PREPARATION OF LOW TEMPERATURE GLAZES

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White, opaque, low-lead glazes maturing at cone 01 and fitting felspar-quartz-clay bodies of comparatively low coefficient of expansion were developed. Special considerations were given to produce glazes with minimum frit and maximum silica ; the former to reduce cost and the latter to lower down the expansion of the glaze. Optimum compositions were found after varying the content of CaO, PbO, ZnO, KNaO, SiO_2, Al_2O_3 and B_2O_3. Batch formulas for a number of successful body-glaze combinations are given.

1. Introduction

Ceramics ranks amongst the still-to-develop industries of the country. In the small scale production that we have, only low temperature hearths are employed. Uufortunately the quality of our home products is not very high and the factors contributing to this are many, namely, raw materials, processing, firing, finishing and lack of proper know how. From the technical point of view firing is the most important factor. Same raw materials with similar processings would produce better products if fired to comparatively higher kiln temperature. Accepting the heat limitations in small scale industries, factors other than temperature must be exploited.

It is, however, not inherent in the low-temperature earthen-ware to be of low quality. Much better standard can be achieved and formulas for bodies and glazes with much improved qualities can be developed within the available temperature limits. It was with this end in view that the present work was undertaken.

2. Material

Two factors were kept in view while selecting the various raw materials: the availability and the purity of the material.

In preliminary experiments, most of the constituents employed were laboratory grade chemicals. In later, comparatively large-scale experiments, utilisation of the indigenous raw material (even when it was comparatively impure) was the main consideration. In nearly all cases, however, quartz, felspar and china clay were of native origin, the analyses of which are as follows:

Quartz: silica, 97.4%; Al_2O_3, 1.865%; Fe_2O_3, 0.035%; CaO, 0.85%; and MgO, 0.15%.

Felspar: silica, 64.60%; Al_2O_3, 22.08%; Fe_2O_3, 0.42%; CaO, 2.80%; and Na_2O/K_2O, 6.85%.

China clay: silica, 44.03%; Al_2O_3, 40·61%; Fe_2O_3, 0.71%; and CaO, 0.75%.

3. Procedure

(i) *Plan of Investigation.*—The object of the present study was to develop low-temperature lead-free, white, opaque glazes which could suit low temperature earthen-ware bodies. During the course of study it was, however, found that, at the desired temperature (1000-1050°C.), it was rather practically impossible to formulate a glaze batch without any lead content—any such glaze invariably crazed, either spontaneously or after a lapse of time, on all the various body compositions upon which it was tried; attempts to prepare low lead-containing glazes became the objective thenceforth.

Quite a number of glazes were prepared. They may be categorized, on the basis of their characteristic constituents, into the following three types:

(1) Those containing no lead, high molecular percentage of boric acid and alkali oxides, low silica and appropriate amount of alumina and lime.

(2) Those containing low precentage of alkali oxides, maximum (12%) boric oxide[1] and comparatively higher amounts of silica, lime and magnesia.

(3) Those containing low to medium amounts of lead oxide, low to nil amount of alkali oxides, medium percentage of boric acid with comparatively higher amounts of lime and silica.

(ii) *Frit and Glaze Compositions and their Preparation.*—Since all the glazes contained soluble or partially soluble constituents like boric acid, borax, red lead etc., fritting of at least a portion of the glaze composition was necessary. The batch compositions of the various frits and glazes employed are given in Tables 1 and 2.

The various frits were smelted individually in small laboratory frit-making furnaces. Raw batches of fine (200 mesh) frit components of 200 g. weight were firstly mixed in a mortar, and then, to ensure thorough mixing, passed through a 60 mesh sieve two times with intermediate rolling on paper. The thoroughly mixed masses were then transferred to fireclay crucibles which were then fired in the frit-making furnace. The firing schedule consisted of raising the temperature at nearly uniform rate up to 900-1000°C. in one and a half hours, and maintaining that temperature for one half hour. (The frits smelted, mixed and poured quite satisfactorily under these conditions. Due to small iron-impurity, the frits were invariably sea-water greenish in hue). Each melt was poured into cold water, wherefrom it was withdrawn, dried, crushed and ball-milled to a fineness of 200 mesh.

The individual glazes were prepared by combining the required amounts of the constituents as shown in Table 2. The batches of 500 g. of dry glaze materials with 300-350 ml. of water were ball-milled to an average fineness of 0.1% on a 200 mesh screen, and were later diluted to proper consistency (sp. gravity 1.4-1.6) by the addition of water. This procedure gave glazes of satisfactory suspension and adhering qualities without the addition of electrolytes or gums.

(iii) *Glaze Application and Firing.*—The glazes were applied to some or all of the bisque-wares, biscuited at 1000-1050°C. (Table 3). The glazes were applied on the body-wares by dipping.

In the earlier experiments the firing was done in laboratory electrical muffle furnace; in later experiments, oil-fired muffle kiln was employed. From the experience gained through hits and trials, a 4-hour heating (3 hours to heat to 700°C. and 1 hour to raise to 1050°C.) for electrical furnace, and a 6-hour heating (4½ hours to attain 700°C. and 1½ hours to raise to 1050°C.) for oil kiln was considered optimum and, in most of the cases, this was the schedule that was followed.

Annealing time for electrical furnace was kept 18 hours and that for oil furnace 36 hours.

TABLE 1.—BATCH COMPOSITION OF FRITS.

Frit No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Borax	20	40	80	80	36	34	34	34	—	—	—	—	—
Boric acid	—	—	10	10	10	5	5	5	25	15	15	20	15
Felspar	—	15	30	30	—	—	—	—	—	—	—	—	—
Quartz	16	80	44	44	32	29	29	29	25	30	30	30	35
Whiting	8	25	20	20	10	8	8	8	8	5	8	8	5
China clay	8	—	8	8	5	5	5	5	7	5	7	7	10
Soda ash	4	—	8	8	—	—	—	—	—	—	—	—	—
Red lead	—	—	—	—	—	19	19	19	15	40	30	25	30
Talc	—	—	—	—	7	—	—	—	—	5	5	5	5
Potassium carbonate	—	—	—	—	—	—	—	—	20	—	—	—	—
Titania	—	—	—	—	—	—	—	—	—	—	5	5	—

TABLE 2.—BATCH COMPOSITION OF GLAZES.

Glaze No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Frit*	70	70	70	70	70	70	70	70	60	60	60	60	60
China clay	3	3	3	3	5	5	5	5	5	10	5	5	5
Talc	3	3	3	7	—	—	—	—	—	—	8	8	6
Whiting	3	3	3	5	—	—	—	—	—	—	—	—	—
Quartz	5	5	5	15	10	15	5	5	5	5	5	5	5
Felspar	10	10	10	—	—	—	—	—	—	—	—	—	—
Zinc oxide	3	3	3	7	5	—	5	5	5	5	5	5	5
Tin oxide	3	3	3	5	5	5	5	5	5	5	7	7	6
Dolomite	—	—	—	5	5	5	5	5	—	—	—	—	—
Lead carbonate	—	—	—	—	—	—	5	5	10	10	10	10	8
Mag. carbonate	—	—	—	—	—	—	—	—	—	5	—	—	—
Titania	—	—	—	—	—	—	—	—	—	—	5	5	10

*Each glaze contains frit of its own number.

(iv) *Crazing Tests.*—The specimen were tested visually for crazing by use of an alcoholic solution of rosaniline dye,[2] firstly just after taking them out of the furnace and secondly after six weeks of firing. In some cases the test was preceded by autoclaving at a pressure of 150 lbs./sq. inch for one hour.

4. Discussion of Results

The results obtained with the various glazes are shown in Table 4. It can easily be observed that all the glazes that contained high percentage of alkali oxides invariably crazed on all the various body-wares; a visual inspection of the crazed meshes would also reveal that greater the amount of alkali oxides, finer was the craze-mesh, or in other words, greater was the amount of crazing. Any knowledge into the mechanism of crazing would also predict the same.[3–6]

Glazes comparatively higher in lime, alumina and silica, when so proportioned as to mature at 1050°C., proved the best as regards their texture, gloss, opacity and craze- resistance.

TABLE 3.—BODY COMPOSITIONS.

Body No.	Clay	Quartz	Felspar	Glass	Bento-nite	Talc
1	100	—	—	—	—	—
2	95	5	—	—	—	—
3	60	—	20	—	—	20
4	60	10	15	—	—	15
5	75	25	—	—	—	—
6	70	30	—	—	—	—
7	60	40	—	—	—	—
8	66	33	—	—	—	—
9	60	—	40	—	—	—
10	50	—	50	—	—	—
11	96	—	—	4	—	—
12	92	—	—	8	—	—
13	70	—	—	30	—	—
14	80	—	—	—	—	—
15	40	20	30	—	10	—
16	40	50	—	—	10	—

5. Conclusion

1. Good low temperature glazes, maturing between cones 06-01 and fitting bodies biscuited at cones 014-013 can be prepared.

2. Craze-free, lead-less, low temperature glazes cannot be prepared.

3. To be craze-free, a low temperature glaze should contain no alkali oxide, considerable boric oxide, some lead oxide and just enough silica to keep the ratio of basic to acidic oxides 1:1.

4. To increase opacity, gloss and whiteness, some zinc, tin and titanium oxides be introduced to the glaze.

5. Bodies containing felspar or talc are better to work at cones 06-01 than those that contain quartz or glass; quartz-containing bodies vitrify at much higher a temperature and glass-containing at much lower.

TABLE 4.—GLAZE RESULTS ON VARIOUS BODIES.

Talc Glaze No.	Effects observed
1	Crazed on all the bodies; was pale yellow in colour and dull in gloss.
2	Crazed on all the bodies; was bluish in hue; was dull in gloss.
3	Comparatively less crazing; was bluish in hue; was duller in gloss.
4 & 5.	Results were similar to that of No. 3 except that the craze meshes were coarser.
6, 7 & 8.	Crazed on all the bodies: on bodies No. 7, 8, 9 and 13 crazing was minimum; only a few craze lines appeared; gloss, colour and texture were promising.
9	All the samples were dull, matt. The glazes, probably, did not mature.
10	Crazed on bodies No. 1, 2, 3, 4, 11 and 12; craze lines appeared on bodies No. 5. 6. 7 and 8 after 6 weeks; gloss, texture and colour were quite good.
11 & 12	Proved quite successful with almost all the bodies; no craze lines were observed on bodies No. 7, 8, 15 and 16 even after autoclaving at 150 lbs./sq. inch pressure; gloss and texture was excellent; colour was creamish white.
13	Did not mature fully and remained dull, matt.

6. Best body glaze frits are:

a. B 4,G 11 (Body No. 4, glaze No. 1)
B 15,G 11
B 16,G 11
B 16,G 12
B 15,G 12
B 4,G 12 Mat. temp. 1000°C. (cone 06)

b. B 4,G 9
B 9,G 9
B 10,G 9
B 15,G 9
B 16,G 9 Mat. temp. 1050°C. (Cone 04)

c. B 4,G 13
B 9,G 13
B 10,G 13
B 15,G 13
B 16,G 13 Mat. temp. 1110°C. (Cone 01)

References

1. Felix Singer, *Ceramic Glazes* (Borax Consolidated Ltd., 1951), p. 24.
2. Danielson and Gordon, J. Am. Ceram. Soc., **33**, 323 (1950).
3. Mellor, Trans. Ceram. Soc. (Engl.) **34**, 1 (1935).
4. Hill, J. Am. Ceram. Soc., **4**, 25 (1921).
5. Stenger, Ber. deut. keram, Ges., **8**, 24 (1927).
6. Schurecht, J. Am. Ceram. Soc., **26**, 93 (1943).