

in excess ethanolic sodium hydroxide, followed by titration of the excess alkalinity, is being given careful study.

3. Investigations now nearing completion concern reactions of the appropriate alkylchlorosilane with silver isocyanate or silver isothiocyanate to yield the following new compounds: $\text{EtSi}(\text{NCO})_3$, b. p. 183° ; $\text{Et}_2\text{Si}(\text{NCO})_2$, b. p. 177° ; $\text{Et}_3\text{Si}(\text{NCO})$, b. p. 165° ; *i*- $\text{PrSi}(\text{NCO})_3$, b. p. 192° ; $\text{PrSi}(\text{NCO})_3$, b. p. 198° ; *i*- $\text{PrSi}(\text{NCS})_3$, b. p. 279° ; $\text{PrSi}(\text{NCS})_3$, b. p. 290° .

Titanium tetrachloride and silver isocyanate yield a solid isocyanate which is nearly insoluble in benzene. Titanium tetrachloride and 1,4-dioxane furnish a pale-colored solid addition compound containing approximately 31% Cl, provisionally identified as $\text{TiCl}_4 \cdot 3\text{C}_4\text{H}_8\text{O}_2$, and being investigated further.

Summary

1. Ethylchlorosilanes and silver isothiocyanate reacted to yield (new) liquids: ethylsilicon triisothiocyanate, $(\text{C}_2\text{H}_5)_3\text{Si}(\text{NCS})_3$, boiling at 276° ; diethylsilicon diisothiocyanate, $(\text{C}_2\text{H}_5)_2\text{Si}(\text{NCS})_2$, boiling at 245.5° ; and triethylsilicon isothiocyanate, $(\text{C}_2\text{H}_5)_3\text{Si}(\text{NCS})$, boiling at 210.5° . Molar re-

fractions, densities and indices of refraction are given.

2. After treatment of a pure alkylsilicon isothiocyanate with 95% ethanol, the resultant (iso)-thiocyanic acid proves to be easily and accurately titrated with standard sodium hydroxide using phenolphthalein as an indicator. This method in many instances has advantages over previously available procedures for determination of (iso)-thiocyanic acid, which polymerizes, and which is a reducer.

3. Automatic, or self-filling and self-adjusting, micropipets herein of volume 0.004–0.016 ml. have served quite well for exact quantitative analysis of unweighed liquid samples, as now demonstrated. From the mercury-standardized volume of the micropipet and from the known density of the liquid at the observed temperature the weight of the liquid is furnished with accuracy otherwise attainable only with use of a microbalance under extreme precautions.

Further investigation is under way regarding the elimination of weighing analytical samples of liquids through use of such micropipets, and of similar equipment.

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Radioactive Tracer Study of Activator Distribution in Infrared Phosphor Systems: Effect of Strontium Oxide^{1,2}

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It has been shown that strontium oxide has a pronounced effect upon the brightness under stimulation of the infrared-sensitive phosphors $\text{SrS}(\text{Sm}, \text{Eu})$, SrCl_2^4 and $\text{SrSe}(\text{Sm}, \text{Eu})$ ($\text{SrSO}_4 \cdot \text{CaF}_2$).⁵ The brightness of the phosphor $\text{SrS}(\text{Ce}, \text{Sm})$, SrCl_2 invariably decreases with the addition of small amounts of strontium oxide. Lattice constant determinations of strontium sulfide or selenide and strontium oxide that has been fluxed together with strontium chloride at 1000° indicate that the amount of oxide which dissolves in the sulfide and selenide is quite small and lies almost beyond the limits of determination by X-ray diffraction.⁶ Inasmuch as quantities of oxide up to several per cent. still have very marked effects upon the luminescent properties of these phos-

phors, these could not be attributed to any change in the nature of the base material caused by the oxide.

The solubility of strontium oxide in fused strontium chloride⁷ at 1000° is sufficiently high so that the quantities of oxide added to the phosphors^{4,5} were in all cases insufficient to saturate the fused strontium chloride. It seemed reasonable to suppose that the oxide alters the nature of the flux, and that this might cause a change in the distribution of the rare-earth activators between the solid base material (strontium sulfide or selenide) and the liquid phase (fused strontium chloride plus dissolved strontium oxide and base). A procedure has been described⁸ for measuring the distribution of the activators europium, samarium and cerium between the solid strontium sulfide or selenide and liquid strontium chloride. This paper deals with the effect of the addition of strontium oxide upon the distribution of the activators in these systems.

Experimental

(a) Apparatus.—The high temperature filtration method⁸ which yielded a partial separation of the solid and

(1) This work was carried out under Contract NObsr 39045 between the Polytechnic Institute of Brooklyn and the Bureau of Ships.

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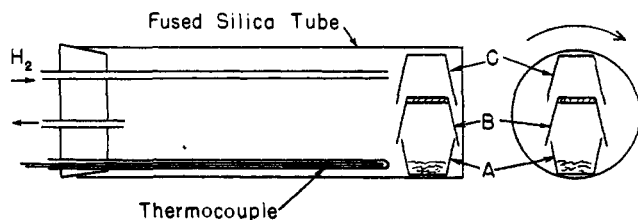


Fig. 1.

liquid phases has been modified so that the separation of the phases can be accomplished directly upon attaining equilibrium with respect to the activator distribution. The apparatus is shown in Fig. 1.

A is a small nickel crucible containing the powdered mixture which is to be studied. B is a nickel filtering crucible with a porous nickel mat and C is a larger nickel crucible used to catch the filtrate. The bank of three crucibles arranged as shown in the figure was placed in a fused silica tube which was then heated to constant temperature in a regulated electric furnace. The temperature inside the tube, measured with a calibrated chromel-alumel couple, was constant to $\pm 5^\circ$. One hour at 1000° was considered sufficient time to establish equilibrium and after that interval the tube was turned through an angle of 180° in the direction indicated. The porous nickel mat allowed the fused salt solution to pass through while retaining the solid phase. An atmosphere of hydrogen was found to be the most convenient.

The filtering crucible was made by drilling about 25 holes, $1/32$ inch in diameter, in the bottom of a nickel crucible. The crucible was then cleaned in nitric acid and heated in hydrogen at 1000° for several minutes and cooled in the hydrogen atmosphere. About $1/4$ inch of 10 micron nickel powder was placed in the bottom of the crucible and compressed at a pressure of 5000 lb./sq. in. Finally the crucible was reheated in hydrogen at 1000° for several minutes. The porous mat prepared in this way is very strong mechanically and is not attacked by the fused salt mixtures used in these investigations.

(b) **Materials.**—The radioactive rare earths used as tracers were described in the previous paper.⁸

The preparation of the strontium sulfide, selenide, oxide and chloride are also described elsewhere.^{4,6}

Results

The activator distribution between the two phases at temperature T , is defined as

$$(1) K_T = \frac{\text{mole fraction of activator in solid phase}}{\text{mole fraction of activator in liquid phase}}$$

K_T can be expressed in terms of values obtained upon the analysis of the residue and filtrate as follows

$$(2) K_T = \frac{[(C'/C) - (N_{o1}'/N_{o1})]}{[(N_{sr}'/N_{sr}) - (N_{o1}'/N_{o1})]}$$

where the primed quantities refer to the residue, and the unprimed ones to the filtrate. C = counts per minute per 0.1 g. of filtrate after the application of the necessary corrections. N_{o1} = moles of chloride found by analysis in 0.1 g. of the filtrate. N_{sr} = moles of strontium found by analysis in 0.1 g. of the filtrate.

In those systems where strontium selenide was the base, it was found more convenient to analyze for selenium instead of chloride. In these cases, the ratio N_{o1}'/N_{o1} is replaced by $(N_{sr}' - N_{se}')/(N_{sr} - N_{se})$ where N_{se} is the number of moles of selenium found by analysis in 0.1 g. of filtrate.

The methods for preparing samples of residue and filtrate for counting, and the determination of their relative activities were described in the previous paper.⁸ Unless otherwise stated, chloride was determined by the Volhard method, strontium gravimetrically as strontium sulfate, and selenium gravimetrically as free selenium.

The distribution constants for the various systems studied are given in Tables I to VI. In all the runs the amount of strontium sulfide or strontium selenide was kept constant at 1.4 g. The total quantity of strontium chloride plus strontium oxide was also kept constant at 0.0340 mole, and only the ratio of oxide to chloride was varied. In the tables the values listed under the heading R are the ratios of the moles of strontium oxide to the moles of strontium chloride used in the particular runs. The total quantities of rare earth activators used were 100 μ g. of samarium, 770 μ g. of cerium and 130 μ g. of europium.

TABLE I
THE DISTRIBUTION OF SAMARIUM IN THE SYSTEM SrS-SrCl₂-SrO

R	C'/C	N_{o1}'/N_{o1}	N_{sr}'/N_{sr}	K_{1010}
0.000	3.479	0.590	1.127	5.38
.0155	0.970	.629	1.128	0.683
.0314	.647	.603	1.103	.088
.0802	.648	.581	1.140	.12
.170	.646	.645	1.090	.002

TABLE II
THE DISTRIBUTION OF SAMARIUM IN THE SYSTEM SrSe-SrCl₂-SrO

R	C'/C	$\frac{N_{sr}' - N_{se}'}{N_{sr} - N_{se}}$	N_{sr}'/N_{sr}	K_{1010}
0.000	1.723	0.749	0.9734	4.35
.0155	0.844	.588	.9927	0.632
.0314	.527	.484	.9871	.085
.0802	.502	.487	.9792	.031

TABLE III
THE DISTRIBUTION OF CERIUM IN THE SYSTEM SrS-SrCl₂-SrO

R	C'/C	N_{o1}'/N_{o1}	N_{sr}'/N_{sr}	K_{1010}
0.000	2.041	0.645	1.108	3.01
.0155	0.734	.621	1.110	0.231
.0802	.626	.614	1.104	.024
.170	.576	.536	1.163	.064 ^a

^a The temperature of this run was 1050° .

TABLE IV
THE DISTRIBUTION OF CERIUM IN THE SYSTEM SrSe-SrCl₂-SrO^b

R	C'/C	$\frac{(N_{sr}' - N_{se}')}{(N_{sr} - N_{se})}$	N_{sr}'/N_{sr}	K_{1010}
0.000	1.847	0.602	0.9912	3.20
.0155	0.712	.591	.9926	0.301

^b Attempts to prepare an infrared-sensitive phosphor using strontium selenide as the base with the activators cerium and samarium have not been successful. Accordingly this system was not studied as completely as the others.

TABLE V

THE DISTRIBUTION OF EUROPIUM IN THE SYSTEMS SrS-SrCl₂-SrO

R	C'/C	$N_{Ce'}/N_{Ce}$ ^c	$N_{Sr'}/N_{Sr}$	K_{1000}
0.000	1.251	0.863	1.014	2.57
.0155	1.417	.666	1.113	1.68
.170	1.612	.573	1.120	1.90
.383	1.076	.609	1.070	1.01

^c Chloride was determined gravimetrically.

TABLE VI

THE DISTRIBUTION OF EUROPIUM IN THE SYSTEM SrSe-SrCl₂-SrO

R	C'/C	$\frac{N_{Sr'}-N_{Se'}}{N_{Sr'}-N_{Se}}$	$N_{Sr'}/N_{Sr}$	K_{1000}
0.000	1.815	0.439	0.963	2.62
.0155	1.523	.525	.975	2.22
.170	1.294	.542	.942	1.88
.383	0.971	.568	.975	0.99

Discussion

The results listed in Tables I to VI show that the samarium and cerium distributions are far more sensitive to the presence of strontium oxide than is the europium distribution. The europium distribution constant is decreased by only about 60% at the highest oxide concentration tried which represents almost complete saturation of the fused strontium chloride. (R for complete saturation of strontium chloride at 1000° has a value of 0.47.) These results are in accordance with the brightness-composition data reported by Stripp and Ward⁴ for the phosphors SrS (Sm, Eu) SrCl₂. Reference to their observations shows that the addition of increasing quantities of strontium oxide to phosphors having a high concentration of europium and a low concentration of samarium caused the brightness to decrease continuously, while if the samarium concentration was higher than that of the europium the brightness first reached a maximum and then decreased. These authors also showed that in this phosphor the peak brightness occurs at about equal concentration of the two activators, the brightness decreasing when either activator is present in excess of the other. From the behavior of the distribution constants as reported here we can see that, in a phosphor containing a high samarium and a low europium concentration, the successive additions of small amounts of strontium oxide would decrease the amount of samarium in the base while leaving the europium concentration in the base virtually unchanged. Thus the composition of the phosphor shifts toward the point

of maximum brightness. On the other hand, in a phosphor containing a low samarium and a high europium concentration, a decrease in the concentration of samarium in the base caused by the addition of strontium oxide causes a shift in the phosphor composition toward *low* samarium concentration thus causing still lower brightness. In an entirely analogous manner, we can explain the difference in brightness between the outside and the inside fracture surfaces of these phosphors as reported in the same paper.

Thus, at least qualitatively, the "oxide-effect" can be explained. Unfortunately we do not have any reliable information as to the original oxide content of the strontium sulfide or selenide used in phosphor preparation so that no quantitative calculations can be made. The strontium selenide used in the preparation of phosphors usually contains much more oxide than the strontium sulfide due to the ready hydrolysis and oxidation of the selenide. Consequently the information concerning the variation of brightness of the SrSe (Sm, Eu) phosphors with oxide content has been quite erratic. It has not been possible in this case to obtain even semiquantitative data. Nevertheless, the conclusion that the major action of the oxide is its effect on the distribution of activators would appear to be justified, but it is not appropriate at this time to exclude other possible effects. For example, it is conceivable and even likely that the oxide ion dissolves in the sulfide lattice to a concentration comparable with that of the activators. So long as we have no means of measuring such low concentrations of oxide ion, its effect on optical properties will remain unknown.

Summary

An improved method is described for determining the distribution of rare earth activator ions between the solid and liquid phases present in infrared-sensitive phosphor systems. The distribution constants, defined as the ratio of the mole fractions of the rare earth ion in the solid and liquid phases, have been determined for the rare earths samarium, cerium and europium in the systems SrS-SrCl₂-SrO and SrSe-SrCl₂-SrO. The distribution constants of samarium and cerium decrease rapidly as the ratio of strontium oxide to strontium chloride increases. That of europium is relatively little affected by strontium oxide. These results explain qualitatively the observed brightness-composition variation in the phosphor SrS (Sm, Eu) SrCl₂, SrO.

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