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CERAMIC COLOURS

Part III.—Blue Stains

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Blue stains compounded of oxides of zirconium, vanadium and cobalt have been studied. Different shades of blue have been developed and optimum compositions and conditions have been established for the respective shades. The stains have been studied for use as underglaze colours, and also as in glaze stains.

This study of blue stains is a continuation of earlier work[1,2] on ceramic colours. Blue stains can be prepared from cobalt or vanadium oxides and both have their own merits. Shades obtained with cobalt cannot be achieved with vanadium and vice versa. However, by the combination of these two type of stains, all the shades of the blue from delicate turquoise to a deep royal blue can be achieved. Vanadium blues can be blended with vanadium yellows to get green shades. These stains have been studied, keeping in view the demands and the conditions prevailing in the local pottery industry which is, at present, importing almost all of its colour requirements. The glaze used in the local pottery, with a little variations in different factories, is frit 80%, clay 10% and quartz 10%. The composition of the frit being glass (ordinary soda lime) 70%, red lead 20% and borax 10% and the body used is talc 52%, K.D. clay 25%, glass 20% and whiting 3%. Locally made stains as well as some of the imported stains do not behave satisfactorily when used under this glaze. We have tried successfully, using the same body and glaze, to stabilise blue as well as other stains by incorporating special flux compositions into these stains as mill additions. After trials in the Laboratories, these stains were provided to local pottery makers who found them satisfactory.

Experimental

Raw materials.—Indigenous materials have been used as far as possible. The imported materials used were of technical grade. The analysis of the indigenous materials used is given in Table 1. Vanadium oxide was added as ammonium metavanadate. B_2O_3 was added in the form of H_3BO_3.

Chemical Composition.—The following four series of stains were studied: (1) ZrO_2–V_2O_5–SiO_2; (2) CoO–Al_2O_3; (3) CoO–SiO_2; (4) CoO–Al_2O_3–SiO_2.

In series 1, several compounds were tried to stabilize V^{+4} into the lattice of $ZrSiO_4$. Only one of them gave good results. Similarly, in series 2,3 and 4, ZnO and H_3BO_3 were found for improving the quality of the stains. suitable

Temperature of Calcination.—Exact firing temperatures for different compositions were located by trial firing. The temperature selected for each composition was such that if overfired it would change into clinkers.

Preparation of Stains.—The ingredients were weighed in batches of 50 g each, mixed thoroughly in an agate mortar and placed in grog-fire-clay crucibles. The firing was done in a globar type electric furnace. After calcination, stains were ground in a mortar and washed with water if necessary. Water washing helped in eliminating

Table 1.—Chemical Analysis of the Raw Materials.

Material	Clay %	Quartz %	Whiting %
L/I	10.00	0.42	43.84
SiO_2	59.10	97.02	0.62
Al_2O_3	29.10	1.22	0.12
Fe_2O_3	0.90	0.15	0.07
K_2O	—	—	—
Na_2O	—	—	—
CaO	0.77	0.88	54.62
MgO	0.19	0.12	0.12

the scummy, spotted appearance of the stains by removing the soluble material. After washing they were milled for about 30–36 hr to pass through 325 mesh sieve in order to secure a uniform texture of the finished product.

Testing of Stains.—All the ceramic stains were tested by mixing them with flux compositions in suitable proportions, after grinding them with water to a fine state of subdivision. Colours were applied to biscuit tiles by spraying or by brush, and the tiles were then glazed with a glaze generally used in local pottery and fired in an electric muffle furnace to maturity. The colours were also tested by using them in glazes of different compositions up to 1200°C. Compositions of glazes showing good results are given in Table 2. Observation and comparison of colours was done visually. Table 2(a) and Table 2(b) show the frit and batch formulae for fluxes used to stablise the shades of the colours.

Results and Discussion

Zirconium–Vanadium Blues.—Vanadium exhibits different colours in different valence states and electronic environments. Pentavalent vanadium (in oxide form) is yellow, tetravalent is blue while trivalent is green. For obtaining a pure shade the whole of the vanadium present must be in a single state of valency. Therefore, when preparing blue stains we must see that no trivalent or pentavalent vanadium is present and we should investigate and discover the optimum conditions for developing pure blue shade. The Zr–V–SiO_2 compositions studied have been shown in Tables 3 and 3(a). The successful compositions are given in Table 3 and the failures are reported in Table 3(a).

No blue colour develops when mixtures of ZrO_2–V_2O_5–SiO_2; $ZrSiO_4$+V_2O_5 or ZrO_2–V_2O_5 are fired because vanadium remains in its pentavalent state and the stains are yellow or greenish yellow. Addition of borax or boric acid brightens the yellow colour. Addition of CaF_2 increases the green tinge. A small amount of vanadium is converted to V^{+4}. This was evidenced when the CaF_2-containing stains were suspended in water and a blue portion was clearly seen. A suitable reducing agent, in appropriate quantity was, therefore, to be used to convert the pentavalent state to tetravalent which has to be stablised[3] in the lattice of $ZrSiO_4$. It is also

TABLE 2.—Glazes

No	K_2O	Na_2O	CaO	MgO	BaO	PbO	ZnO	Al_2O_3	B_2O_3	SiO_2	ZrO_2
1	0.187	—	0.431	0.097	0.107	0.178	—	0.396	—	1.892	—
2	0.0509	0.1895	0.2908	—	—	0.1449	0.3239	0.1425	0.078	0.840	0.054
3	0.20	—	0.25	0.15	0.10	—	0.30	0.22	0.375	2.50	—

TABLE 2(a).—FRITS FOR FLUXES.

No.	Na_2O	K_2O	CaO	PbO	Al_2O_3	B_2O_3	SiO_2
1	0.102	0.057	0.397	0.444	0.222	0.205	2.447
2	0.482	0.085	0.433	—	0.208	0.335	1.897
3	0.163	0.076	0.244	0.517	0.142	0.327	1.970

TABLE 2(b).—BATCH COMPOSITION OF FLUXES

Flux No.	Frit No.			Feldspar	$CaCO_3$	Dolomite	China clay	Quartz	Barium carbonate	ZnO
	1	2	3							
1	55.5	—	—	9.5	5.0	3.6	10.2	16.2	—	—
2	12.5	31.5	—	—	5.0	5.0	12.0	23.0	5.0	6.0
3	—	30.0	—	—	5.8	5.5	16.1	28.3	5.5	8.8

clear from Table 3 that V^{+4} enters the lattice of $ZrSiO_4$ easily when $ZrSiO_4$ is formed at the same time from ZrO_2 and SiO_2. If we introduce ZrO_2 and SiO_2 in the form of $ZrSiO_4$, a very small amount of vanadium enters $ZrSiO_4$ lattice as V^{+4} and the stains have a light shade. Moreover, if the reducing agent is more than the appropriate amount the stains have more greenish tinge and when the reducing agent is not added in sufficient quantity we get a dirty green shade. Composition No. 2 has been found to be the best. This means that ZrO_2 and SiO_2 should be introduced in molar (1:1) proportions, and ammonium metavanadate 4.85% and the reducing agent about 6.8% of the total compositions.

Cobalt Blues.—Cobalt oxide cannot be used alone as a ceramic colour because at high temperature and in reducing atmostphere, the oxygen is given off, forming bubbles which are trapped in the glaze as it cools,[4] and with low temperature glazes containing a large amount of fluxes it has a ten tendency to flow. Therefore, cobalt blues are prepared, in the spinel form $CoO.Al_2O_3$ which is stable in reducing conditions also or in the form of cobalt aluminosilicate or cobalt silicate. Reaction of CoO and Al_2O_3 starts between 900°–950°C when α-Al_2O_3 is formed and the reaction rate greatly increases during the change of γ-Al_2O_3 to α-Al_2O_3.[5] CoO and SiO_2 begin to react at 900°C and form a violet silicate.[6]

TABLE 3.—ZIRCONIUM–VANADIUM BLUE (Temperature 800–900°C).

No.	ZrO_2	Microzone	SiO_2	NH_4VO_3	Reducing agent	AlF_3	Shade
1.	61.5	—	30.0	3.0	7.0	—	Turquoise blue<2
2.	,,	—	,,	5.0	7.0	—	(Best)
3.	,,	—	,,	7.0	7.0		Bright turquoise blue <1,2
4.	,,	—	,,	9.0	7.0	—	<1,2
5.	,,	—	,,	3.0	9.0	—	Turquoise blue <1—2
6.	,,	—	,,	3.0	11.0	—	,, <1—2
7.	,,	—	,,	3.0	13.0	—	,, <1—2
8.	,,	—	,,	5.0	9.0		,, >1—2
9.	,,	—	,,	5.0	11.0		,, >1—2
10.	,,	—	,,	5.0	13.0		(Less blue than 2, brighter than 3,4)<1.
11.	,,	—	,,	7.0	9.0		,, < 8
12.	,,	—	,,	7.0	11.0		,, < 8
13.	,,	—	,,	7.0	13.0		,, < 8
14.	,,	—	,,	9.0	9.0		,, < 8
15.	,,	—	,,	9.0	11.0		,, < 8
16.	,,	—	,,	9.0	13.0	—	Less blue than 10
17.	,,	—	,,	5.0	13.0	4.0	Less than 16
18.	,,	—	,,	5.0	11.0	6.0	Less than 17
19.	,,	—	,,	5.0	9.0	8.0	Less than 18
20.	,,	—	30.0	4.0	15.0	—	Between 17 and 18
21.	40.0	—	—	2.0	8.0	—	Less than 18
22.	40.0	—	40.0	4.0	6.0	—	More than 16 and less than 10
23.	—	91.0	—	4.0	8.0	—	Very light blue.

TABLE 3(a).—(Temperatures 850–900°C)-

No.	Microzone	ZrO_2	SiO_2	NH_4VO_3	H_3BO_3	Other ingredients	Remarks
1.	85.0	—	—	2.0	13.0	—	Yellow at 850°C bright at 900°C
2.	80.0	—	—	1.0	—	Borax, 19.0	
3.	80.0	—	—	0.5	19.5	—	} Light yellow
4.	80.0	—	—	1.0	—	CaF_2, 19.0	
5.	90.0	—	—	1.0	—	KNO_3, 9.0	
6.	85.0	—	—	2.0	—	KNO_3, 13.0	} White
7.	85.0	—	—	2.0	—	NH_4Cl, 8.0; $CaCo_3$, 5.0	
8.	—	50.0	42.0	2.0	20.0	—	
9.	—	40.0	40.0	2.0	18.0	—	} Light greenish yellow
10.	—	35.0	35.0	2.0	10.0	CaF_2, 10.0	
10-A	—	35.0	35.0	2.0	10.0	CaF_2, 10.0; Sb_2O_3, 10	No change greenish tinge.
11.	90.0	—	—	2.0	6.0	CaF_2, 2.0	
12.	90.0	—	—	3.0	4.0	CaF_2, 3	Increase 11-13
13.	90.0	—	—	4.0	3.0	CaF_2, 3	White
14.	60.0	—	20.0	2.0	10.0	CaF_2, 8	
15.	60.0	—	20.0	2.0	10.0	—	} Light yellow
16.	—	60.0	32.0	5.0	10.0	SnO_2, 3	

TABLE 4.—COBALT BLUE .

No.	CoO	Al_2O_3	SiO_2	Clay	ZnO	H_3BO_3	SnO_2	Temperature of Calcination °C	Shade
1.	29.5	51.0	—	—	—	—	—	1300	Royal blue with reddish tinge
2.	24.5	51.0	—	—	5.0	—	—	1250	Royal blue brighter than 1
3.	19.5	51.0	—	—	10.0	—	—	1250	2
4.	19.5	51.0	—	—	10.0	5.0	—	1250	3
5.	29.5	—	30.0	—	—	—	—	1200	Violet
6.	24.5	—	30.0	—	5.0	—	—	1200	(More blue than 5)
7.	19.5	—	30.0	—	10.0	—	—	1200	(More blue than 6)
8.	19.5	—	30.0	—	10.0	5.0	—	1200	(More blue than 7)
9.	29.5	51.0	30.0	—	—	—	—	1200	Royal blue with reddish tinge
10.	29.5	51.0	30.0	—	10.0	—	—	1200	brighter than 9
11.	29.5	51.0	30.0	—	—	—	10.0	1200	more reddish tinge than 8,9
12.	29.5	51.0	30.0	—	10.0	—	10.0	1200	reddish tinge greater than 10,11, & 12).
13.	15.0	—	—	51.0	—	—	—	1200	Medium blue
14.	30.0	—	—	51.0	—	—	—	1200	Darker than 13.
15.	15.0	—	—	51.0	—	10.0	—	1200	
16.	15.0	—	—	51.0	5.0	—	—	1200	Bright medium blue (brighter than 12, 13).
17.	10.0	—	—	51.0	10.0	—	—	1200	
18.	10.0	—	—	51.0	10.0	5.0	—	1200	Medium blue Darker than 17
19.	25.0	—	—	—	25.0	—	—	1100	Bluish green
20.	35.0	—	—	—	15.0	—	—	1100	Greenish blue
21.	15.0	—	—	—	35.0	—	—	1100	Bluish green

Cobalt blue compositions investigated are shown in Table 4 $Co.Al_2O_3$ compositions are royal blue with a reddish tinge. Addition of ZnO brightens the colour and reduces reddish tinge. Additions of H_3BO_3 make the colour brighter and helps in the formation of the spinel at lower temperature.[7] Cobalt silicate compositions are violet in colour, ZnO and H_3BO_3 additions effect the compositions in a manner compareable to $Co.Al_2O_3$ compositions. $CoO-Al_2O_3-SiO_2$ compositions are also royal blue with a reddish tinge. Compositions containing CoO and clay have medium dull blue colour which brightens by the addition of ZnO and H_3BO_3. SnO_2 has no effect, as regards colour, on these compositions except that they become opaque.

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