X-RAY STUDY OF THE SYSTEM LEAD MONOXIDE - ANTIMONY PENTOXIDE -STANNIC OXIDE*

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A study of antimony yellow in the system, PbO-Sb_2O_5-SnO_2 was made by X-ray analysis and the spectro-reflectance measurements. Seven compositions were tried for investigation at temperatures ranging from 700 C. to 1100° C., and the results indicated that the antimony yellow containing tin oxide is the solid solution of pyrochlore type having the general formula $A_2B_2O_7$ or M_4O_7.

Introduction

The system, PbO-Sb_2O_5-SnO_2, is an example of antimony yellow or Naples yellow which is defined as the basic antimonate of lead and is one of the most important types of ceramic pigments. Although ceramic pigments have been the subject of interest to different ceramists in the past, the mineral compositions of most pigments are still not clear. Encyclopaedia of the Ceramic Industries[1] supply various recipes for the preparation of antimony yellows, but their compound formation in high temperature reactions have not been described. Parmelee[2] simply adds, "Antimony performs two important functions in silicate fusions, such as, in glazes; it acts both as an opacifier and as a colouring agent. When used alone, it does not appear to be capable of yielding coloured melts; the yellow ascribed to it is caused either by the presence of the oxides of lead or iron."Seger[3] also suggests several compositions for the pigments but does not mention anything about the nature of the solid state reactions.

Antimony yellow having the simplest composition, $2PbO.Sb_2O_5$, has been reported[4] to have formed pyrochlore— the mineral, pyrochlore is a complex oxide having the general formula $A_2B_2O_7$, where A=Na, Ca, K, Mg, Fe_2, Mn_2, Sb_3, Pb, Ce, La, Di etc., and B=Cb, Ta, Sn, Fe^3, W-, but it is a common fact that antimony yellow for use in ceramics has more complicated compositions, as in which case, it is essential to add tin oxide, aluminium oxide and iron oxide, singly or together, as secondary constituents.

Antimony yellow was orginally the pigment for lead glazes, and it is said that the effects of the secondary oxides are to make the pigments more stable and more useful for glazes which contain less lead oxide and mature at a higher temperature. It was, however, still unknown whether there is any formation of pyrochlore in the present system, and thus, this investigation was undertaken.

*This work was done at the Nagoya Government Industrial Research Institute, Japan.

In all the experiments, mixtures of different ingredients of definite proportions were calcined at several suitable temperatures, and the reaction products were studied by X-ray analysis and the spectro-reflectance measurements.

Experimental

Raw materials used were: (a) Red-lead (for PbO)-chemically pure sample, (b) Antimony pentoxide-guaranteed reagent, and (c) Metastannic acid (for SnO_2)-chemically pure sample with 14% moisture.

Seven compositions (Table 1) in the PbO-Sb_2O_5-SnO_2 system in which the ratio of metals to oxygen is 4:7 were used for investigation.

TABLE 1.—MOLAR COMPOSITION OF ANTIMONY YELLOW.

Expts.	N1	N2	N3	N4	N5	N6	N7
PbO	2.0	6.2	4.33	2.3	2.67	3.67	1.0
Sb_2O_5	1.0	3.0	2.00	1.0	1.00	1.00	—
SnO_2	—	0.6	1.00	1.0	2.00	5.00	3.0

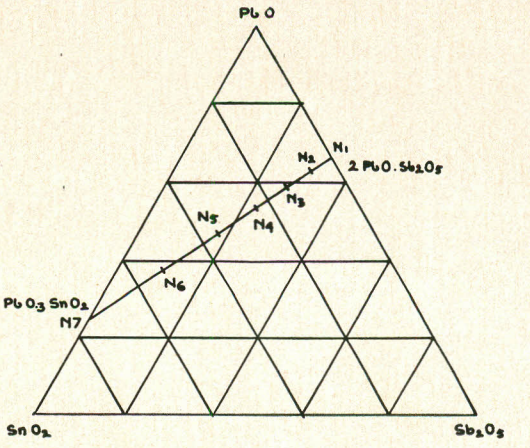

FIG. 1

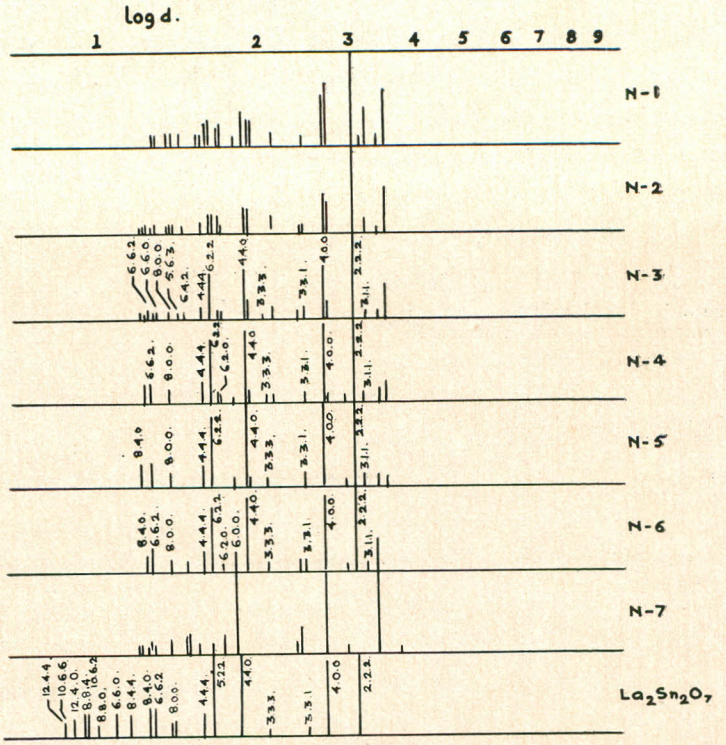

Fig. 2.—X-ray analysis of products from seven different compositions.

FIG. 2.

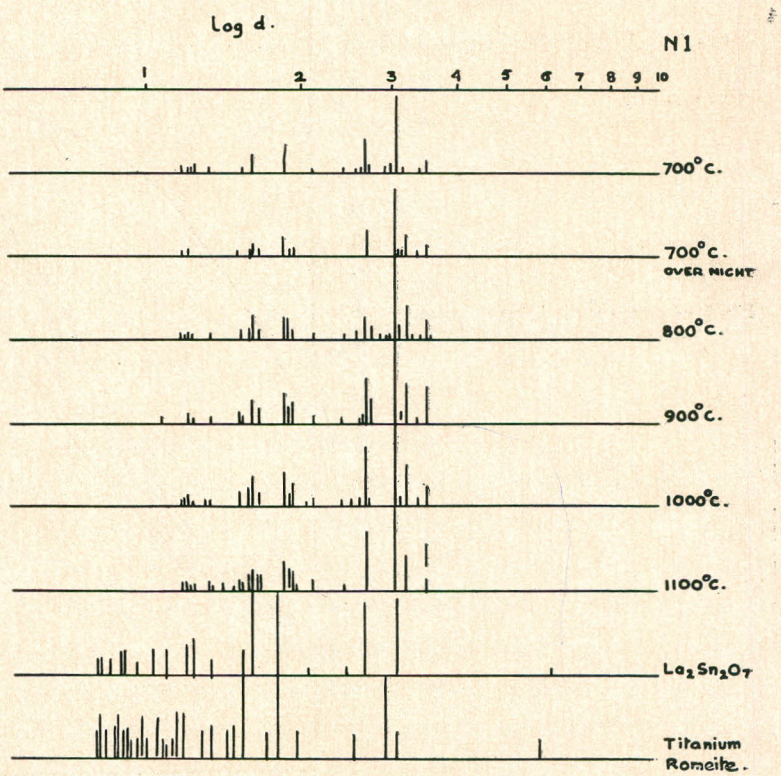

Fig. 3.—Log d values for sample N 1 fired at different temperatures.

FIG. 3.

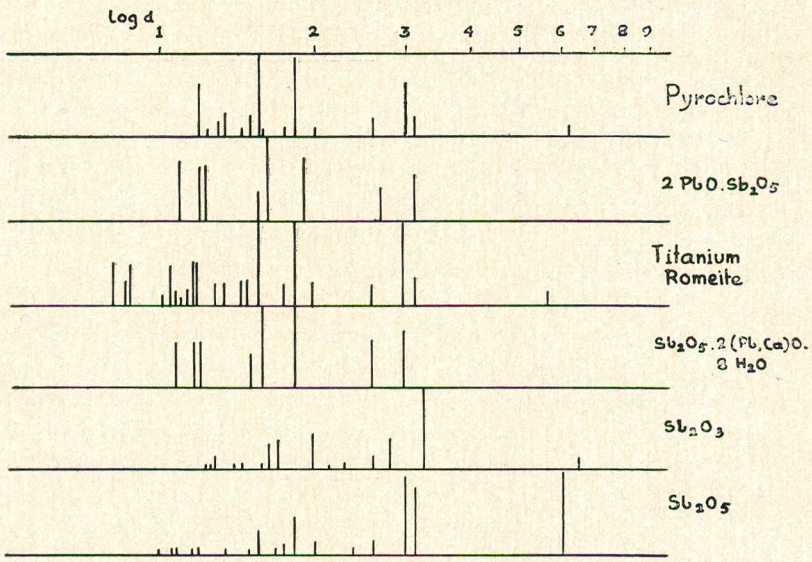

Fig.. 4.—Log d values for serveral compo unds along with a standard pyrochlore.

FIG. 4.

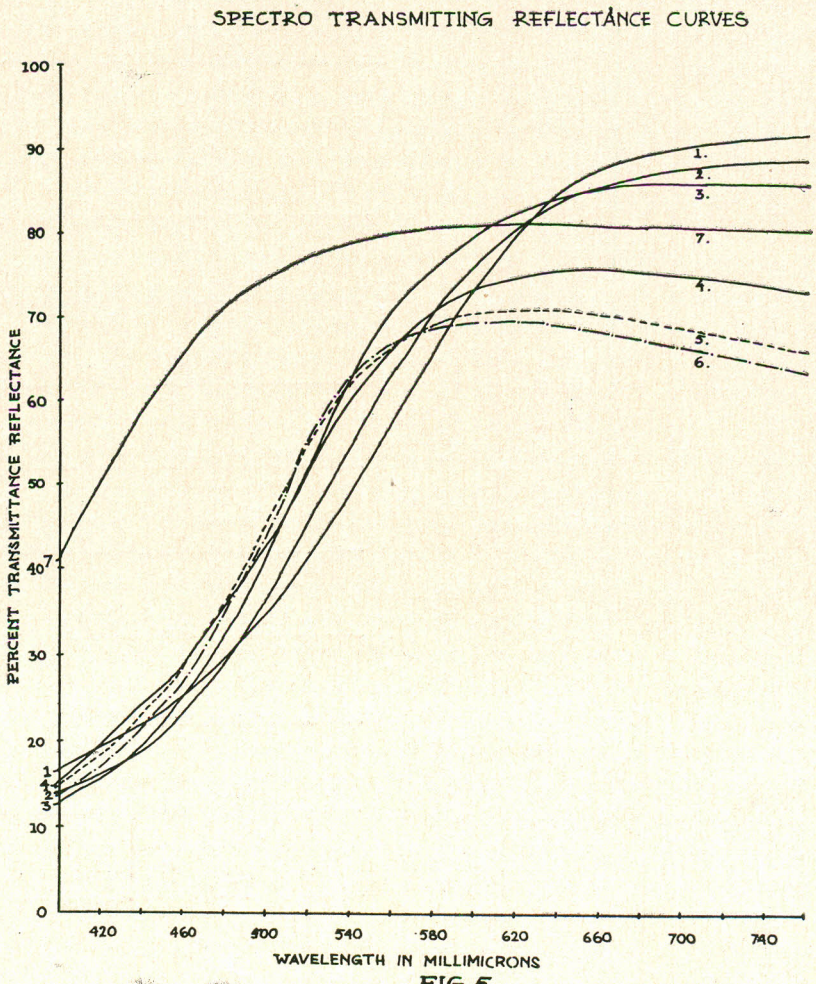

Fig. 5.—Spectro transmitting reflectancce curves for the seven products.

FIG.5.

For such experiment, 50 g. total of the ingredients were accurately weighed, made a thin paste with water, ground and mixed intimately by automatic mortar-pestle. After drying at 110°C., the samples were again ground (in dry condition) and fired at 700°, 800°, 900°, 1000° and 1100°C. (7-g. samples were taken for firing in each experiment, and the desired temperature was, in each case, kept constant for 2 hours).

The reaction products were ground fine, washed with dilute hydrochloric acid and water respectively in order to remove unreacted oxides, dried, and studied by X-ray analysis (X-ray diffraction patterns) and by the spectro-reflectance measurements (Hitachi Spectro-photometer, EPR-1). Calculation of the X-ray data and thereby the determination of the nature of the compound formed were made in the usual way.[5,6] Colours of the reaction products at different firing temperatures were also noted as shown in Table 2.

TABLE 2.

Temp. °C.	N1	N2	N3	N4	N5	N6	N7
700	Bistre	Bistre	Bistre	Buff	Buff	Light cinnamon	Cream straw
700	Yeilow orange	Cadmium yellow	Naples yellow	Brilliant yellow	Cream yellow	Cream yellow	Ivory yellow
750*	,,	,,	,,	,,	,,	,,	,,
800	,,	Yellow orange	Yellow orange	Buff	Buff	Light cinnamon	Cream straw
900	,,	Cadmium yellow	Brilliant yellow	Cream yellow	Cream yellow	Cream yellow	Ivory yellow
10000	,,	,,	Naples yellow	Brilliant yellow	,,	,,	,,
1100	,,	,,	,,	,,	,,	,,	,,

* In these two experiments, the desired temperatures were kept constant overnight as against 2 hours in other cases.

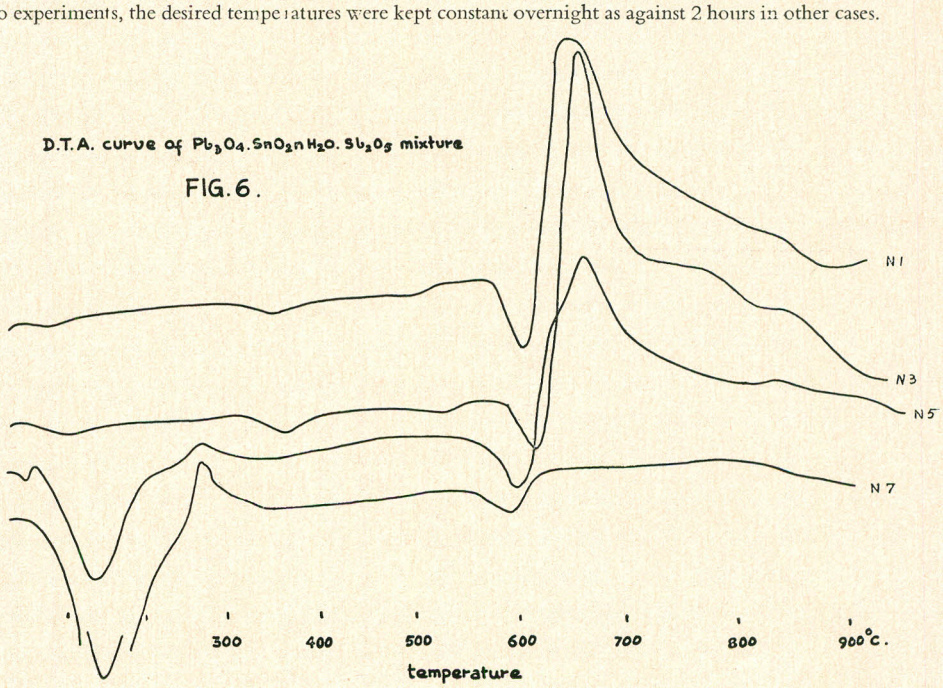

Fig. 6.—D.T.A. curve of $Pb_2O.\ SnO_2nH_2O$ Sb_2O_5 mixture.

Results and Discussion

The resuts of X-ray analysis of all the seven products fired at the optimum temperature of 1100°C. are shown in Fig. 2 by log d values along with the log d values of lanthanum stannates standard pyrochlore compound (log d values have been plotted against intensities of the X-ray lines. In Fig. 2, most of the prominent peaks of the reaction products are seen to coincide with those of lanthanum stannate which shows the formation of pyrochlore). Sample No. N1 fired at different temperatures are represented in Fig. 3 by log d values; whereas, for the sake of comparison, log d values of several compounds along with a standard pyrochlore are given in Fig. 4. Spectro-reflectance curves which have been shown in Fig. 5 state that all these pigments are compounds of the same nature. Differential thermal analysis (D.T.A.) curves have been given in Fig. 6.

It could, thus, be said, on the basis of the results of X-ray analysis and the spectro-reflectance curves, that the antimony yellow containing tin oxide is the solid solution of the pyrochlore type having the general formula $A_2B_2O_7$ or M_4O_7 All the compounds on the line binding Pb_2O (Sb_2O_5 and $PbO_3.SnO_2$ in the triangle-diagram Fig. 1) satisfy this condition.

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