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COLOURED GLAZES BASED ON SURFACE CLAY

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Surface clay (red clay) has been used as a base for various coloured glazes such as yellow, brown, maroon, black and light blue, maturing between 1000°–1100°. Iron content of the clay has been utilized for developing these colours. Additional Fe_2O_3 and MnO_2 have been added for effecting desirable changes in the shade of some glazes.

INTRODUCTION

Surface clay is the cheapest raw-material and this has been the main reason for carrying out this study. We have tried to develop coloured raw glazes which may be used for artware and can be applied on the earthenware body-composition usually used in local pottery industry at Gujrat and Gujranwala. Surface clay might have been used in isolated cases as a glaze component but no systematic study has been reported for the development of coloured glazes based on surface clay. Effect of iron content on the colour of ceramic products has been studied by Macvay and Parmellee [1]. They have pointed out the possibility of producing red, tan and brown colours in engobes and other ceramics products. Hostetter and Roberts [2] have studied the effect of glass composition on the colour imparted by iron oxide. Konnision [3] has studied the effect of iron-content on the colour of clay.

EXPERIMENTAL

Red clay, K.D. pottery clay, feldspar, quartz, talc, laterite and soda-lime glass (ordinary bottle glass) were the raw-materials used. The chemical analysis is reported in Table 1.

In addition to the technical grade zinc oxide, white lead, manganese dioxide and calcuim fluoride were also used.

Procedure

Washed surface clay, quartz and feldspar, were ground to 100 mesh. Various constituents of glaze were mixed in proper proportions and the mix was ball-milled for 5–6 hr after the addition of water. The consistency of the glaze was adjusted and it was applied to test pieces by dipping or spraying in the green state as well as after biscuit firing at 900°. In the case of earthenware body used by local pottery industry the glaze was applied to pieces fired at 900° as well as at 1150°. The compositions of these two bodies are: Gujrat body containing talc (50%), K.D. pottery clay (25%), whiting (6%), glass (14%) and quartz (5%), and Artware body containing K.D. pottery clay (60%), feldspar (18%) and quartz (22%).

Test pieces from these bodies were made by routine casting procedure.

Table 1. Chemical analysis

	Red clay	K.D. pottery clay	Quartz	Feldspar	Talc	Laterite	Soda-lime glass
I/L	6.20	13.60	0.21	0.35	7.72	9.65	0.10
SiO_2	59.60	47.10	97.13	66.90	58.10	12.28	70.00
Al_2O_3	19.28	32.98	1.39	21.28	2.52	23.57	3.30
Fe_2O_3	5.38	1.12	0.035	0.026	1.13	49.33	0.25
CaO	3.74	1.40	0.88	0.12	0.73	0.24	8.80
MgO	2.70	1.04	0.35	0.09	29.15	1.23	2.70
Na_2O	2.07	1.50	–	8.67	0.42	–	14.10
TiO_2	0.3	0.76	–	–	–	3.99	–
K_2O	0.63	0.48	–	2.25	0.20	–	0.58

Table 2. Yellow glazes

Composition No.	Clay (%)	Feldspar (%)	Quartz (%)	ZnO (%)	White lead (%)	Glass (%)	Talc (%)	Colour (%)
1	90–80			10–20				Yellow
2	70–50			30–50				Dirty cream
3	50			5	45			Brownish yellow
4	50			10	40			Yellow
5	50			15	35			"
6	50			20	30			"
7	45.5		45.5		9			"
8	43.5		43.5		13			Good yellow
9	41.7		41.7		16.6			"
10	45.5				9.0	45.5		Reddish up to 1000°
11	43.5				13.0	43.5		& yellow above 1050°
12	41.7				16.6	41.7		"
13	45.5	45.5			9.0			Reddish yellow
14	43.5	43.5			13.0			"
15	41.7	41.7			16.6			"
16	40.0	40.0			20.0			"
17	38.5	38.5			23.0			"
18	45.5				45.5		9.0	Bronish yellow
19	43.5				43.5		13.0	"
20	41.7				41.7		16.6	"
21	40.0				40.0		20.0	"
22	38.5				38.5		23.0	"
23	31.3		12.4		31.3	18.8	6.2	Bright yellow
24	30.3		12.1		30.3	18.2	9.1	"
25	29.4		11.75		29.4	17.7	11.75	"

DISCUSSION

Variations in the colour of ceramic products containing only iron oxide as a colouring agent are due to the fact that iron can exist in the Fe^{++} and Fe^{+++} form and the ratio of Fe^{++} to Fe^{+++} is the controlling factor as regards the shade of the colour [1–3]. This ratio can be controlled or modified by factors such as composition of the glaze, firing temperature and the atmosphere of the furnace. In glazes (glasses) Fe^{3+} behaves as a network former and Fe^{2+} as a network modifier [3].

Yellow Glazes. Hostetter *et al.* [2] have produced a lemon yellow shade in a soda-lime-silica glass composition by controlling the Fe^{2+}/Fe^{3+} ratio. In the present study for developing a yellow glaze the presence of 10–20% ZnO is necessary to keep the Fe^{2+}/Fe^{3+} ratio within such values where the shade is yellow. In the absence of ZnO the white lead component of the glaze helps Fe^{3+} to act as a network former and the glaze turns brown. Even in the presnece of ZnO, if the amount of white lead is more than 30% the colour changes to brown. ZnO can be replaced by talc and the same yellow shade can be obtained.

Compositions giving yellow shade have been reported in Table 2. It is clear from the results that a glaze with good yellow shade can be obtained by adding ZnO or quartz to red clay. Other additions are made to have desirable physical properties in the glaze. When 10–20% of ZnO is added to red clay, the yellow colour is developed but the glaze remains matt even above 1100°. Substitution of 35–40% of clay in the above composition with white lead gives good yellow glaze maturing above 1000°. Addition of quartz to red clay in the presence of fluxes, also produces yellow shade. When 1–20% of white lead is added to a 1:1 mix of clay and quartz, a good yellow-coloured glaze is obtined which matures above 1050°.

Physical properties, like texture and lustre are improved by increasing the amount of white lead to 30% and replacing 12% clay and 10% quartz with talc and glass. Small additions of CaF_2 increase the brightness of the glaze.

Brown Glazes. For brown coloured glazes the presence of white lead is necessary because it helps Fe^{3+} to enter into four-fold coordination just like silicon atoms and the

Table 3. Brown glazes

Composition No.	Clay	White lead	Glass	Laterite	Quartz	Temp. (°C)	Colour
1	60	40				950	Reddish brown
2	50	50				900	Brown
3	38.5	38.5	19.2	3.8		1050	Brown
4	37.6	37.6	18.8	6.0	–	1050	Brown
5	37.0	37.0	18.5	7.5	–	1050	Reddish brown
6	36.5	36.5	18.25	8.75	–	1050	Coffee brown
7	35.7	35.7	17.9	10.7	–	1050	Coffee brown
8	31.25	31.25	18.7	6.3	12.5	1100	Choccolate brown
9	30.3	30.3	18.2	6.05	15.15	1100	Brown
10	29.4	29.4	17.65	5.9	17.65	1120	Reddish Brown

Table 4. Black glazes

Composition No.	Clay	Glass	White lead	MnO	Temp. (°C)	Colour
1	42.4	12.7	42.4	2.5	1040	Brown-reddish black
2	41.3	12.4	41.3	5.0	"	Black
3	40.7	16.3	40.7	2.4	"	Brownish-reddish black
4	39.7	15.9	39.7	4.7	"	Black
5	39.1	19.5	39.1	2.3	"	Brownish black
6	38.2	19.1	38.2	4.5	"	Black

Table 5. Fritted glazes

S.No.	Red clay	White lead	Quartz	Glass	Zinc oxide	Talc	Laterite	MnO_2	Colour
1	50.0	30.0	–	–	20.0	–	–	–	Yellow
2	43.5	9.0	45.5	–	–	–	–	–	"
3	41.7	16.6	41.7	–	–	–	–	–	"
4	30.3	30.3	12.1	18.2	–	9.1	–	–	"
5	37.0	37.0	–	18.5	–	–	7.5	–	Brown
6	31.25	31.25	12.5	18.7	–	–	6.3	–	"
7	39.7	39.7	–	15.9	–	–	–	4.7	Black

colour of Fe^{+++} in such environment is brown. When the iron is completely in the four-fold coordination we can get very uniform brown glazes. The amount of white lead sufficient to help iron enter the four-fold coordination completely, is about 30%. In the case of lower amount the glaze remains brick red.

Choccolate-coloured glaze is obtained by the addition of white lead to red clay. For a good choccolate colour, the amount of white lead should be more than 40%. Below 40% the colour remains brick-red. Choccolate-coloured glaze matures at 1050°. Addition of glass up to 20% in a 1:1 mixture of clay and white lead produces

reddish brown colour but, when additional Fe_2O_3 is introduced in the form of laterite, the colour changes, first to coffee-brown and then to blackish brown. Compositions in Table 3 have very good coffee-brown shade with metallic lustre. The amount of laterite necessary to produce coffee-brown is 7–10%. More than 10% laterite imparts a balckish tinge. When about 12% quartz is added to a composition containing 6% laterite at the expense of clay and white lead, we get a choccolate-brown colour. Increasing additions of quartz lighten the colour and with 18% quartz in the glass we get a light brown colour with a metallic lustre.

Black Glazes. Composition presented in Table 4 show that a 1:1 mixture of red clay and white lead gives a choccolate colour. Addition of soda-lime glass up to 20% imparts desirable properties of texture and gloss alongwith metallic lustre. Metallic lustre and gloss increase with, increasing glass content. These glazes mature at about 1050°.

Fritted Glazes. Some of the glaze compositions given in Tables 2–4 were fritted to see their behaviour as regards the colour and other properties. The frit compositions are presented in Table 5. It has been found that the fritted composition when applied with an addition of 5% K.D. clay as mill addition give satisfactory results. The colour remains the same but there is a slight change in the shade of the colour.

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