

LOW-LEAD BORO-SILICATE GLAZES FOR ARTWARE

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Systematic studies have been made of the substitution of zinc oxide by magnesium oxide in the low-lead boro-silicate glazes maturing at cone 06(980°C.). In investigations have been extended to the study of the effect of zinc oxide when included in frit or in mill batch. Glazes of excellent visual and physical properties have been produced with magnesia as a glaze ingredient. Zinc oxide has proved to give its full effect when included in mill batch rather than when it is a part of the frit. Some really good glazes for practical purposes have been developed.

Introduction

This investigation is restricted to the production of lead boro-silicate glazes for artware, maturing at cone 06(980°C.). Limiting values of the more common RO fluxes evaluated in the preliminary laboratory studies are employed. The glazes falling within the range of triaxials planned are, therefore, expected to possess good texture with only slight variations. Zinc and zincless compositions have been formulated. A moderate quantity of zinc oxide imparts superior lustre, improves finish and enhances opacity but its detrimental effect on the underglaze colour¹ is a serious drawback. The replacement of zinc oxide by magnesium oxide in the frit not only removes the above mentioned defect but also provides a cheap and readily available alternate flux. Lead oxide, however, is the ingredient which produces the main fluxing action.

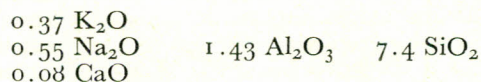
The advantage of fritting, besides rendering the soluble constituents insoluble, is that almost all the chemical reactions are completed on frit-smelting. Chemical reactions between the glaze constituents are accompanied by evolution of gases. It is, therefore, a distinct gain to pre-melt the glaze materials in frit furnace and thereby to eliminate an important cause of bubbles, blisters and the related surface imperfections.

Opaque glazes seem to be more suitable for our conditions, because the body used hitherto and elsewhere in Pakistan, does not fire to a pure white state. Transparent glazes, on the other hand, not only will refract the defects of the body but also will combine with the metallic impurities scattered throughout, to form coloured spots.

The information presented here may readily be applied as a basis for developing working formulas by the artware manufacturers.

Raw Materials

Indigenous raw materials, for the most part, are employed for the body and the glaze preparation, indigenous potash feldspar with empirical formula,



and molecular weight 674 is employed in all the glazes reported here. The fusion temperature of the feldspar was found to be 1200°C.

Finely-ground native dolomite of molecular formula 1.0 CaCO₃, 0.76 MgCO₃ and marble chips are the sources of MgO and CaO. Quartz with 97.5 percent SiO₂ and Mianwali clay (89 percent clay content, 0.96 percent Fe₂O₃ and the rest as free silica) are the other materials of this group.

Small quantities of the regular commercial grade chemicals such as borax, boric acid, zinc oxide and zircon are among the imported materials.

Procedure

1. *Plan of Investigation.*—These studies are based upon a lead-boro-silicate glaze composition designated as A-7 in the triaxial A and Table 1. The glaze contains 0.5 molecular equivalent of PbO which is replaced partially by zinc oxide. In another attempt, magnesium oxide is substituted for zinc oxide. This substitution did not impair the desirable properties of the glaze, nor did it elevate the maturing temperature significantly. As a means of verifying this observation and obtaining definite and workable limits for magnesium oxide, a more detailed investigation of this particular point was made. Two triaxial fields, each having 10 glaze compositions, were planned for the study of this point. They have similar components of the base group at the corners, except

TABLE I.—BATCH COMPOSITIONS OF THE FRITS FOR TRIAXIAL A.

Frit No.	Feldspar	Quartz	Marble chips	Red lead	Borax	Boric acid	Zinc oxide
A-1	18.3	34.2	18.0	14.0	9.5	6.2	—
A-2	17.4	33.4	14.4	20.1	9.1	5.6	—
A-3	18.2	34.8	15.1	14.0	9.5	5.9	2.5
A-4	16.8	32.2	11.1	25.6	8.8	5.5	—
A-5	17.5	33.5	11.6	20.0	9.2	5.7	2.4
A-6	18.3	35.0	12.1	14.1	9.6	5.9	5.0
A-7	16.2	31.0	8.0	31.1	8.5	5.2	—
A-8	16.8	32.2	8.3	26.1	8.8	5.5	2.3
A-9	17.6	33.8	8.7	20.2	9.2	5.7	4.8
A-10	18.4	35.2	9.1	14.2	9.6	6.0	7.5

that zinc oxide in triaxial A is replaced by magnesium oxide in triaxial B. In these compositions, zinc oxide and magnesium oxide are incorporated in frits. A third triaxial (C) has been planned to conduct a comparative study of the effect of zinc oxide when it is a part of frit (triaxial B) or when it is in mill batch.

2. *Frit Preparation.*—Carefully-weighed ingredients of all the frit batches (100 mesh fineness) were mixed in an edge runner. The firing was accomplished in an oil-fired furnace. Thoroughly mixed frit batches of 500 g. each were smelted in a Mianwali fireclay crucible, the temperature was raised gradually to 1100°C. in about an hour, and maintained for half an hour. The molten mass was disintegrated in water. The shattered mass thus obtained was dried and ground to an approximate fineness of -100 mesh screen. Frit compositions are given in Tables 2 and 3.

3. *Test on Frit.*—Solubility in water: The solubility of frit particles in water was determined according to the procedure adopted by Koenig.²

4. *Glaze Preparation.*—The glazes were milled individually to a fineness of approximately 0.5 percent residue on a 200 mesh screen. The specific gravity of the glaze slip was adjusted to 1.4. These glazes were applied by spraying on bisque tiles of compositions; Mianwali clay 48 percent, quartz 30 percent, feldspar 20 percent and lime 2 percent. The glazing of the laboratory trials were done for 8-10 hours to come off with a soaking period of one hour. Compositions of the glazes are given in Table 4.

5. *Tests on Glaze Surface.*—Thermal Shock Test: The glazed pieces were allowed to undergo 10 cycles of quenching with a temperature drop of 125°C., the range being 150 to 25°C. Examination

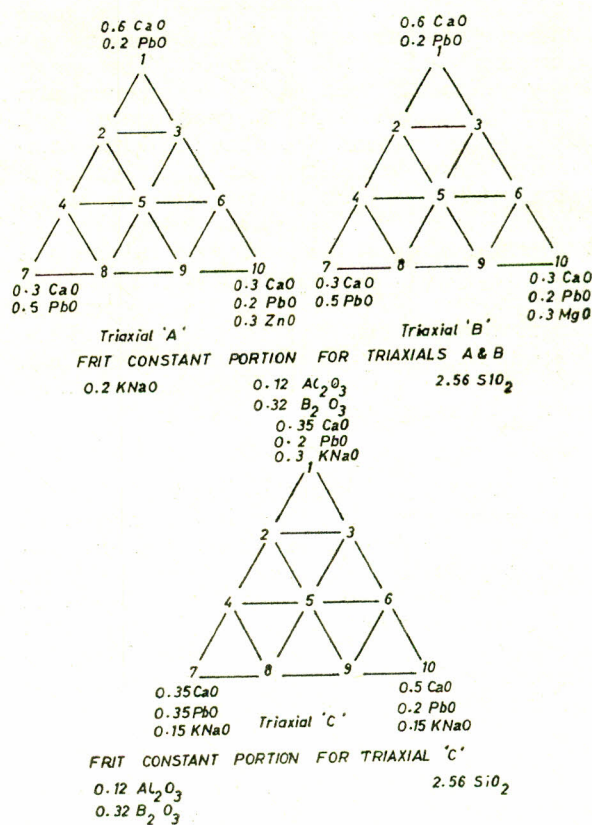


Fig. 1.

tion for the crazing was made by dipping the pieces in a 0.5 percent alcoholic solution of rosaniline.⁴

Results and Discussion

Glaze composition designated as A-7 in the triaxial A was found to mature at cone 0.6. It had a smooth, bright, blemish-free surface. From its visual qualities it could be used on the table wares. But the glaze suffered from a disadvantage of being soft.³ Spontaneous crazing was developed after a few weeks. From Table 5, it can be seen that the glaze under study has the maximum solubility. These defects, however, were removed by the partial replacement of lead oxide by calcium oxide, zinc oxide and magnesium oxide in triaxials A and B. A close study of Table 5 would reveal that the desired qualities of craze resistance and decreased solubilities are somewhat achieved,¹ although some time at the cost of superior gloss and surface.

A comparative study of the glazes of triaxial A and B from Table 5 shows that the glazes with 0.1 molecular equivalent of MgO have improved texture, lustre and matured at the temperature comparable with those having the same amount of zinc oxide. This may be explained by saying that the presence of MgO helps⁵ CaO to form a low melting eutectic, but magnesium oxide in higher amounts tend to raise the melting point due to its refractory nature. Thus, glaze No. A-6, A-9, B-6 and B-9 with 0.2 molecular equivalent of either ZnO or MgO had almost comparable surface characteristics, except for the maturing temperature of the glazes which was raised a little. It was, therefore, observed that the glazes A-6 and A-9 of triaxial A and the corresponding glazes in triaxial B, when fired to cone 06, gave smooth surfaces but the glazes of the latter group seemed to be under-fired and had a slight tendency towards a dull finish. However, when fired to 1000°C. with a soaking period of one hour, they had surfaces comparable with the corresponding zinc glazes (A-6 and A-9). The glazes with zinc oxide and magnesium oxide contents higher than 0.2 molecular equivalent, tend to develop significant surface imperfections and dull finish. Consequently the glaze No. A-10 crawled,⁵ exposing tiny places at the corner regions of the tiles, while slight pitting was observed at the semibright middle portion. Glaze B-10, on the other hand, was semi-matt with many pin-holes distributed evenly throughout.

Almost all the glazes of triaxial C had satisfactory commercial texture, except those which were high in calcium oxide,^{5,6} and lower in alkali and lead oxide contents. The latter developed egg-shell texture (C-3, C-9 and C-6 in Table 4). The glazes higher in alkali³ lower in calcium oxide and lead oxide, on the other hand, were

soft and crazed spontaneously. Comparing the glazes of this group with those of triaxial A, it was observed that the glazes of the former group were whiter and more opaque, while the latter were somewhat opalescent although lustrous. Amongst glazes A 5, A-6 and C-4, the first two glazes had comparatively much lower opacity than glaze No. C 4. This might be due to the fact that the glaze A 5 and A-6 contained zinc oxide as frit component, while in glaze C 4, it was a mill constituent. Zinc oxide in frit reacts with the available silica at the elevated temperature of 1100°C. to form soluble $Zn\ SiO_3$ and would thus produce opacity only to the extent to which the latter component gets devitrified and separates out. On the contrary, when zinc oxide is added as a mill ingredient, the firing temperature being comparatively lower (1000°C.), it would essentially remain distributed through the melt in the form of undissolved particles, producing thereby maximum opacity.

Almost all the glazes of triaxial A, B and C passed all the ten cycles of thermal shock except A-4, A-5, A-7, B-3, B-6 and C-1 which could endure less than 5 cycles only.

Parmelee⁷ reported that a proportionality existed between the solubility of lead-less borosilicate glazes and their acid and basic ingredients. A close study based upon the solubility of the lead-boro-silicate frits revealed that an interesting relationship also existed between solubility and molecular equivalents of various oxides in the frit. This relationship, worked out from experimental observations, expressed the percent loss of weight or the solubility. It can be derived from the following equation:

$$\text{Percent solubility} = \frac{\text{Mole KNaO} + \text{Mole } B_2O_3 + 0.43 \times \text{Mole PbO}}{\text{Mole CaO} + \text{Mole } SiO_2 + 0.8 \times \text{Mole ZnO}}$$

The values calculated according to this equation showed close proximity with the observed values (Table 5). Unlike the glazes containing ZnO, value of the solubility for those containing MgO could be calculated without taking into consideration its molecular equivalent.

Zinc and calcium² tend to lower the solubility of the lead borosilicate glazes in the given order. This fact could be easily observed in Table 5. Glazes No. B-3 and B-6 contained 0.2 mol. equivalent of PbO. The former contained 0.5 molecular equivalent of calcium oxide and zinc oxide were 0.4 and 0.2 molecular equivalent,

TABLE 2.—BATCH COMPOSITIONS OF THE FRITS FOR TRIAXIAL B.

Frit No.	Feldspar	Quartz	Marble chips	Red lead	Borax	Boric acid	Dolomite	magnesium carbonate
B-3	18.2	34.8	11.0	14.0	9.5	5.9	6.6	—
B-5	17.5	33.5	7.7	20.2	9.2	5.7	6.2	—
B-6	18.3	35.0	4.0	14.1	9.6	5.9	13.2	—
B-8	16.8	32.0	4.6	26.0	8.8	5.5	6.1	—
B-9	17.6	33.6	0.9	20.2	9.2	5.8	12.7	—
B-10	18.4	35.0	—	14.1	9.6	5.9	14.8	2.1

TABLE 3.—BATCH COMPOSITIONS OF THE FRITS FOR TRIAXIAL C.

Frit No.	Feldspar	Quartz	Marble chips	Red lead	Borax	Boric acid	Sodium carbonate
C-1	18.8	36.0	10.8	14.5	19.2	—	9.7
C-2	18.5	35.4	10.7	17.7	15.6	2.1	—
C-3	18.9	36.0	12.5	14.5	15.9	2.2	—
C-4	18.2	34.9	10.5	21.0	9.5	5.9	—
C-5	18.6	35.6	12.3	17.8	9.7	6.0	—
C-6	19.0	36.2	14.1	14.6	10.0	6.1	—
C-7	18.0	34.4	10.4	24.1	3.7	9.4	—
C-8	18.3	35.0	12.1	21.1	3.8	9.7	—
C-9	18.7	35.8	13.9	17.9	3.8	9.9	—
C-10	19.0	36.5	15.8	14.7	3.9	10.1	—

Glaze constant portion for triaxial A and B.

0.2 K NaO	0.28 Al ₂ O ₃	3.2 SiO ₂
	0.32 B ₂ O ₃	0.20 ZrO ₂

Glaze constant portion for triaxial C.

0.28 Al ₂ O ₃	3.26 SiO ₂
0.23 B ₂ O ₃	0.20, ZrO ₂

TABLE 4.—PERCENTAGE BATCH COMPOSITIONS OF THE GLAZES FOR THE TRIAXIALS A, B AND C.

Glaze No.	Frit	Mianwali clay	Quartz	Zircon	Zinc oxide
1	2	3	4	5	6
Triaxial A.					
A-1	76.0	11.5	2.5	10.0	—
A-2	77.0	11.0	2.5	9.5	—
A-3	75.5	11.6	2.7	10.2	—
A-4	77.9	10.5	2.4	9.2	—
A-5	77.4	10.8	2.5	9.3	—
A-6	76.5	11.2	2.6	9.7	—
A-7	78.8	10.1	2.3	8.8	—
A-8	78.0	10.4	2.5	9.1	—
A-9	77.3	10.7	2.5	9.5	—
A-10	76.5	11.1	2.6	9.8	—

(Continued)

(Table 4 Continued):

1	2	3	4	5	6
Triaxial B.					
B-3	75.6	11.5	2.7	10.2	—
B-5	77.0	11.0	2.5	9.5	—
B-6	75.6	11.6	2.6	10.2	—
B-8	77.8	10.5	2.4	9.3	—
B-9	76.7	11.0	2.6	9.7	—
B-10	75.5	11.6	2.7	10.2	—
Triaxial C.					
C-1	73.0	11.2	2.6	9.9	3.3
C-2	73.5	11.0	2.5	9.8	3.2
C-3	73.0	11.2	2.6	9.9	3.3
C-4	74.0	10.8	2.5	9.5	3.2
C-5	73.5	11.0	2.6	9.7	3.2
C-6	73.0	11.2	2.6	9.9	3.3
C-7	74.6	10.5	2.5	9.3	3.1
C-8	74.0	10.8	2.5	9.5	3.2
C-9	73.0	11.2	2.6	9.9	3.3
C-10	73.0	11.2	2.6	9.9	3.3

TABLE 5.—PERCENT SOLUBILITY OF THE FRITS IN DISTILLED WATER AT BOILING AND SOME OTHER PROPERTIES.

Glaze No.	% Solubility		Texture	Gloss	Cycles of thermal shock endured (150-25°C.)	
	Observed	Calculated				
1	2	3	4	5	6	
Triaxial A.						
A-1	0.19	0.192	pin hole	bright	10	
A-2	0.22	0.212	egg shell	do	10	
A-3	0.20	0.198	smooth	do	10	
A-4	0.23	0.246	egg shell	do	4	
A-5	0.19	0.219	smooth	do	2	(developed delayed crazing)
A-6	0.2	0.205	smooth	do	10	
A-7	0.27	0.271	smooth	v. bright	3	do
A-8	0.25	0.256	smooth	bright	10	
A-9	0.23	0.227	egg shell	dull dry	10	
A-10	0.21	0.212	partially crawled	semi bright		
Triaxial B.						
B-3	0.196	0.196	smooth	bright	2	(developed delayed crazing)
B-5	0.22	0.216	do	do	10	
B-6	0.204	0.194	do	semi-bright	4	
B-8	0.26	0.25	do	v. bright	10	
B-9	0.21	0.116	do	less bright	10	
B-10	0.205	0.20	pin hole	dull (semi mat)		

(Table 5 Continued):

(Table 5 Continued):

1	2	3	4	5	6	
Triaxial C						
C-1	0.23	0.242	smooth	bright	5	do
C-2	0.21	0.233	do	v. bright	10	
C-3	0.20	0.222	egg shell	less bright	10	
C-4	0.26	0.223	smooth	v. bright	10	
C-5	0.20	0.212	smooth	bright	10	
C-6	0.19	0.20	egg shell	bright	10	
C-7	0.22	0.213	smooth	bright	10	
C-8	0.21	0.202	smooth	bright	10	
C-9	0.18	0.191	egg shell	less bright	10	
C-10	0.18	0.182	pin hole	slightly dull	10	

respectively. The observed solubility was 0.196 and 0.204, respectively, which showed that the replacement of 0.1 molecular equivalent of calcium oxide with the same amount of zinc oxide had increased the solubility to some extent. Similar inference may be drawn from the comparison between the other members of triaxials B or A and B.

Conclusions

(1) The presence of MgO and ZnO confers a valuable property of craze resistance to the lead-borosilicate glazes. (2) Magnesium oxide and zinc oxide upto 0.2 molecular equivalent distinctly improve the gloss and texture of the glaze. (3) MgO and ZnO in quantities more than 0.2 molecular equivalent lend the glaze a dull and dry finish. (4) Replacement of PbO and alkalis by CaO, MgO and ZnO contributes to the hardness and durability of the glaze. (5) ZnO is more effective in mill batch as a contributory factor towards opacity, but it produces superior lustre when incorporated in frit. (6) The replacement of ZnO by MgO does not materially increase the maturing temperature of the glaze. Besides, the underglaze decoration can be attempted with satisfactory results. (7) Glazes A-6 and A-9 of triaxial A and glazes B-6 and B-9 of triaxial B gave good results when fired to 980°C. and 1000°C., respectively. B-5 and B-8 are the best among the

MgO bearing glazes. They can be used with underglaze colour with advantage. Most of the glazes of triaxial C except C-1 and C-10 may be used for artware.

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