LEAD INDUSTRIES ASSOCIATION, INC.
292 MADISON AVENUE
NEW YORK, N. Y. 10017

February 20, 1964

SUBJECT: REPRINT ON LEAD ENAMELS

To Members of the Lead Industries Association, Inc:

We have obtained copies of the attached reprint on low-temperature, lead-bearing enamels for steel for distribution to enamelers, frit manufacturers, graduate and under-graduate students in enameling, and others for whom this study might prove useful.

This work was done at the University of Illinois under a research fellowship sponsored by the International Lead Zinc Research Organization.

Particularly where students in enamel classes are concerned, we think this piece will serve to encourage further work with lead. In addition, this reprint will be offered in the "Lead Library" listing in LEAD magazine, which is sent to about 8,000 ceramists.

Members may obtain 25 copies of this reprint free of charge, and larger quantities at our cost of 11 cents per copy.

Very truly yours,

Jerome F. Smith

Jerome F. Smith

dmz

Enclosure

Look Ahead with Lead

[Reprinted from The American Ceramic Society Bulletin, Vol. 42, No. 11, November 1, 1963]

Molybdenum trioxide (MoO_3) in combination with lead produces lead molybdate crystals which may serve as an opacifier in low temperature enamels. Crystallization characteristics of lead molybdate, with respect to composition of the enamel and firing temperature, were studied. The influence of size and number of crystals determined the reflectance characteristics in the visible spectrum of the enamel. Methods used in this investigation were X-ray analysis, differential thermal analysis, and electron microscopy.

Crystallization Characteristics of Lead Molybdate in Low-Temperature Enamels

R. B. AMIN

Engineering Research Laboratory, Engineering Department
E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

R. L. COOK

University of Illinois, Urbana, Ill.

LOW-TEMPERATURE ENAMELS having opacity comparable to conventional white enamels and firing temperature as low as 1200°F are difficult to formulate. Generally, a lead-borosilicate type of glass is used for the low temperature enamel. If a crystalline material with a high index of refraction is to be used as an opacifier, it should be such that it can be easily crystallized into a large number of small crystals in the lead-borosilicate enamel glass matrix. The weakened structure of lead borosilicate glass seems to favor the crystallization of large ionic complexes like MoO_4^{-2}, WO_4^{-2}, CrO_4^{-2}, and UO_4^{-2}. Lead molybdate, $PbMoO_4$, is a crystalline compound having a tetragonal scheelite structure like $CaWO_4$ and a high index of refraction (2.304–2.402). The melting point of $PbMoO_4$ is 1919°F, which is high enough to give a stable crystalline precipitate during the firing process of the enamel. The purpose of this investigation was to study the crystallization characteristics of lead molybdate in low-temperature enamels based on lead-borosilicate glasses and its reflectance characteristics in the visible spectrum.

There is very little information available in literature about the use of lead molybdate as an opacifier in low temperature enamels; however, Kautz[3] has described low-temperature enamels in which large amounts of lead molybdate in the mill batch produced a cream-white opaque enamel with good adherence at a firing temperature of about 920°F.

Experimental

A series of frit compositions were formulated to study the effects of various frit constituents on the crystallization characteristics of lead molybdate in low-temperature enamels. Percent oxide compositions of the frits are given in Table I.

Heat Treatment of the Frits and X-Ray Analysis

Heat treatment of the frits was carried out in a tube furnace. Fifteen grams of dry ground frit (1% on 200 mesh sieve) was heat treated for 15 minutes at various temperatures between 1000° and 1300°F. The heat treated frits were quantitatively analyzed by X-ray diffraction analysis using an internal standard technique.

Enamel Panel Preparation

The dry ground frits were also used for the slip preparation. The mill batch used is as follows:

Ground frit	100.00
Colloidal silica	1.75
Water	35.00

Cleaned enamel grade iron panels with nickel deposition of 0.10 to 0.12 g per square foot were preoxidized at 1000°F for 5 minutes. The panels were sprayed directly at a weight of application of 25 g per square foot and were fired for 15 minutes at various temperatures between 1000° and 1300°F. The reflectance characteristic in the visible spectrum of the panels was obtained on a recording spectrophotometer.

Presented at the Sixty-Fourth Annual Meeting of The American Ceramic Society in New York, N. Y., May 2, 1962 (Ceramic-Metal Systems Division, No. 14-E-62).

[1] W. A. Weyl, Coloured Glasses, p. 141. Society of Glass Technology, Sheffield, England, 1951. 541 pp.; *Ceram. Abstr.*, 1952, September, p. 159d; reprinted by Dawson's Pall Mall, London, 1959. 541 pp.

[3] Karl Kautz, "Molybdenum in Enamels: III, Typical Molybdenum Enamels," *J. Am. Ceram. Soc.*, **28** [3] 76–82 (1945).

Table I. Compositions of Enamels No. 1 to No. 12

Weight percent

Composition No.	Na_2O-PbO-B_2O_3 variations (1)	(2)	(3)	MoO_3 concentration (4)	(5)	(6)	(7)	$NaNO_3$ concentration (8)	(9)	(10)	(11)	LiO substitution (12)
SiO_2	27.00	27.00	27.00	29.47	29.15	28.54	27.68	27.40	30.53	29.85	29.19	27.00
PbO	25.65	25.65	30.65	32.30	31.00	31.29	30.34	30.04	33.45	32.72	32.01	30.65
Na_2O	17.55	15.05	12.55	13.23	13.09	12.84	12.42	12.30	13.71	13.40	13.10	10.05
LiO												2.50
B_2O_3	10.21	12.71	10.21	10.25	10.05	10.12	10.11	10.01	11.15	10.90	10.66	10.21
ZnO	5.11	5.11	5.11	5.37	5.32	5.21	5.06	5.01	5.56	5.45	5.33	5.11
MoO_3	5.11	5.11	5.11		1.06	3.13	6.06	7.00	5.28	5.45	5.33	5.11
$NaNSF_4$	8.41	8.41	8.41	8.87	8.77	8.60	8.53	8.24		2.23	4.59	8.41

Results and Discussion

Effect of Na_2O–PbO–B_2O_3

Frits No. 2 and No. 3 were opaque and showed all the intense peaks of lead molybdate on the X-ray diffraction pattern. Frit No. 1 showed only one, the most intense peak of lead molybdate; the other peaks were not well defined. None of these frits showed any visual sign of crystals at the smelting temperature of 1800°F. It appears that a considerable amount of lead molybdate was dissolved in the frit at the smelting temperature, but the frit becomes a supersaturated solution with respect to lead molybdate as it is cooled.

Figure 1 shows the plots of percent lead molybdate crystallized versus the temperature of heat treatment for frits No. 1, No. 2, and No. 3. These results show that an increase in Na_2O content above 15.05% at the expense of either PbO or B_2O_3 resulted in an increase in the solubility of lead molybdate in the firing range of the enamel. Frit No. 1 may have maximum crystal content at a temperature lower than 1000°F.

After the heat treatment at 1000°F, frits No. 2 and No. 3 showed a bluish coloration while frit No. 1 did not. The bluish coloration was thought to be due to the first stage of crystal growth in which the crystals are very small and there is an effect of Rayleigh scattering. The bluish coloration turned more white as the temperature of heat treatment was increased.

In order to get good glossy enamel, the firing temperature of enamel No. 2 was about 1125°F, and that of enamel No. 1 and No. 3 was 1150°F. The spectrophotometer curves of these enamels are given in Fig. 2. Here, also, the increased solubility of lead molybdate crystals in the firing range of the enamel No. 1 is noticeable.

Effect of MoO_3 Concentration

Composition No. 3 was selected as a base for this study. To the base composition less the molybdenum trioxide (Composition No. 4), additions of 0.6, 1.06, 3.13, 5.11, 6.06, and 7.00% of molybdenum trioxide were made (Compositions No. 4 to No. 8). The frit with no addition of MoO_3 was clear and did not show any peaks on the X-ray diffraction pattern. The frit with 1.06% addition of MoO_3 was slightly opaque but did not show any peaks on X-ray diffraction pattern. Frits with 3.13, 5.11, 6.06, and 7.00% additions of MoO_3 showed the peaks of lead molybdate. Figure 3 shows the role of MoO_3 concentration on the amount of lead molybdate crystallized after heat treatment. There is an increase in the amount of lead molybdate crystallized with each increment of molybdenum trioxide. These results of X-ray analysis showed good correlation with the spectrophotometer curves (Fig. 4). There was a marked increase in reflectance value with an in-

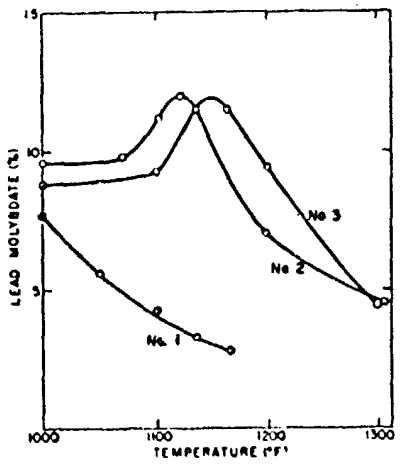

Fig. 1. Effect of Na_2O-PbO-B_2O_3 variation on the crystallization of lead molybdate in compositions 1, 2, and 3.

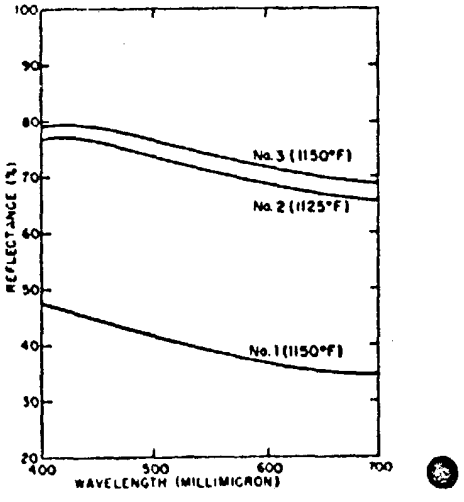

Fig. 2. Effect of Na_2O-PbO-B_2O_3 variation on the reflectance of enamels 1, 2, and 3.

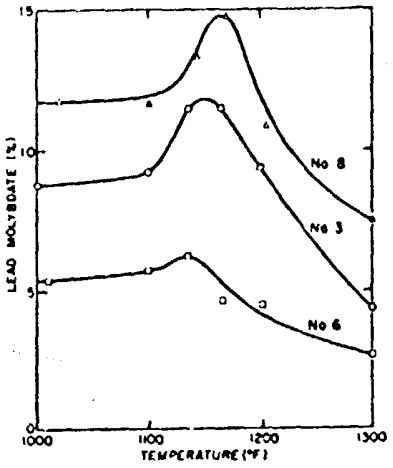

Fig. 3. Effect of MoO_3 concentration on the crystallization of lead molybdate in compositions (6) 3.13% MoO_3, (3) 5.11% MoO_3, and (8) 7.00% MoO_3.

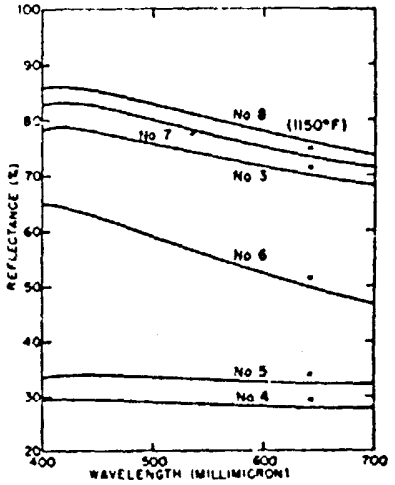

Fig. 4. Effect of MoO_3 concentration on the reflectance of compositions (4) 0.0% MoO_3, (5) 1.04% MoO_3, (6) 3.13% MoO_3, (3) 5.11% MoO_3, (7) 6.04% MoO_3, and (8) 7.00% MoO_3.

crease in molybdenum trioxide content. A composition with no molybdenum trioxide addition had a reflectance value of slightly less than 30%. Probably most of this reflectance is due to the presence of bubbles in the enamel structure. X-ray diffraction patterns of this frit, heat treated at various temperatures between 1000° and 1200°F, did not show presence of any crystalline material.

Effect of Na_2SiF_6

Frit No. 3 contained 8.41% Na_2SiF_6; in this base composition less the Na_2SiF_6 (Composition No. 9), additions of 0.0, 2.23, and 4.39% of Na_2SiF_6 were made (Compositions No. 9 to No. 11). Frits with 2.23 and 4.39% addition of Na_2SiF_6 were opaque white and showed peaks of lead molybdate. The frit with no addition of Na_2SiF_6 was clear and did not show any peaks. Figure 5 shows that, with increasing amounts of Na_2SiF_6, the maximum amount of lead molybdate crystallized by heat treatment has been shifted to a higher temperature and, also, the amount of lead molybdate was increased. With no addition of Na_2SiF_6, the maximum amount of lead molybdate crystallized in the frit was not more than 2 to 3%. Figure 6 shows that the reflectance value was increased with increase in Na_2SiF_6 addition, and there was less effect of Rayleigh scattering. It appears that the increase in Na_2SiF_6 addition not only increased the amount of lead molybdate crystallized but also increased the size of the lead molybdate crystals.

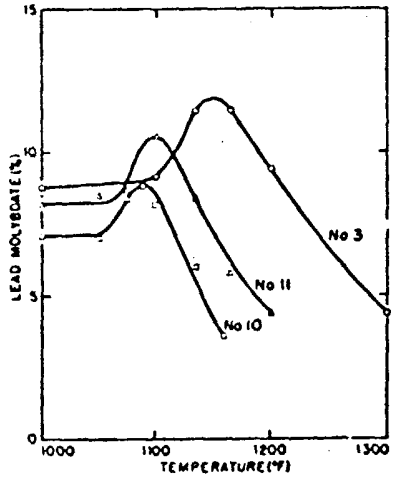

Fig. 5. Effect of Na_2SiF_6 on the crystallization of lead molybdate in compositions (10) 2.23% Na_2SiF_6, (11) 4.39% Na_2SiF_6, and (3) 8.41% Na_2SiF_6.

Effect of Li_2O Substitution

In base composition No. 3, 2.5% LiO was substituted for NaO (Composition No. 12). The effect of LiO on the crystallization of lead molybdate is shown in Fig. 7. The maximum for the amount of lead molybdate crystallized was shifted from 1140° to 1065°F and, also, the solubility of lead molybdate was increased. The spectrophotometer curves (Fig. 8) show that the firing temperature and the reflectance value were reduced with Li_2O substitution. Enamel No. 12, when overfired at 1150°F, gave a very low reflectance value of about 12%. There were three factors contributing to this decrease in reflectance: (1) the lead molybdate crystals were dissolved at the higher firing temperature; (2) the lithia substitution made the enamel glass more fluid, and the bubbles were removed from the enamel matrix during the firing process; and (3) the lithia containing enamel glass was very reactive and dissolved appreciable amounts of iron oxide formed during the preoxidation process of the cleaned metal.

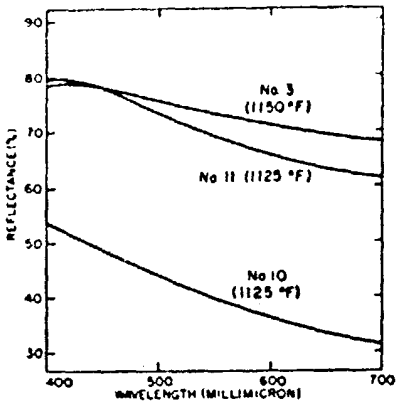

Fig. 6. Effect of Na_2SF_4 on the reflectance of compositions (10) 2.23% Na_2SF_6, (11) 4.39% Na_2SF_6, and (3) 8.41% Na_2SF_6.

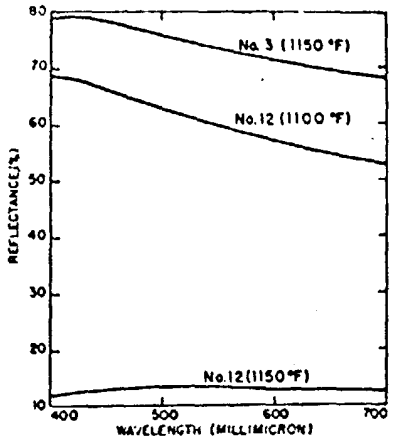

Fig. 8. Effect of Li_2O on the reflectance in compositions (3) 12.55% Na_2O, 0.0% Li_2O, and (12) 10.05% Na_2O, 2.5% Li_2O.

Differential Thermal Analysis

Various frits showed visual sign of crystal growth by change in coloration from bluish white to white as the temperature of heat treatment was increased from 1000° to 1150°F. Frits No. 3 and No. 12 were selected for this investigation. A manually controlled DTA apparatus was used.

The thermograms of frits No. 3 and No. 12 are given in Fig. 9. An endotherm due to the water removal was observed at 300° to 375°F for both the frits. In frit No. 12 substitution of 2.5% Li_2O for Na_2O showed a decrease in temperature of crystal growth exotherm from 1175° to 1075°F. A decrease in temperature from 1150° to 1065°F was also observed for maximum crystal content on heat treatment of the frit.

Electron Microscopy

A microscopic investigation of heat treated thin films of enamel glass (frit No. 3) did not provide enough information about the crystal habit and the size of the lead molybdate crystals. This was due to the small size, probably below 0.25μ, of the lead molybdate crystals. This fact was also evident from the spectrophotometer curves of the enamel panels. They showed higher reflectance value in the shorter wavelength region of the visible spectrum because of the small size of the crystals.

Enamel No. 3 was selected for electron microscope study. Panels with an application of 25 g per square foot and fired at 1150°F for 15 minutes were used for the replication. A cleaned panel was etched for 2 minutes by 5.0% glacial acetic acid solution in water. An intermediate replica of the etched surface was prepared using Fax Film plastic tape. Carbon replica was prepared from the intermediate replica. Carbon replica was examined in an RCA-EMU model electron microscope. An electron micrograph (Fig. 10) shows one dense and a few sparse areas of lead molybdate crystals. This study showed that most of the lead molybdate crystals present in the enamel glass matrix were acicular. Some irregularly shaped crystals were also present. The longitudinal dimension of the crystals ranged from 0.05 to 0.2μ. The other irregularly shaped crystals were all below 0.15μ in size. These results explain the Rayleigh scattering observed in the spectrophotometer curve of enamel No. 3. The color of the lead molybdate crystals in macro size is pale yellow, but, due to the small size of the crystals below 0.2μ, the enamel appears bluish

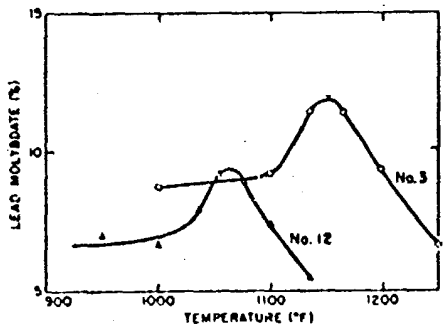

Fig. 7. Effect of Li_2O on the crystallization of lead molybdate in compositions (3) 12.55% Na_2O, 0.0% Li_2O and (12) 10.05% Na_2O, 2.5% Li_2O.

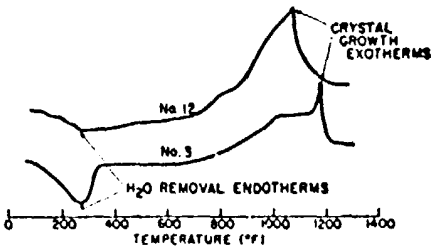

Fig. 9. Thermograms of frits (3) 12.55% Na_2O, 0.0% Li_2O and (12) 10.05% Na_2O, 2.5% Li_2O.

Fig. 10. Electron micrograph of lead molybdate crystals in enamel No. 3.

white. The cream-white color observed by Kautz[3] was probably due to the larger size of the lead molybdate crystals.

Summary

1. Lead molybdate crystallized in a low-temperature enamel glass matrix into a large number of small crystals and imparted to the enamel a reflectance value of 75 to 80%. The opacity obtained is comparable to the white enamels in which conventional opacifiers, such as titania, zirconia, and antimony oxide, are used.

2. The observation of melt condition and the results of X-ray diffraction analysis indicated that many of the frits were supersaturated with lead molybdate.

3. The various enamel constituents have marked influence on the crystallization of lead molybdate.

a. A sodium oxide content of more that 15.05% in these enamels increased the solubility of lead molybdate to a considerable extent and adversely affected the opacity.

b. An increase in molybdenum trioxide content from 1.06 to 7.08% increased the amount of lead molybdate crystallized and the reflectance value.

c. Sodium silicofluoride additions up to 8.41% increased the temperature of maximum amount of lead molybdate crystallized by heat treatment and, also, the amount that was crystallized.

d. Substitution of 2.5% lithia for soda lowered the temperature of maximum crystal content by 85°F, increased the solubility of lead molybdate, and lowered the firing temperature of the enamel.

4. Differential thermal analysis of two frits (No. 3 and No. 12) showed the crystal growth exotherms. The temperature of the exotherms were close to the temperature at which maximum amount of lead molybdate crystal content was observed on heat treatment of the frits.

5. Electron microscope study of the lead molybdate crystals present in enamel No. 3 showed that most of the crystals were acicular and some were irregularly shaped. The size of the crystals ranged from 0.05 to 0.2μ. The small size of the crystals gave an explanation for the Rayleigh scattering. ☆

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