

DEVELOPMENT OF AVENTURINE GLAZES

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Aventurine glazes, using Pakistani raw materials in their formulation have been developed. The covered (a) variation in RO group (Na, K, Ca and Pb), (b) variation in R_2O_3 group (B_2O_3 , Al_2O_3 and Fe_2O_3), (c) variation in RO_2 (SiO_2) and effects of application and firing techniques of glazes. The glazes were fired up to $1000^\circ C$. Some good Aventurine glazes (containing Fe) were obtained and conditions that affect the results were also established.

Aventurine quartz and aventurine felspar have scales of mica, haematite and gothite, which give off fire-like flashes when held in bright lights. For the first time in 1849, Wohler¹ produced such effects in glazes which resembled aventurine felspar, and these glazes were therefore named aventurine glazes.

Aventurine glaze is one in which individual crystal in the magma separates out and appears to be flitter or spangle suspended in the glass. The aventurine effect can be obtained by adding a metallic oxide in such quantities that when heated to a molten mass, the matrix becomes saturated with the oxide; and when the glaze cools thin crystals or spangles of the oxide separate out from the supersaturated magma. The commonly used oxides for this purpose are those of iron, chromium and copper. Iron oxide is more common and gives the best aventurines.

Many workers have made investigations in this field. An aventurine effect by applying an engobe of iron or uranium oxide and then covering the same with a borax glaze.¹ Thirty-five parts of iron oxide per 100 parts of the glaze, and 20% finely-ground metallic iron produced aventurine glazes with variations in colour.² The addition of artificial haematite crystals to the glaze produces the same effect.³ High amounts of SiO_2 require high amounts of Fe_2O_3 , as high as 0.71 moles.⁴ These glazes were studied rather extensively by making changes in RO and R_2O_3 groups while the SiO_2 contents were kept constant.⁵ In another study,⁶ iron was substituted by Cr and Cu. All these glazes were fired between cone 02 to cone 3.

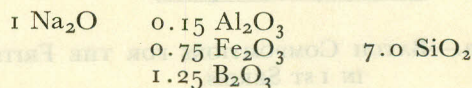
In the present investigation, the authors have not only changed the limits of ranges of RO and R_2O_3 which the previous research workers had covered but have also included the study of effects of variations in $RO_2(SiO_2)$.

Experimental

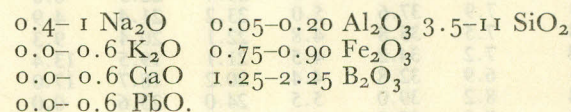
Plan of Investigation.—The investigation consists of four systematic fields i.e. effects of (1) variation

in B_2O_3 and Fe_2O_3 ; (2) variation in Al_2O_3 content; (3) variation in RO group (Na, K, Ca, Pb); (4) variation in RO_2 group (SiO_2). Effects of firing conditions and glaze application have also been studied.

From previous investigations it was found that the formula:



gave the best composition for the aventurines. In preliminary investigation Fe_2O_3 was varied from 0.75 to 0.95 mole, keeping other constituents constant. It was found that 0.95 mole Fe_2O_3 gave dark coloured glaze without crystallisation, while 0.75 mole, gave yellow coloured glaze with crazing. The rest of the glazes gave crystals, although the colour developed darker shades with increase in Fe_2O_3 contents. Keeping in view all the previous investigations the following ranges of various constituents were selected as the base:



In the first series, Fe_2O_3 and B_2O_3 were varied as shown in Fig. 1. Ascending alphabets represent rise in B_2O_3 while rising numbers show the respective rise in Fe_2O_3 contents. Batch compositions so formulated are given in Tables 1a and 1b. The two best compositions C_4 and D_1 were selected from these series and variation in Al_2O_3 content was made. Batch compositions are given in Table 2.

Figure 2, the triaxial, shows the variation in RO group. Since Pb and Ca have very little favourable effect upon crystallisation, while Na_2O , is most suitable, 0.4 mole of Na_2O was kept constant and the remaining 0.6 mole of RO group was replaced by K_2O , CaO , and PbO . Ten compositions as shown in Tables 3a and 3b were

Fig. 1.

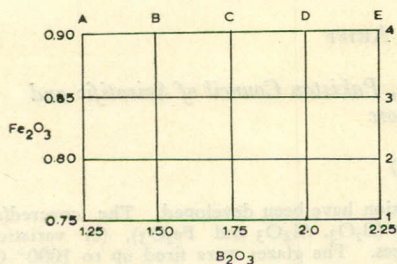


Fig. 2.

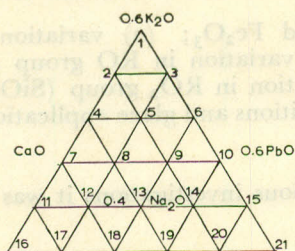


TABLE 1a.—BATCH COMPOSITIONS FOR THE FRITS IN I ST SERIES.

Frit No.	% Felspar	% Borax	% Sodium carbonate	% Quartz	% Fe ₂ O ₃	% Boric acid
A-1	8.5	40.5	5.4	25.0	20.4	0.0
B-1	8.1	38.6	5.1	23.8	19.4	5.0
C-1	7.7	36.6	4.9	22.6	18.5	9.5
D-1	7.35	35.00	4.65	21.6	17.6	13.7
E-1	7.0	33.6	4.5	20.7	16.9	17.4
A-2	8.4	40.0	5.3	24.7	21.4	0.0
B-2	8.0	38.0	5.1	23.4	20.4	5.0
C-2	7.7	36.2	4.8	22.4	19.4	9.4
D-2	7.4	34.7	4.6	21.3	18.5	13.5
E-2	7.0	33.2	4.4	20.4	17.8	17.3
A-3	8.3	39.4	5.2	24.4	22.5	0.0
B-3	7.9	37.6	5.0	23.2	21.4	4.9
C-3	7.5	35.8	4.8	22.1	20.4	9.3
D-3	7.2	34.2	4.5	21.1	19.5	13.4
E-3	6.9	32.8	4.4	20.2	18.7	17.0
A-4	8.2	39.0	5.5	24.0	23.6	0.0
B-4	7.8	37.0	5.0	23.0	22.4	4.8
C-4	7.5	35.5	4.6	21.8	21.4	9.2
D-4	7.1	33.8	4.5	20.8	20.4	13.4
E-4	6.8	37.5	4.3	20.0	19.6	16.9

TABLE 1b.—MILL BATCHES OF THE GLAZES IN I SERIES.

No.	Frit %	Clay %	Quartz %	No.	Frit %	Clay %	Quartz %
A-1	65.3	1.67	33.0	A-3	66.0	1.6	32.4
B-1	66.0	1.62	32.3	B-3	66.8	1.6	31.6
C-1	66.8	1.58	31.6	C-3	67.7	1.55	30.8
D-1	67.8	1.53	30.45	D-3	68.3	1.5	30.2
E-1	68.2	1.5	30.2	E-3	69.0	1.48	29.5
A-2	66.0	1.6	32.2	A-4	66.5	1.6	32.1
B-2	67.0	1.6	31.2	B-4	67.0	1.6	31.3
C-2	67.8	1.5	30.7	C-4	67.9	1.53	30.6
D-2	68.6	1.5	29.8	D-4	68.5	1.5	30.0
E-2	68.7	1.5	29.8	E-4	69.3	1.46	29.20

formulated from three frits K₁, K₇ and K₁₀. Base glaze composition was as shown at C₄.

In case of variation in the SiO₂ content, C₄ again was taken as base composition and additions of SiO₂ were made in mill batch. The compositions formulated are shown in Table 4.

Preparation of Frit and Glaze.—Frit batches, according to the compositions shown in the tables, were weighed and thoroughly mixed, smelted in grog crucibles and quenched in water. The frit thus formed was dried and ground in an edge-runner up to 100 mesh. Glaze batches were formulated by adding frit clay, quartz and strong ammonium hydroxide as deflocculant. The glaze was ground in pebble mill up to a fineness of 200 mesh.

Glaze Application and Firing.—Small test pieces were cast in the form of crucibles, ash trays and figurines etc. from a slip having a composition of clay 55%, felspar 30%, and quartz 15%. Glazes were applied on the pieces already biscuited at 1000°C by dipping as well as spraying. Thickness of the glaze varied from 1 mm to 2 mm.

Test pieces were fired in electric muffle furnace. The maximum temperature attained was 1000°C in most of the cases. Cooling was done in the following way:—

- (1) Test pieces were soaked for 30 to 45 min and then the furnace was allowed to cool in 16 hr.
- (2) Test pieces were soaked for ½ hr controlled cooling was done to 800°C in 4 hr and then the furnace was allowed to cool in 14 hr.
- (3) The above was repeated with controlled cooling down to 750°C.

TABLE 2.—BATCH COMPOSITION OF GLAZES IN II SERIES.

No.	Mol. eq. of Al ₂ O ₃	Frit %	Clay %	Quartz %
1C ₄	0.1	69	—	31
2C ₄	0.15	67.9	1.53	30.6
3C ₄	0.20	67.0	3.0	30.2
4C ₄	0.25	66.0	4.5	24.6
1D _I	0.1	69.0	—	31
2D _I	0.15	67.8	1.53	30.4
3D _I	0.20	66.6	3.0	30.4
4D _I	0.25	65.5	4.5	30.0

TABLE 3a.—BATCH COMPOSITIONS OF FRITS IN III SERIES.

No.	Felspar	Borax	Boric acid	SiO ₂	Fe ₂ O ₃	K ₂ CO ₃	CaCO ₃	Pb ₃ O ₄
K-1	4.8	19.5	19.10	21.10	23.3	12.2	—	—
K-7	4.9	20.2	19.7	24.2	21.9	—	9.1	—
K-10	4.4	18.2	17.6	21.6	19.6	—	—	18.6

TABLE 3b.—BATCH COMPOSITION OF GLAZES IN III SERIES.

No.	Frit K-1	Frit K-7	Frit K-10	Clay	Quartz
K-1	66.0	—	—	3.5	30.2
K-2	44.6	21.2	—	3.48	30.7
K-3	42.9	—	24.4	3.3	29.4
K-4	22.6	43.0	—	3.5	31.0
K-5	21.6	20.5	24.5	3.4	31.0
K-6	20.8	—	47.3	3.3	28.7
K-7	—	65.0	—	3.5	31.5
K-8	—	41.6	24.8	3.4	30.0
K-9	—	20.0	47.7	3.3	29.0
K-10	—	—	69.0	3.2	27.8

TABLE 4.—BATCH COMPOSITIONS OF THE GLAZES IN IV SERIES.

No.	Moles of SiO ₂	Frit C ₄ %	Quartz %	Clay %
S-1	3.5	93.5	4.3	2.2
S-2	4.0	88.6	9.3	2.1
S-3	4.5	84.5	13.6	2.2
S-4	5.0	80.5	17.5	1.9
S-5	5.5	77.0	21.4	1.8
S-6	6.0	73.5	24.8	1.7
S-7	6.5	70.5	27.8	1.6
S-8	7.0	68.0	30.6	1.6
S-9	7.5	63.3	33.3	1.5
S-10	8.0	63.0	35.6	1.4
S-11	9.0	58.6	40.0	1.4
S-12	10.0	54.9	43.8	1.3
S-13	11.0	51.5	47.2	1.2

- (4) Test pieces were soaked at 1000°C for $\frac{1}{2}$ hr and then controlled cooling was done up to 800°C in 1 hr and again at this temperature, the test pieces were allowed to cool down to room temperature in 13 hr.
- (5) Test pieces were fired at 1000°C and were allowed to cool without any soaking.
- (6) Test pieces were soaked at 950°C (maximum) and controlled cooling was done to 750°C in 3 hr and then furnace was cooled to room temperature in 13 hr.

Discussion

From the observations in Table 5, it is found that the lower amounts of B₂O₃ and Fe₂O₃ (A-1, A-2 and B-1) give yellow colour to the glaze, with lot of crazing. When either of the two is increased, a marked increase in crystal growth is observed. Higher amounts of Fe₂O₃ increase the maturing temperature of the glazes and the development of crystals. This is evident from the compositions A-3 and A-4 which have considerable Fe₂O₃ melt at higher temperature as compared to A-1 and A-2. Because of higher percentage of Fe₂O₃, the colour of the glazes darkens, crystals become more prominent and uniform, and crazing is minimised.

When B₂O₃ is increased, crystal growth is enhanced again, colour of the glaze darkens but there is no appreciable change in the melting temperature of the glazes. D_I and E_I prove these conclusions.

In between these limits, the results are as expected, i.e. B-2, C-3 and C-4 show gradual difference in colour and crystal formation. In fact these compositions are amongst the best ones. Still higher amounts of B₂O₃ and Fe₂O₃ do not give good results. Best aventurines are obtained in the ranges, B₂O₃ from 1.50 to 2.0 moles and Fe₂O₃ from 0.80 to 0.90 mole.

Alumina, when varied from 0.10 to 0.25 mole gives best results when it is 0.10 mole. Higher alumina does not favour crystallisation.

When Na₂O is replaced by K₂O, CaO and PbO (Fig. 2) crystal growth is minimised but the glaze exhibits many pleasant shades of colours. K_I gives a chocolate colour. This colour becomes lighter and lighter as we move towards PbO apex (Fig. 2) i.e. K₆, K₉ and K₁₀ give the lightest shades. A pleasant bluish tinge is imparted when we move towards CaO, i.e. K₄, K₇ and K₈ are

TABLE 5.—RESULTS.

Glaze No.	Colour	Crazing	Crystallization	Approximate melting temp.°C
A-1	Yellow-purple	crazed	None	980
B-1	"	"	fair	"
C-1	Purple	not visible	"	"
D-1	"	"	"	"
E-1	"	"	"	"
A-2	Yellow-purple	crazed	none	990
B-2	"	not visible	fair	"
C-2	Purple	"	"	"
D-2	"	"	"	"
E-2	"	"	"	"
A-3	Dark red	"	good	1000
B-3	"	"	"	"
C-3	"	"	"	"
D-3	"	"	"	"
E-3	"	"	very good	"
A-4	Red-black	"	good	"
B-4	"	"	very good	"
C-4	"	"	excellent	"
D-4	"	"	good	"
E-4	"	"	"	"
1C-4	Red-black	crazed	fair	"
2C-4	"	not visible	very good	"
3C-4	"	"	good	"
4C-4	"	"	none	"
K-1	Purple	not visible	fair	"
K-2	Purple with bluish tint	"	"	"
K-3	Purple with Brown tint	not visible	very little	"
K-4	Purple with more bluish tint	not visible	very little	"
K-5	Purple	"	"	"
K-6	Purple with brownish tint	"	"	"
K-7	Dominantly bluish purple	"	"	"
K-8	Lighter bluish tint	"	"	"
K-9	Purple	not visible	none	"
K-10	Brownish tint	"	"	"
S-1	Purple	crazed	fair	
S-2				
S-3				
S-4	"	none	very good	
S-5				
S-6				
S-7	"	none	very good	
S-8				
S-9				
S-10	"	"	good	
S-11				
S-12				
S-13				

darker; K₇ being most bluish in colour. No crazing is seen in these glazes and all of them have good gloss and smooth surface.

Variation in SiO₂ content from 3.5 moles to 11.0 moles has revealed that low SiO₂ contents give very little crystals. The number of crystals increases as we increase SiO₂. 7.0 to 9.0 moles of SiO₂ give the optimum range for best crystals, while SiO₂ as high as 11.0 moles does not hinder crystal growth.

Application of these glazes requires special attention. Skilled workmanship is essential. Uneven coating or any streak on ware spoils the uniformity of the crystals. Thin application of the glazes does not give rise to crystals because the glaze is not sufficient in which crystals can develop. Thick application gives rise to flowing and uneven crystal growth. 1 mm to 2 mm thickness gives good results.

Development of crystals depends upon the rate of cooling. Slow cooling between 1000°C and 750°C is most favourable for crystal growth, when cooling was done as in firing at Nos. 2,3 and 4 mentioned under para 'Glaze application and firing'; the results were not different from one another. In case of firing No. 1, some crystals were observed. In case of firing No. 5, no crystallisation was noted, as the glaze got less time to melt and form crystals. No. 6, again gave good results. These firing confirm the results of Norton⁴, on control of crystalline glazes.

The glaze which gives the best results has the following composition.

1.0 Na ₂ O	0.15 Al ₂ O ₃	7.0 SiO ₂
	0.90 Fe ₂ O ₃	
	1.75 B ₂ O ₃	

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