Studies on the Oxy-acid Phosphors. IV. Application of Polarography to the Analysis of Activators, Especially, in Calcium Silicate Phosphors*)

By Yoshihide KOTERA, Michiko YONEMURA and Tadao SEKINE

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Introduction

In the preparation of the phosphors, the amount of activators is one of the most important factors for determining their characteristics, and it is usually calculated by the mixing ratio for the batch before firing. As certain activators may be dissipated during the firing, it is necessary to determine the residual amount for discussing properties of resulting phosphors in connection with the amount of activators. We have determined this amount for several phosphors by means of polarography.

Especially, for calcium silicate phosphors activated by manganese and lead, whose characteristics depend upon the atmosphere during the firing, it is proved that the atmosphere during firing gives remarkable changes in the residual amount of activators and that the brightness of phosphors is affected by this amount.

Experimental and its Results

(1) Analysis of Activators in Phosphors by Polarography.—We tried to analyse activators in various phosphors by means of polarography.

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The procedures are described as follows.

(*a*) *Manganese in Zn_2SiO_4: Mn and $(Zn, Be)_2SiO_4$: Mn.*—Manganese was analysed by the procedure which was reported by Spalenka[1].

1.5–2.0 g. of the unfired and fired sample were dissolved in conc. HCl. This solution was evaporated up to dryness, to which warm distilled water was added. After silica was removed by filtration, 20–40 ml. of 6N HCl were added to the filtrate. 1 ml. of this solution was taken as a sample for polarography, and, after addition of one to two drops of H_2O_2, 2.5 ml. of the mixed solution of saturated sodium sulfite solution (solution No. 3 in the Spalenka's receipt) and methol solution (solution No. 4), 5 ml. of ammonia solution (solution No. 5), and 10 ml. of the mixed solution of cyanide solution (solution No. 6) and caustic soda solution (solution No. 7), it was analysed by polarography. The solutions used in this procedure were prepared by the method of Spalenka's.

In order to detect manganese in the silica obtained by filtration, it was fused with Na_2CO_3 and NaOH in a platinum crucible, but manganese was not found in its polarogramm.

Zn_2SiO_4: Mn was prepared by firing the batch for 3 hours at 1150°C, the batch containing 1 g. ZnO, 0.4 g. SiO_2, 0.003 g. NaF and 0.01 g. Mn. As for $(Zn, Be)_2SiO_4$: Mn, the batch used contained 1 g. ZnO, 0.5 g. SiO_2, 0.03 g. BeO, 0.05 g. Mn and 0.03 g. $(NH_4)_2S_2O_8$.

The results are shown in Table I and Fig. 1.

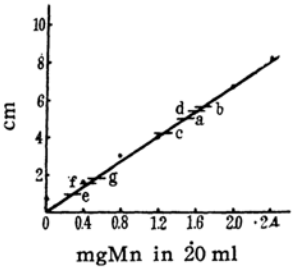


Fig. 1. Determination of Mn in Zn_2SiO_4: Mn, $(Zn, Be)_2SiO_4$: Mn and the mixed white phosphors.
a: Zn_2SiO_4: Mn (unfired)
b: Zn_2SiO_4: Mn (fired)
(a, b: 0.2 g. sample in 20 ml)
c: $(Zn, Be)_2SiO_4$: Mn (unfired)
d: $(Zn, Be)_2SiO_4$: Mn (fired)
(c, d: 0.05 g. sample in 20 ml)
e: 3500°K white f: 4500°K white
g: warm white
(e, f, g: 0.05 g. sample in 45 ml)

TABLE I

CONTENT OF MANGANESE IN Zn_2SiO_4: Mn and $(Zn, Be)_2SiO_4$: Mn

	unfired	fired
Zn_2SiO_4: Mn	0.0075 g. Mn/g.	0.0084 g. Mn/g.
$(Zn, Be)_2SiO_4$: Mn	0.025 g. Mn/g.	0.033 g. Mn/g.

(*b*) *Manganese and antimony in the mixed white phosphors.*—"3500°K white", "4500°K white" and "warm white", which were prepared in U.S.A. and expected to be the mixture of calcium halophosphate phosphor activated by manganes and antimony and other phosphors, were used as samples. 0.2 g. of sample were fused with 1.6 g. of Na_2CO_3, the fused mass was dissolved in HCl, and the volume of solution thus obtained was adjusted to 40 ml., the acidity of which was found to be that of 3N HCl.

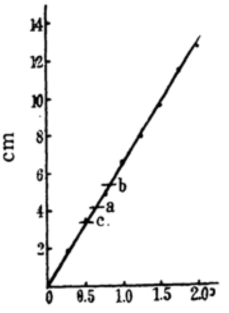
The antimony in this solution was analysed directly by the method of Page and Robinson[2], while manganese was analysed by the procedure described above. The standard solution of antimony was prepared by dissolving Sb_2O_3 in $CaCl_2$ solution, which was previously made acidic by the addition of HCl.

The results obtained are shown in Table II and Fig. 2.

TABLE II

CONTENT OF MANGANESE AND ANTIMONY IN THE MIXED WHITE PHOSPHORS

	manganese	antimony
3500°K white	0.015 g./g.	0.0065 g./g.
4500°K white	0.021	0.0085
warm white	0.024	0.0053



Eig. 2. Determination of Sb in the mixed white phosphors
a: 3500°K white
b: 4500°K white
c: warm white
(a, b, c: 0.1 g. sample in 20 ml.)

(*c*) *Copper in ZnS: Cu.*—Being dissolved in HCl, ZnS: Cu was analysed by the usual polarographic procedure, and it is confirmed that the copper content remained unchanged during the usual firing.

(2) *Analysis* of Activators in Calcium Silicate Phosphors and the Measurement of Their Brightness.

(*a*) *Preparation of calcium silicate phosphors.*—The batch containing 1.0 g. SiO_2, 2.0 g. $CaCO_3$, 0.08 g. $MnSO_4$, 0.02 g. PbF_2 and 0.8 g. $(NH_4)_2S_2O_8$, was fired at 1120°C for 2 to 6 hours in various atmospheres. Two kinds of silica were used for the batch, one being prepared from ethyl silicate, the other from sodium silicate. The atmosphere during firing was controlled by the precedure described in a previous paper[3].

(*b*) *Analysis of activators in the phosphors and the measurements of their brightness.*—The fired products were dissolved in HCl and

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[1] M. Spalenka, *Z. anal. Chem.*, **128**, 42 (1948).

[2] J. E. Page and F. A. Robinson, *J. Soc. Chem. Ind.* (London), **61**, 93 (1942).

[3] Y. Kotera and T. Sekine, This Bulletin, **28**, 129 (1955).

the solution evaporated up to dryness repeatedly, and then, after filtration, it was adjusted to 30 ml., which had acidity of 3 N HCl. The lead in this solution was analysed directly according to Terui[4]. Manganese was analysed according to Hohn[5], after the solution of 50 g. of NH_4Cl and 50 ml. of conc. NH_3 in 500 ml. of water was added to the solution of the sample and the total volume was expected to be 20 ml. The standard solution of lead was prepared by dissolving $PbCl_2$ in HCl.

The measurement of brightness under the excitation by 2537 Å was carried out by the procedure described in a previous paper[6].

(*c*) *The effects of atmosphere and firing time on the residual amount of activators and the brightness.*—The results obtained are shown in Table III and Fig. 3. These results were analysed by the completely randomized block designs for the residual amount of lead and manganese and the brightness, the atmosphere and the firing time being taken as factorial effects. Care concerning randomization was taken, for example, a large quantity of the batch was prepared by mixing, of which the divided portions were taken and fired in the same furnace. The effects of the atmosphere and the time are significant at the 1% and 5% levels respectively. As the brightness would be changed with the residual amount of lead or manganese, the correlation coefficients between one of these residual amounts and the brightness were calculated. Multiple correlation coefficient was 0.926 (significant at the 1% level), and partial correlation coefficient was 0.850 (signif. at the 1% level) in the case of lead, while it was −0.408 (not signif.) in the case of manganese. From these values, it is concluded that

(i) The amount of lead has a more important effect upon the brightness than manganese.

(ii) These effects go by contrary, viz., the brightness is increased either with the increase of the amount of lead, or with the decrease of that of manganese.

TABLE III

THE RESIDUAL AMOUNTS OF ACTIVATORS AND THE BRIGHTNESS OF CALCIUM SILICATE PHOSPHORS

	Firing time (hr.)	Atmosphere				
		air	H_2O	O_2	H_2	N_2
Lead content	2	0.0021	0.0013	0.0014	0.0007	0.0013
	4	0.0019	0.0015	0.0011	0.0004	0.0013
	6	0.0017	0.0013	0.0011	0.0002	0.0011
Manganese content	2	0.0039	0.0039	0.0036	0.0057	0.0056
	4	0.0040	0.0043	000037	0.0057	0.0057
	6	0.0040	0.0043	0.0039	0.0057	0.0057
Brightness	2	9.5	7.0	8.2	1.6	6.9
	4	9.1	6.5	7.4	1.6	7.2
	6	9.0	5.1	7.5	1.4	5.9

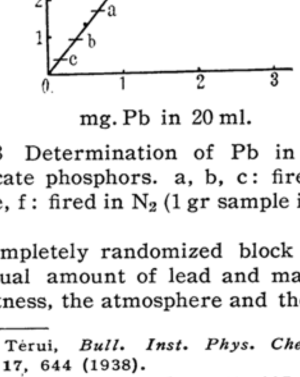

Fig. 3 Determination of Pb in calcium silicate phosphors. a, b, c: fired in H_2 d, e, f: fired in N_2 (1 gr sample in 20 ml.)

In order to verify these results, the analysis of covariance was carried out and the effects of atmosphere and firing time on the brightness were investigated, the amount of manganese or lead being taken as additional factorial effects. These results are listed in Table IV, from which it is concluded that

TABLE IV

TABLE OF THE ANALYSIS OF COVARIANCE

(a) When the amount of lead is taken as addditional effects

Source of variation	Degree of freedom	Sum of squares	Mean squares	F
firing time	2	119.58	59.79	2.98
atmosphere	4	1601.79	400.45	$19.95^{\#\#}$
average linear response	1	8447.76	8447.76	$420.91^{\#\#}$
error	7	140.47	20.07	

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4) Y. Terui, *Bull. Inst. Phys. Chem. Research* (Tokyo), **17**, 644 (1938).

5) N. Hohn, *Z. Electrochem.*, **43**, 127 (1939).

6) Y. Kotera and T. Sekine, This Bulletin, **27**, 13 (1954).

(b) When the amount of manganese is taken as additional effects

Source of variation	Degree of freedom	Sum of squares	Mean squares	F
firing time	2	76.90	38.45	1.72
atmosphere	4	4946.15	1236.53	$63.80^{\#\#}$
average linear response	1	5150.88	5150.88	$265.78^{\#\#}$
error	7	135.67	19.38	

significant at the 1% level, #, signif. at the 5%.

(i) The F-ratio for the atmosphere variation is significant at the 1% level while that for the firing time variation is not significant.

(ii) As the linear response is separated, the analysis of covariance gives clarified results, and as for the selection of additional factorial effects, the amount of lead is preferable to that of manganese, which would be expected from the values of the correlation coefficients and from Table IV.

From the results of the randomized block design, the effect of firing time on the brightness is significant at the 5% level, but, this effect on the residual amounts of both lead and manganese is also significant at the 5% level, and it is verified from the analysis of covariance, that the changes of brightness are almost always caused by the changes of residual amounts of activators.

The significance of the effects difiers between five kinds of atmosphere, as is listed in Table V. It is to be noted that better results were not obtained for hydrogen, which has hitherto been considered to be an adequate atmosphere for the preparation of this phosphor⁷⁾.

Table V

The significance of effects of the atmospheres

amount of lead	$\text{air} \overset{\#\#}{>} H_2O,\ N_2,\ O_2 \overset{\#\#}{>} H_2$
amount of manganese	$H_2,\ N_2 \overset{\#\#}{>} H_2O \overset{\#}{>} \text{air} \overset{\#}{>} O_2$
brightness	$\text{air} \overset{\#\#}{>} O_2 \overset{\#}{>} N_2,\ H_2O \overset{\#\#}{>} H_2$

(*d*) *Effect of the source of silica on the residual amounts of manganese and lead.*—The results described above were obtained for the silica, which was prepared from ethyl silicate, and they were compared with those for the silica prepared from sodium silicate. These results are shown in Table VI, in which the values are expressed by percentage of the residual amounts of activators remaining after firing to those present before firing. The values above 100 may be caused by the fact that, although activators were not dissipated, the decrease in weiget was brought out by the evolution of gas produced during the raction for formation of the host lattice. From these results, it is shown that, if the silica from sodium silicate is used instead of one from ethyl silicate, lead is decreased remarkably, and manganese decreases only a little, so the decrease in brightness might be expected.

Table VI

Effects of the source of silica on the residual amount of manganese and lead

	Source of silica	Atmosphere				
		air	H_2O	O_2	H_2	N_2
Amount of lead	Ethyl silicate	50	31	33	17	31
	Sodium silicate	16	16	23	—	7
Amount of manganese	Ethyl silicate	74	74	68	107	106
	Sodium silicate	107	104	111	106	122

Discussion

The amount of activators was determined for various phosphors before and after firing by means of polarography. These procedures were considered to be one of the most effective methods to control the production of phosphors. Almost all of the activators, which are now used for the present phosphors, could be analysed by employing polarographic methods. We found it, however, difficult to detect some of impurities in the raw materials of phosphors, for example, iron in purified ammonium diphosphate.

Manganese or copper was not dissipated during firing, while antimony or lead seemed to be lost in that period. The fact that the amount of manganese in Zn_2SiO_4 : Mn or $(Zn, Be)_2SiO_4$: Mn was increased during firing, may be explained by the assumption that the water contained in these batches, probably as silicic acid, was lost during firing. The reason why antimony content differs between 3 samples of white phosphors might be found in their different contents of one kind of calcium halophosphate phosphors.

The factorial design of experiment, which is used for the determination of effects of atmosphere and firing time on the brightness, seems to be one of the most powerful methods for the control of the phosphor production and gives a good result for the case of calcium silicate phosphor. In this case, the residual amounts of activators were analysed by polarography and used as the additional factorial effects for the analysis of covariance of the brightness. The results obtained from this analysis could clarify the effects of atmosphere and firing time on the residual amounts of activators and the brightness separately. From these results, it is shown in the calcium silicate phosphors, that lead

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7) H. C. Froelich, *Trans. Electrochem. Soc.*, **93**, 101 (1948).

has a more significant effect upon the brightness than manganese and the change of atmosphere causes that of the amount of activators and the brightness. The fact, that, with the increase of the amount of lead the brightness is increased, while manganese has an opposite effect, is in accord with the previous results⁷⁾, but we could not obtain such a decisive results when hydrogen was employed as an atmosphere, as reported previously. As to the source of silica, it will be preferable to use one from ethyl silicate, because the increase of the brightness may be expected.

Summary

The amount of activators, which are now used for the present phosphors, was determined by means of polarography. The results obtained shows that manganese or copper is not dissipated during firing, while antimony or lead is dissipated in that period.

As for calcium silicate phosphors activated by manganese and lead, the residual amounts of activators were analysed by polarography and, these amount being taken as the additional factorial effects, the analysis of covariance was carried out to see the effects of atmosphere and firing time on the brightness. The results obtained show that the amount of lead has a more significant effect upon the brightness than manganese and the change of atmosphere causes that of the amount of activators and the brightness.

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Government Chemical Industrial
Research Institute, Tokyo
Hatagaya, Tokyo