ORIGINAL PAPERS AND DISCUSSIONS

THE USE OF SUBSTITUTES FOR TIN OXIDE IN GLAZES

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A search of our *Transactions* reveals that little work has been done with substitutes for tin oxide in glazes, outside of the enameled iron field. In enamels for cast iron and sheet steel the principal substitute for tin oxide has been antimony oxide. A review of the *Transactions* develops the following references:

J. B. Shaw, in "The Allowable Limits of Variation in the Ingredients of Enamels for Sheet Steel," Vol. XI, p. 151, says: "SnO₂ produces opacity alone, but it may be entirely replaced with ZnO plus Sb₂O₃, with equally good results; 0.13 equivalent of ZnO plus Sb₂O₃ or SnO₂ is sufficient to produce a good white opacity by using two coats of white."

Homer F. Staley, in "The Control of Fusibility in Enamels," Vol. XIII, p. 506, states: "While bone ash can be used as a weak opacifying agent to some extent, it is liable to cause minute pin-holes in the enamel and vesicular structure in any part of the piece that should happen to be overheated."

R. E. Brown, in "The Replacement of Tin Oxide by Antimony Oxide in Enamels for Cast Iron," Vol. XIV, p. 752, writes: "The effect of Sb₂O₃ is to increase the maturing temperature, and to increase the whiteness and opacity when employed between the limits of 0.0-0.9 equivalent Sb₂O₃." To produce a good white with SnO₂ 0.15 equivalent was required.

Homer F. Staley, "Antimony Compounds as Opacifiers in Enamels," Vol. XVIII, p. 188: "Oxide of antimony enamels of good gloss can be made." "Opaque whites are produced by controlling the heat treatment and composition."

Emley and Young, "The Production, Manufacture and Use of Compounds of Barium," Vol. XVIII, p. 247: "Barium salts are also used extensively in the preparation of mat glazes. An important use of barium is in the manufacture of enamels for iron. When tin oxide is used as an opacifier, the presence of barium is very desirable. . . ."

Ercill C. Hill, "White Terra Cotta Glazes at Cones 6-7," Vol. XVII, p. 383, found that: "The opacity and white color of the glazes increases with the increase of SnO_2 . It also increases with increase of ZnO , and with increase of BaO when the ratio of CaO to BaO is less than 1 : 1. Increase of SnO_2 is more effective in increasing opacity than either ZnO or BaO ."

Kirkpatrick, Arnold and Geiger, "An Attempt to Fit Enamels to Plastic Clay Bodies," Vol. XVIII, p. 145, found that 0.12 equivalent of SnO_2 was sufficient to produce opacity in an enamel for bricks.

J. B. Shaw, "Antimony Oxide as an Opacifier in Cast Iron Enamels," *J. Am. Ceram. Soc.*, Vol. I, p. 511, asserts that: "Extreme care in proportioning the raw materials, very careful and thorough mixing, and proper smelting, will insure the successful use of antimony oxide."

Homer F. Staley, "Enamels for Cast Iron," *J. Am. Ceram. Soc.*, Vol. I, p. 706, says that sodium metantimonate has been extensively used in America during recent years as an opacifying agent for cast iron enamels which are leadless, or with low or medium lead. He states that "The essential difference between sodium metantimonate enamels and those in which the oxide of antimony is used as the chief opacifier is that the latter contain much larger amounts of sodium nitrate."

These references show that practically all of the investigations into the matter of substitutes for tin oxide as an opacifier has had to do with enamels for metals. The work done by Hill in the field of terra cotta glazes covers the ground very well, but he tried only ZnO and BaO to determine their effects upon SnO_2 .

Scope of this Investigation.—In the work under consideration twelve different substitutes were used to replace tin oxide in four

different types of glazes. The corresponding number in each of the four series contains the same opacifier.

SERIES R.—Raw lead glaze at cone 02

			Batch weights
0.70 PbO			167.7 White lead
.10 K ₂ O	0.15 Al ₂ O ₃	1.7 SiO ₂	55.7 Feldspar
.10 CaO		.10 SnO ₂	10.0 Whiting
.10 ZnO			8.1 Zinc oxide
			12.9 China clay
			54.0 Flint
			14.9 Tin oxide

SERIES F.—Fritted wall tile glaze at cone 02

			Batch weights
Frit 0.24 K ₂ O			133.7 Feldspar
.28 Na ₂ O	0.24 Al ₂ O ₃	3.56 SiO ₂	123.6 Flint
.48 CaO		1.12 B ₂ O ₃	48.0 Whiting
			106.9 Borax
			69.4 Boric acid
Glaze 0.49 PbO		2.25 SiO ₂	193.5 Frit
.12 K ₂ O	0.19 Al ₂ O ₃	.571 B ₂ O ₃	126.4 White lead
.15 Na ₂ O		.10 SnO ₂	18.1 China clay
.24 CaO			19.5 Flint
			14.9 Tin oxide

SERIES T.—Terra cotta raw glaze at cone 6

			Batch weights
0.200 KNaO			111.4 Feldspar
.375 CaO	0.325 Al ₂ O ₃	2.50 SiO ₂	37.5 Whiting
.175 BaO		.10 SnO ₂	34.5 Barium
.250 ZnO			20.2 Zinc oxide
			32.2 China clay
			63.0 Flint
			14.9 Tin oxide

SERIES P.—Raw porcelain glaze at cone 9

			Batch weights
0.36 K ₂ O			174.9 Feldspar
.23 ZnO	0.54 Al ₂ O ₃	4.00 SiO ₂	30.0 Whiting
.35 CaO		.10 SnO ₂	16.2 Zinc oxide
.06 BaO			9.8 BaCO ₃
			38.7 China clay
			78.0 Flint
			14.9 SnO ₂

Substitutes Used for SnO_2 .—In the first number of each series 0.10 SnO_2 was used, and in the succeeding numbers the same amount by weight of the substitutes was used to replace the tin oxide. Some of these substitutes are so composed that it is not possible to use them by equivalents, and as they are all purchased by weight, that is the only practical method of comparison when price is considered.

- Glaze 1—Tin oxide marketed by Roessler & Hasslacher Chemical Co.
- Glaze 2—Terrar from Roessler & Hasslacher Chemical Co.
- Glaze 3—Zirconium oxide from A. D. Camp, Cleveland.
- Glaze 4—Zirconium oxide from Aluminum Alloys Co., Niagara Falls, N. Y.
- Glaze 5—Zirconium oxide (pure) from Pennsylvania Salt Co.
- Glaze 6—Fluorspar.
- Glaze 7—White antimony oxide.
- Glaze 8—Aluminum oxide (hydrated)
- Glaze 9—Kryolith, from Roessler & Hasslacher Chemical Co.
- Glaze 10—Leukonin, from Roessler & Hasslacher Chemical Co.
- Glaze 11—Stannolite, from Wenger's, Ltd., England.
- Glaze 12—Phosphorite, from Wenger's, Ltd., England.
- Glaze 13—Lithopone, from Harrison Bros., Philadelphia.

Data on Substitutes.—"Terrar" is an imported product largely used in the enamel iron industry before the war made it impossible to obtain it. It is probably composed largely of zirconium oxide and zirconium silicate. "Leukonin" is also used in enamel iron work, and is essentially sodium metantimonate. It is not recommended for general glaze purposes. "Stannolite" and "Phosphorite" are compounds whose composition is unknown. They are said to be used very extensively in England for opacifiers in place of tin oxide. "Lithopone" is a compound of 30 per cent zinc sulphide and 70 per cent barium sulphide. It is now being used very largely by the rubber manufacturers in place of zinc oxide.

Firing.—All glazes were made up in batch weights in grams, thoroughly ground in a ball mill, and applied to small grogged body tiles which had previously been fired to cone 9. Series "R," "F" and "T" were fired in a large test kiln to the indicated heats. Series "P" was fired in a large sanitary kiln requiring 120 hours for firing.

Results from Firings.—

SERIES R.

- R- 1—Semi-opaque. Milky white. Not well glossed.
- R- 2—Less opaque than 1. Not so white.
- R- 3—Not quite so opaque as 2. Bubbled.
- R- 4—About the same as 2.
- R- 5—Similar to 3. Bubbled.
- R- 6—Clear glaze. Crazed.
- R- 7—Slight opacity. Full gloss.
- R- 8—Clear glaze.
- R- 9—Clear glaze. Badly crazed.
- R-10—Same opacity as 7.
- R-11—Same opacity as 7.
- R-12—Clear glaze. Crazed.
- R-13—Clear glaze. Not fully matured.

Tin oxide shows the best opacity in this series. Would require at least 0.15 equivalent for good opaque glaze. None of the substitutes offer much encouragement, although "terrar" might show results if used in much larger amounts than is required of the tin oxide.

SERIES F

- F- 1—Semi-opaque enamel. Glossy.
- F- 2—Slightly more opaque than 2, but blistered.
- F- 3—Not quite so opaque as 1. Dull surface.
- F- 4—Less opaque than 3. More gloss.
- F- 5—Clear glaze. Full gloss.
- F- 6—Clear glaze. Full gloss.
- F- 7—Slight opacity. Full gloss.
- F- 8—Clear glaze. Full gloss.
- F- 9—Clear glaze. Full gloss. Crazed.
- F-10—Slight opacity. Less than 7. Full gloss.
- F-11—Slight opacity. Less than 7. Full gloss.
- F-12—Clear glaze. Glossy.
- F-13—Same as 11. Crazed.

Tin oxide is the best opacifier in this group. The commercial zirconium oxide in 2 is the next best. The pure zirconium oxide in 5 shows no opacity whatever. It is evident that this type of fritted glaze is not at all suited to use for opaque purposes. Glaze "R" and glaze "F" are about equal.

SERIES T

- T- 1—Good opaque enamel. Glossy.
- T- 2—Fair opaque enamel. Glossy. Not quite so white as 1.

- T- 3—Good white opaque. Beaded. Not quite so white as 1.
- T- 4—Fair opacity, but less than 2. Glossy.
- T- 5—Good white opaque. Not quite equal to 1.
- T- 6—Only slight opacity. Crazed.
- T- 7—Opaque white. Almost equal to 1 except that it is bubbled.
- T- 8—Fair opaque white. Mat surface.
- T- 9—Slightly more opacity than 6. Semi-glossy.
- T-10—Good opacity. Glossy. Not fully freed from bubbles.
- T-11—Semi-opaque. Glossy.
- T-12—Semi-opaque. Glossy.
- T-13—Semi-opaque. Slight gloss.

There are more opaque glazes in this series than in the first two. Zirconium oxide (pure) in 5 seems equal to tin oxide for opacity, but the glaze is not quite so white. Antimony oxide is equal to tin oxide for opacity but the glaze is not fully developed. Aluminum oxide produces a very good opaque mat glaze. Leukonin seems almost equal to tin oxide for opacity, color and gloss.

SERIES P

- P- 1—Good opaque white. Crawled some.
- P- 2—Semi-opaque white. Same as "T"-2.
- P- 3—Same opacity as 1. Not so white. Crawled.
- P- 4—Same as 2.
- P- 5—About the same as 3. Not quite so good as 1.
- P- 6—Almost a clear glaze.
- P- 7—Flocculent opaque white. Crawled.
- P- 8—Semi-opaque. Less than 2 and 4.
- P- 9—Clear glaze. Glossy.
- P-10—Slight opacity. Glossy.
- P-11—Semi-opaque; less so than 8.
- P-12—Slight opacity. Glossy.
- P-13—Slightly opaque, material in suspension.

Tin oxide still seems to be the best opacifier, although "terror" and zirconium oxide, especially the pure, seem to offer possibilities of being good substitutes. More material might be required for the same opacity as from tin oxide, but the other defects can no doubt be overcome.

General Conclusions

1. Zinc oxide is of great assistance in producing opacity with tin oxide and with the substitutes, as is shown in series "T" and "P."

2. Barium exerts a marked influence on opacity, as shown in a comparison of series "T" with series "P."

3. Zinc and barium oxide have more influence on opacity than the clay content.

4. A glaze of type "T," with both barium and zinc, is most favorable for opacity. This applies to tin oxide as well as the substitutes.

5. Where they can be used leukonin and antimony oxide are cheaper than tin oxide. Zirconium oxide is the best substitute for tin oxide if it can be procured at a sufficiently low price.