RAW LEADLESS OPAQUE GLAZES AT CONE4

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The investigation covers three aspects of raw leadless, boron-free, opaque glazes maturing at Cone 4. Studies have been made of the effect of (1) the RO fluxes (calcium, barium, magnesium, strontium and zinc oxides) upon fusibility, gloss and texture, (2) the variation of alumina-silica ratio for a promising glaze composition and (3) tin oxide, titania and zirconia, on the opacity and colour. Some typical glaze compositions for bright and mat glazes have been suggested to be tried on an industrial scale. They are the whitest with excellent gloss and opacity.

Introduction

The advantages of lead borosilicate glazes are their easy maturing and high gloss but the presence of poisonous lead and characteristic surface imperfections, however, are objectionable features of these glazes. Boric oxide, alongwith other soluble constituents, tends to make the glaze soft and somewhat soluble, even after being incorporated in frits. With a view to removing these defects, attempts have been made to develop raw leadless boron-free glazes from the indigenous raw materials. Raw glazes maturing at cone 04-2 have been reported in literature.[1-2] These glazes contain colamonite as their main flux, but this mineral is not available locally, and it was therefore necessary to explore the use of other minerals for this purpose. Some of the difficulties in formulating the new glazes were in respect of their fusibility but they were, however, eliminated to some extent by the incorporation of suitable fluxes, although, some times at the cost of superior gloss and texture. The present work includes the study of the effect of various fluxes, opacifiers, and variation of alumina-silica ratio for some glazes, upon the fluidity, opacity, gloss and texture of the glazes. The glazes developed during the course of this investigation are suitable for wall tiles and pottery. The desired qualities achieved are economy, simplicity of preparation, ease of application and possibility of single firing.

Materials

Many indigenous raw materials were utilized during the course of this work, along with small quantities of imported chemicals, in order to find some better workable combinations. (1) Indigenous potash felspar with empirical formula

$$\left.\begin{array}{l}0.37\ K_2O\\0.55\ Na_2O\\0.08\ CaO\end{array}\right\}\ 1.43\ Al_2O_3\ 7.4\ SiO_2$$

with a molecular weight of 674 and a fusion temperature of 1200°C.[2] Finely ground native dolomite of molecular formula 1.0 $CaCO_3$ 0.76 $MgCO_3$ and marble chips were the sources of MgO and CaO. Quartz with 97.5% SiO_2 and Mianwali Clay with 89% clay content were the other materials of this group. (3) Regular grades of some commercial chemicals like $BaCO_3$, tin oxide, zinc oxide and zircon.

Experimental

1. *Plan of Investigation.*—After preliminary investigation, a tentatively good glaze, with the following emperical formula was developed:

$$\left.\begin{array}{l}0.24\ K_2O+Na_2O\\0.45\ CaO\\0.10\ BaO\\0.21\ ZnO\end{array}\right\}\ 0.32Al_2O_3\quad \begin{array}{l}3.2\ SiO_2\\0.13\ ZrO_2\end{array}$$

This composition was chosen as a basis for further investigations. In the first phase of work, the alkali content in the glaze composition was held constant at 0.24 eq. with alumina and silica contents at 0.32 and 3.2 eq. respectively and the effect of the variation in the amount of more than one of the oxides of barium, calcium, magnesium, strontium and zinc were studied. Various glaze compositions thus compounded are shown in Table 1.

In the second phase the effect of the variation of alumina-silica content was studied upon one of the promising glaze composition No. A11, found in the first part of this investigation, as indicated in Table 2.

Finally, glaze No. A11 was again selected in order to study the effect of tin oxide, titanium oxide and zirconia opacifiers, as shown in Table 3.

2. *Glaze Preparation.*—The individual glazes were prepared by mixing the molecular equivalents of the components of the formulations 2-3. The batches of 1000 g. of dry powdered materials were mixed with the required quantity of water and milled in a laboratory pebble mill for 6 hours to such a fineness that not more than 1% is retained on a 200 mesh screen.

3. *Glaze Application and Firing.*—The glazes were applied by dipping or by spraying to the bisque wall tiles and crucibles. These glazed pieces were fired in a laboratory electric furnace for 8 to 12 hours from room temperature to cone 4.

4. *Crazing Test.*—The glazed test pieces were maintained at 150°C. for 1 hour and then plunged in water at 20°C. This was repeated five times.

TABLE 1.

Glaze No.	CaO	BaO	MgO	SrO	ZnO
A-1	0.70	—	0.06	—	—
2	0.65	0.06	.05	—	—
3	0.65	—	0.11	—	—
4	0.60	—	0.06	—	0.10
5	0.50	0.16	—	—	0.10
6	0.50	0.10	—	—	0.16
7	0.50	0.06	—	—	0.20
8	0.50	—	—	0.06	0.20
9	0.50	—	—	0.10	0.16
10	0.50	—	—	0.16	0.10
11	0.50	—	—	—	0.26
12	0.45	0.10	—	—	0.21
13	0.45	0.16	—	—	0.15
14	0.45	0.21	—	—	0.10
15	0.40	—	0.12	—	0.24
16	0.40	—	0.16	—	0.20
17	0.40	—	0.26	—	0.10
18	0.30	0.16	—	0.15	0.15
19	0.30	0.10	0.06	0.10	0.20
20	0.30	0.06	0.10	0.20	0.10
21	0.26	0.05	0.21	—	0.24

TABLE 2.

Glaze constant portion : 0.24 K_2O+Na_2O, 0.5 CaO, X Al_2O_3, Y SiO_2, 0.26 ZnO, 0.2 ZrO_2

Glaze No.	Al_2O_3 X	SiO_2 Y
B-1	0.40	2.7
2	0.40	3.1
3	0.40	4.1
4	0.35	2.4
5	0.35	2.8
6	0.35	3.7
7	0.30	2.0
8	0.30	2.5
9	0.30	3.0
10	0.24	1.7
11	0.24	1.9
12	0.24	2.6
13	0.22	2.4

TABLE 3.

Glaze constant portion: 0.24 K_2O+Na_2O, 0.5 CaO, 0.26 ZnO; 0.3 Al_2O_3; , 3.2 SiO_2, XSnO_2, X TiO_2. XZrO_2

Glaze No.	SnO_2 X	Glaze No.	TiO_2 X	Glaze No.	ZrO_2
A-1	0.10	B-1	0.10	C-1	0.10
2	0.12	2	0.13	2	0.15
3	0.13	3	0.15	3	0.18
4	0.14	4	0.18	4	0.22
5	0.16	5	0.22	5	0.25
6	0.18	6	0.26	6	0.28

After this test, alcoholic solution of rosaniline[4] was applied to the pieces to observe the crazing.

5. *Colour Capacity and Texture.*—Visual methods were relied upon to determine the colour, opacity and texture for want of proper measuring equipments.

Discussion of the Results

The various results obtained are given in Tables 4, 5 and Fig. 1. A study of this data leads to the following important conclusions.

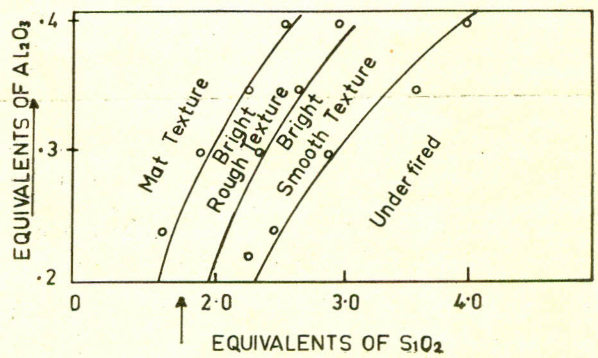

Fig. 1.

Calcium oxide in amount more than 0.5 eq. and in the absence of strong fluxes like baria and strontia tends to raise the maturing temperature of the glaze, and develop a mat texture at an alumina-silica ratio below 1:8. When calcium oxide[4] from 0.7 to 0.45 eq. is the sole member of RO group along with soda felspar as a flux and small amount of zinc oxide, the glazes produced had good gloss but develop egg shell texture. In corporation of magnesia in the form of dolomite along with calcia in amounts of 0.1–0.15 equivalents lower the maturing temperature appreciably and improve the lustre. Amounts higher than 0.2 eq. of MgO, however, favour crystallisation.

Baria[5] has proved to be a better flux and produces lustrous glazes when compared with those obtained from CaO-MgO combination. Thus glaze A-6 and A-14 have smooth and bright finish, while A-2 and A-16 tend to have a dull finish. Barium oxide in small additions improved the lustre, but amount exceeding 0.2 eq. promotes crystallisation and mat texture. A regular small increment in the amount of SrO in the glazes make them more fusible. The glazes start maturing at Cone 3, and possess good lustre. A continued addition render the texture semi-bright, egg shell and somewhat foamy. Zinc oxide[6] imparts a superior gloss and decreases the softening temperature of the glaze. The glazes with a Ba-Zn combination are more brilliant and of smooth texture than those with SrO. The best glazes of this group are: A-6, A-7, A-12 and A-13.

TABLE 4.—VISUAL RESULTS OF THE GROUP A GLAZES.

Glaze No.	Texture	Gloss	Glaze No.	Texture	Gloss
A-1	Egg shell	Semi mat	A-11	Smooth	Bright
2	Egg shell	Semi bright	12	Smooth	Very bright
3	Smooth	Crystalline mat	13	Smooth	,,
4	Pinholes	Semi mat	14	Pinholes	,,
5	Pinholes	Bright	15	,,	,,
6	Smooth	Very bright	16	,,	Mat
7	Smooth	,,	17	Egg shell	Crystalline mat
8	Smooth	,,	18	Smooth	Bright
9	Pinholes	,,	19	Egg shell	,,
10	Egg shell	Semi bright	20	Slightly foamy	Semi bright
			21	Smooth	Very bright

Almost all the glazes pass the thermal shock test and do not show any sign of crazing even several weeks after the test.

It can be seen from Fig. 1 that the range for the bright glazes is fairly appreciable. Glazes with Al_2O_3 content as low as .22 equivalent and ratio above 1:7 produces brilliant glazes. Low and moderate alumina content produces glazes of better finish than with higher alumina content. Glaze with low alumina content and alumina-silica ratio less than 1:8 develop a mat texture while those with a ratio above 1:11 were under fired at Cone 4. Glazes with low alumina content showed a tendency to crazing on thermal shock test.

The best composition for these types of glazes are from 1:9 to 1:10 alumina-silica ratio with silica content of .28 to .34 equivalents. Any attempt to cross these limits results in the decrease of gloss and pronounced surface imperfections. All the bright glazes, except those low in alumina content, pass all the cycles of thermal shock tests.

Tin oxide has long been known to produce superior white opacity. 0.1 eq. produces a fair degree of opacity. But 0.1-0.3 eq. of tin oxide produces more favourable effects particularly in the presence of ZnO, which by itself, materially increases, the opacity, gloss and texture. 0.1 to 0.26 eq. of TiO_2 was studied but it is observed that 0.14 to 0.18 gives the desirable effect. Quantities higher than this, tend to develop from cream to yellow colour with a gradual loss of brilliancy. The glazes with TiO_2 content 0.2 eq. and above are semi-bright to semi-mat with smooth texture.

Zircon has been found to be a better opacifier than zirconia, although the quantities employd to get the same effect was a bit higher. It helped the glaze to mature somewhat earlier. Best opacity and texture was found with ZrO_2 content, from 0.18 to 0.22 eq. Fineness of this chemical has also an appreciable influence on the opacity and texture. BaO and SrO, when present in a glaze, tend to dissolve zirconia somewhat (glazes No. A18 and A19), thus decreasing the opacity. Zinc and barium oxides are found to assist the zirconia opacifiers (glazes No. A6 and A12). All the glazes compounded in this part except those with TiO_2 content exceeding 0.25 eq. passed all the cycles of thermal shock test.

Conclusions

(i) Raw leadless boron-free glazes of the desired fusibility, gloss and texture can be produced by the use of calcium, barium and zinc oxides as the, major constituents of the RO group. (ii) MgO when added together with lime, lowers the maturing temperature of the glaze. Amounts of MgO higher than 0.15 eq. produce crystalline mat. (iii) SrO renders the glazes more fusible, but amounts higher than 0.15 eq. produce egg-shell or foamy texture. (iv) Glazes with relatively low alumina content and alumina silica ratio of 1:10 are brighter and of fine finish. (v) Glazes containing 0.12 eq. SnO_2, 0.18 TiO_2 and 0.2 of Zirconia give the desired opacity. (vi) Zinc and barium from 0.05–0.2 equivalents assist the zirconia opacifiers while SrO in amount exceeding 0.1 equivalent tends to dissolve the opacifier. (vii) Some of the best bright and mat glazes found during the course of the investigations are: Bright: A-6, A-12 and A-21. Mat: A-3, A-16 and A-17.

TABLE 5.—VISUAL RESULTS OF GROUP C GLAZES.

Glaze No.	Opacity	Colour
A-1	Fair	Bluish-white
2	Good	White
3	Good	Very white
4	Excellent	Very white
5	Excellent	Very white
6	Excellent	Very white
B-1	Poor	White
2	Fair	White
3	Good	Cream-white
4	Good	Cream
5	Good	Pale
6	Good	Yellow
C-1	Poor	Less white
2	Fair	Cream-white
3	Fair	Cream-white
4	Good	White
5	Excellent	Very white
6	Excellent	Very white

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