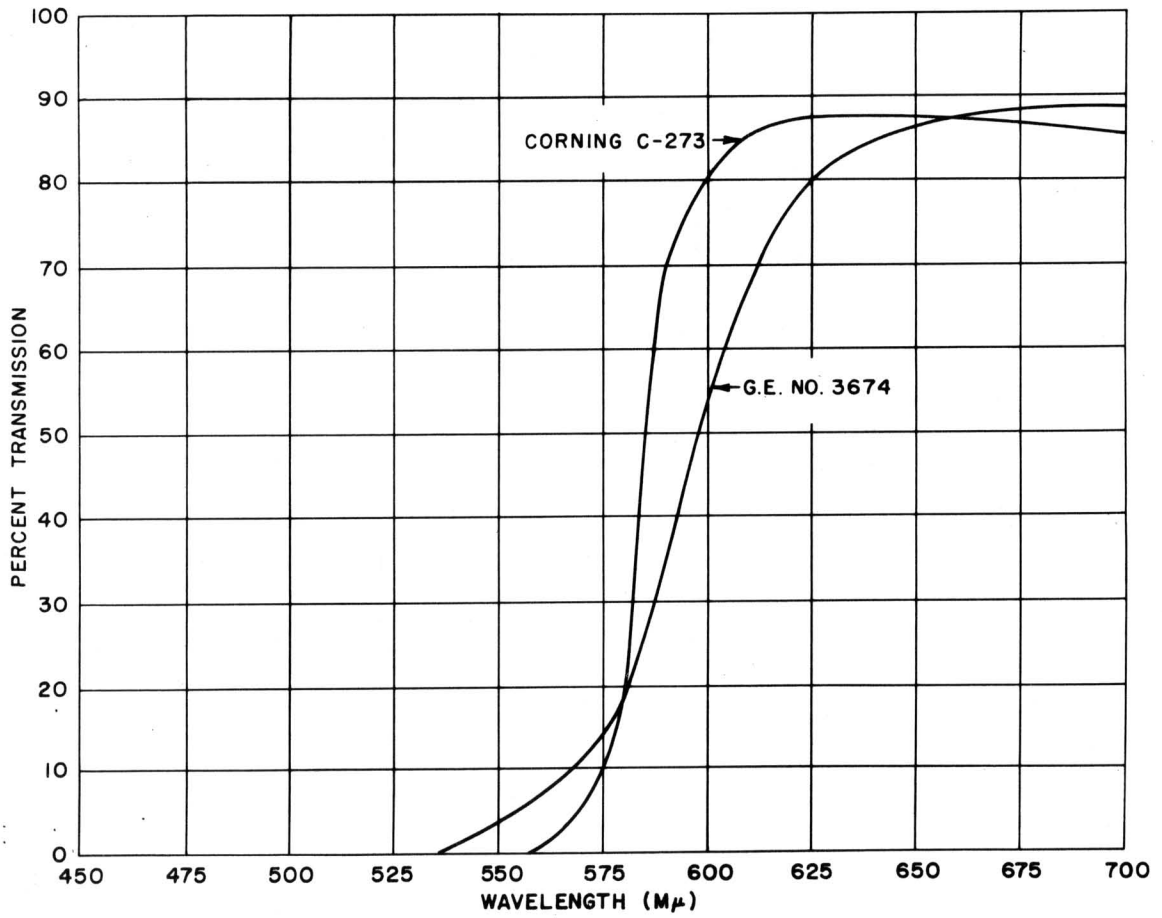
CORNING vs G.E. RED FILTER

Figure 30

SPECTRAL ENERGY DISTRIBUTION OF LONG PERSISTENCE PHOSPHOR
WITH G.E. NO. 3674 RED FILTER ON TUBE FACE
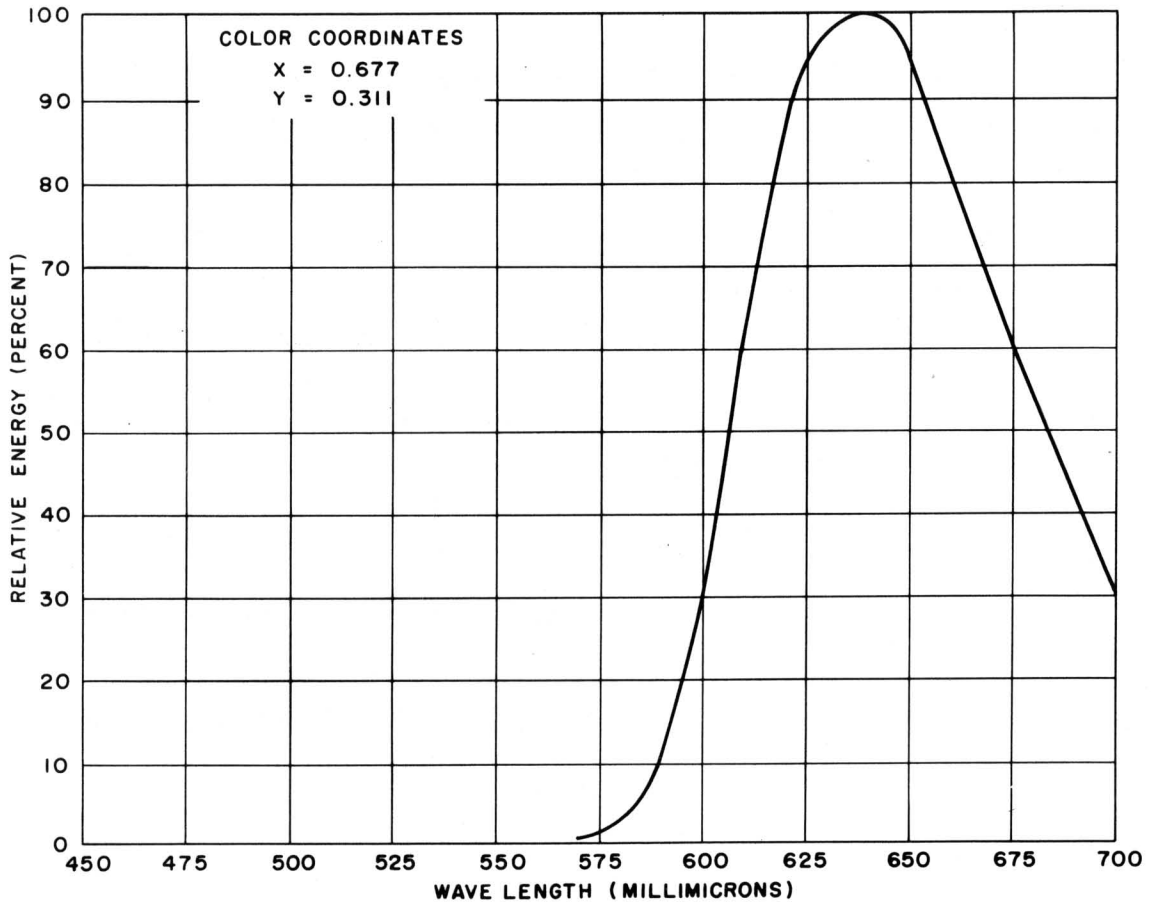
COLOR COORDINATES
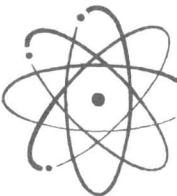X = 0.677
Y = 0.311

Figure 31

XV.   REFERENCES

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