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CERAMIC COLOURS

Part IV.—Green Stains

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A comprehensive study is made on the preparation and use of the various green colours, having different shades. Optimum conditions and composition have been established for stains as well as glazes. The stains have been studied for use as under-glaze, over-glaze and also as in-glaze stains. The colours can be applied at various temperature ranging from 900-1200°C.

The use of ceramics stains has continued to increase, and the range of the colours widened due to intensified research and development. This investigation, a continuation of earlier work[1-3] on ceramic colours, deals with green ceramic stains development. The study has been made, keeping in view the increasing demands prevailing conditions in the local pottery industry which is, at present, importing almost all its colour requirements. Imported colours are selling at a high price in the market. The cost of those stains when manufactured on a commercial scale will cost half the price of imported one, thus saving a large amount of foreign exchange. The glaze being used by the local potters, mentioned in the previous work[3] changes the shades of the locally made as will as some of the imported stains, when used under the above mentioned glaze. By incorporating special flux composition into these stains we have tried them out successfully using the local body and glaze. After laboratory trials, these stains were provided to the local pottery maker who found them satisfactory.

Ceramic green colours may be divided into the following generals classification:

1. Those containing chromium,
2. those without chromium—chiefly the green made from ziroconium—vanadium grouping,
3. there is a third type of green colours from Cu, and,
4. those containing nickle oxide.

Raw Material

Indigenous materials have been used as far as possible. The imported materials used were of technical grade. The chemical analysis of the material is given in the Table 1. Chromium oxide was obtained from potassium dichromate.

Chemical Composition

The following series of stains were studied:

1. Chrome green Cr_2O_3
2. Victoria green Cr_2O_3–$CaCO_2$–SiO_2
3. Blue green Cr_2O_3–CoO(cobalt oxide)
4. Copper green CuO–ZnO
5. Nickle green NiO–Cr_2O_3

Zirconium–vanadium green were not investigated because of the relative high price of the raw materials. This shade of green can be made by blending[4] Zr–V–yellow and Zr–V–blue (turquoise).

Preparation of Stains

1. *Chrome Green.*—Chrome green colour was prepared by calcining dichromate of sodium or potassium. Charcoal, coal, sulphur,[5] ammonium chloride,[6] burnt gypsum and salt peter were tried as reducing agent.

Following reactions take place:

(i) $Na_2Cr_2O_7+2C = Cr_2O_3+Na_2CO_3+CO$

(ii) $K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 = 2NaCl+4H_2O+N_2$

(iii) $2Na_2Cr_2O_7 + 2 CaSO_4 = 2 Cr_2O^3+2Na_2SO_4+2CaO + 3O_2$

Potassium dichromate was thoroughly mixed with finely divided reducing agent and mixture was placed in a clay grog crucible. The mixture was heated in an electric furnace at 600–850°C. Best results were attained with ammonium chloride or sulphur as reducing agent at 600–800°C for 4 hr. heating. Ninety per cent theoretical yield of 98% of Cr_2O_3 was obtained. After ignition the products were ground and washed until there is no yellow colouration in the washing water. 8–15% of reducing agent yields the maximum Cr_2O_3.

Cr_2O_3 so prepared was mixed with different quantity of china-clay and fired at 1050°C. Pure Cr_2O_3 as well as calcined mixture (Cr_2O_3+clay) were applied as underglaze, in-glaze and overglaze colour.

2. *Victoria Green.*—Victoria green colour was prepared by calcining silica, $CaCO_3$ and dichromate of sodium or potassium. Compositions and shades are shown in the Diagrame 1 and Table 3 respectively.

Addition of CaF_2 (fluorspar) or $BaCO_3$ or, plaster brightens the colour intensity. Compositions were calcined at various temperature ranging between 1000–1250°C. Potassium-dichromate dissolved in hot H_2O was mixed with other ingredients.

3. *Blue Green Colour.*—Blue green colours were made from Cr_2O_3, CoO and clay. Composition and shades are shown in the Diagram 2 and 3 and Table 2 and 3 respectively. Different composition were calcined at various temperatures ranging from 1000–1250°C for 1 hr. Similarly CoO and ZnO blue green was prepared.

4. *Copper Green.*—Copper oxide and zinc oxide when calcined together gives nice green colour. Compositions tried are shown in Table 4. Mixtures were calcined at 1000°C for 1 hr.

5. *Nickel Chromium Green.*—NiO and Cr_2O_3 when calcined at 1000–1100°C gives beautiful green colour. Different composition and shades are shown in Table 5. Best compositions are only mentioned here.

Washing and Grading

All the green stains prepared from $K_2Cr_2O_7$ are thoroughly washed with water till the rinsing water does not show any yellow colouration. Washed colours are then ground to a fineness of 325 B.S. sieve in order to secure a uniform texture of the furnished product.

Application of the Stains

Stains were applied in-glaze, under-glaze and over-glaze. 3–10% of the stains was added to the glaze and was applied to biscuit tiles by spraying or by dipping. Tiles were then fired in an electric muffle furnace to maturity.

In case of under-glaze and over-glaze application the stains were mixed with flux compositions 3 in suitable proportions. This mixture is then applied to biscuit tiles or on the finished pieces for under-glaze and over-glaze testing. Suitable glaze is then applied on the pieces by spraying or dipping

TABLE 1.—CHEMICAL ANALYSIS OF THE RAW MATERIALS.

Material	Clay 1	Clay 2	Quartz	Whiting
L/1%	10.62	12.52	0.42	43.84
SiO_2	48.52	46.32	97.02	0.62
Al_2O_3	33.30	37.74	1.22	0.12
Fe_2O_3	0.65	0.32	0.15	0.07
CaO	3.24	0.78	0.88	54.62
MgO	1.25	0.11	0.12	0.12
Na_2O	1.25	0.74	—	—
K_3O	0.10	0.86	—	—

TABLE 2.

No.	Cr_2O_3 (%)	Clay (%)	Colour on calcining	colour after application
1	10	90	Dirty green grey	Dirty grey
2	20	80	Dirty green	Light green
3	30	70	Green	Green
4	40	60	Green	Green
5	50	50	Dark green	Dark green
6	60	40	,,	,,
7	70	30	,,	,,
8	80	20	,,	,,
9	90	10	,,	,,

TABLE 3.

Diagram No. 1		Diagram No. 2		Diagram No. 3	
Composition	Colours of the stain	Colour for clay	Colour for Al_2O_3	Colour for clay	Colour for Al_2O_3
1	Dark green	Dark green	Dark green		
2	Dark green	Dirty dark green	Dark green	Light green	Light green
3	Dark green	Dirty dark green	Dark green	White	White
4	Green	Dark Bluish green	Dark Bluish green	Green	Green
5	Green (tends towards Vic. green)	Dark blue green	Dark green	Dirty light	Light green
6	Green	Dark blue	Dark green	White	White
7	Green	Dark blue green	Green blue	Green	Green
8	Vic. green	Blue green	Bright blue green	Blue green	Blue green
9	Vic. green	Blue green	Bright blue green	Light blue green	Blue green
10	Green	Dark green	Bright green	White	White
11	Light green	Dirty greenish blue	Greenish blue	Green	Green
12	Light green	Bright green blue	Green blue	Blue green	Blue green
13	Apple green	Green blue	Greenish blue	Blue green	Bright green
14	Light green	Dirty blue green	Blusih green	Blue green	Blue green
15	Light green	Greyish green	Greyish green	White	White
16	White	Dark blue	Dark blue	Black	Black
17	White	,,	,,	Dark blue	Dark blue
18	White	,,	,,	Dark blue	Dark blue
19	White	,,	,,	Dark blue	Dark blue
20	White	,,	,,	Blue	Blue
21	White	,,	,,	White	White

and fired till glaze maturing. Firing of over-glaze colour was done on a low temperature i.e. 700–800°C. Glaze compositions are shown in Table 6.

Results and Discussion

Chrome Green.—Sodium or potassium dichromate when heated in reducing condition forms Cr_2O_3. Any one of the following; coal, charcoal, ammonium chloride or sulphur was applied as reducing agents. Best results were obtained with ammonium chloride or sulphur when applied as reducing agents. Maximum yield of 95% Cr_2O_3 was obtained with 10–18% sulphur. Mixture of sulphur and potassium dichromate was calcined for 2–4 hr at 600–850°C. The mixture melts at a higher temperature such as at 1000°C.

To have a beautiful green shade 1-5% of Cr_2O_3 can be used as in-glaze colour. Cr_2O_3 when used as such has a tendency to swell, fume or volatilize to some extent during the firing process and is thus absorbed into the refractory of the furnace. When tin whites or pastel colours containing tin are fired in this furnace, chrome reacts with tin and a chrome–tin pink is formed. For this reason, chromium oxide is usually calcined with silica and Al_2O_3 to completely react with Cr_2O_3. China clay was used instead of silica and alumina. Best colour was obtained with a mixture of Cr_2O_3 and china-clay in the ratio of 3:7, optimum temperature being 1050°C. The colour intensity increases with the increase of Cr_2O_3. Colour applied with a higher percentage of Cr_2O_3 does not look pleasant.

Victoria Green.—Calcination of silica, calcium carbonate and potassium dichromate gives a very beautiful bright green colour, but it is very transparent. Fig. 1 shows the compositions studied. Addition of fluorspar (CaF_2) helps the easy formation of victoria green. It also helps in stablizing the colour. Small additions of red-lead, $BaCO_3$ and plaster further stablize the colour. Compositions forming victoria green stains are shown by the shaded area in the Fig. 1, with a fix addition of 24% CaF_2, 2% red-lead, 2% $BaCO_3$ and 3% plaster. Compositions were fired at different temperatures between 950–1150°C. Mixture melts at higher temperature such as at 1050°C. Optimum temperature for the formation of victoria green was found to be 1000°C. Compositions ranging between $K_2Cr_2O_3$ 33–39% $CaCO_3$ 18–24% SiO_2 18–26% $CaF_2$16–25%, red lead 1–5%, $BaCO_3$ 1–3%, plaster 1–3% give victoria green colour.

In opaque glazes colour does not apply satisfactorily, for the tone always has a grey cast and lacks brilliance. When colour is applied thinly as an under-glaze, there is often a blackening[4] of the colour at the interface of bisque and the colour. Chrome green and victoria green have particular requirement for glaze. They must not contain zinc oxide, because zinc in glaze reacts with chromium in the stain and result in a rather undesirable dirty green. The use of the tin oxide must also be avoided as tin oxide of the glaze reacts with chromium of the stain, a chrome-tin pink is formed. This developes a very undesirable pink under tone in the green. Zircona and microzone are desirable. opacifier for victoria green and chrome green colours. 5–10% of thoroughly washed and ground to 350 mesh stain gives beautiful green shades.

Blue Green.—Composition of blue green stains prepared by calcination of Cr_2O_3, CaO and clay are shown by the Fig. 2. Colour of the stains are

TABLE 4.

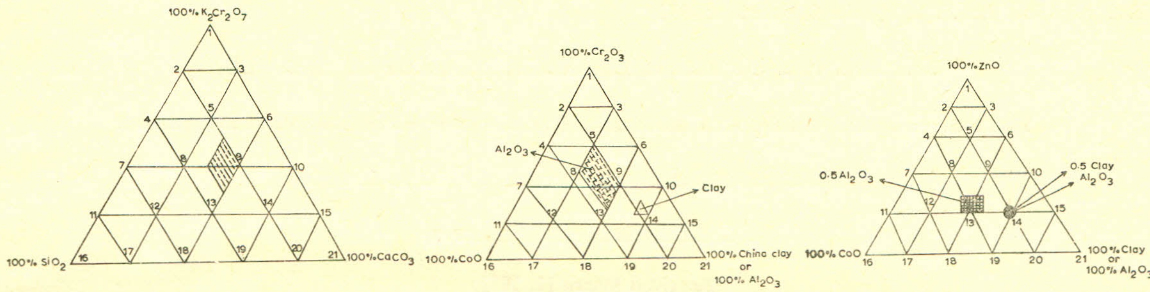
No	CuO %	ZnO %	Colour after calcination	In-glaze
1	10	90	Grey	Dirty grey
2	20	80	Grey	Grey
3	30	70	Greyish green	Dirty green
4	40	60	Slightly greyish-green	Green
5	50	50	Green	Green
6	60	40	Green	Dark green
7	70	30	Blackish green	Black
8	80	20	Black	Black
9	90	10	Black	Black

TABLE 5.

No	NiO %	Cr_2O_3 %	Colour after calcination	In-glaze
1	10	90	Chromium green	Light greyish green
2	20	80	Dark green	Greyish green
3	30	70	Dark green	Greyish green
4	40	60	Green	Green
5	50	50	Green	Green
6	60	40	Blackish green	Blackish green
7	70	30	Greenish black	,,
8	80	20	Greenish black	Greenish black
9	90	10	Light greenish black	,,

TABLE 6.—GLAZE COMPOSITIONS (%).

No.	K_2O	Na_2O	CaO	MgO	BaO	ZnO	PbO	Al_2O_3	B_2O_3	ZrO_2	SiO_2
1	0.189	0.051	0.291	—	—	0.324	0.145	0.143	0.08	0.05	0.84
2	0.187	—	0.431	0.097	0.107	—	0.178	0.396	—	—	1.892



Flourspar =24%; Red lead 2-3%; Ba CO_3 = 3% With fixed addition to each Composition.

tabulated by the side table. It is clear from this table that colour changes beautifully with change of composition. High chromium oxide and low cobalt oxide containing compositions are of greener-blue-green colour. When the amount of chromium oxide is gradually decreased with an increase in the amount of cobalt oxide, the shades from green colour. When the amount of chromium oxide is gradually decreased with an increase in the amount of cobalt oxide, the shades from green-blue green to the blue blue-greens are obtained. Best blue green colours are formed within the singly shaded portion of the Fig. 2.

Similar colours are obtained by replacing clay by alumina. Best shades are obtained withing the doubly shaded area.

Compositions in the two shaded areas, when calculated correspond to the following molecular formula: (i) with clay, 0.5 Cr_2O_3, 0.5CoO, 0.5 clay; (ii) with a alumina, 0.5 Cr_2O_3, 0.5 CoO, 0.5 alumina.

Blue green colours obtained from the calcination of CoO, ZnO and clay or alumina are shown by the Fig. 3. In case of cobalt oxide, zinc oxide and lcay or alumina stains, the shades change from dark blue to bluish green as the amount of cobalt oxide decreases. Best green of this type is obtained within the shaded areas. Singly shaded area indicates the colour with that of clay and double shaded area is that of alumina.

Colours formed with alumina are brighter than that with clay. Best greens of this type have following molecular formula: 0.5 CoO, 0.5 ZnO, 0.5 clay; 0.5 CoO, 0.5 ZnO, 1.0 Al_2O_3. Intensity of the colour is maximum at 1100°C.

Stains with Al_2O_3 are of turquoise blue shades. So far as their application is concerned the low percentages of blue green stains result in glazes an undesirable dirty grey colour. Blue green gave very attractive body stain, developing a strong turquoise colour.

Copper Green.—Copper oxide when calcined with zinc oxide at 1100°C forms a very attractive green colour. From the Table 3 it is obvious that the beautiful green is obtained when the amount of the two oxides are nearly equal. As the amount of copper oxide is increased, the colour of the stain so formed changes from grey to green and finally to black. Molecular formula for the best colour being CuO–ZnO.

Tin oxide or microzone may be used as an opacifier in the glaze. Zinc oxide is also essential consistituent of this glaze. If the glaze is alkaline, a turquoise blue colour results; but when the glaze is acidic, a beautiful green colour is developed.

This combination should not be used in glaze that fires above 1175°C. Above this temperature colour tinge does not remain uniform.

Nickle Chrome Green.—Nickle oxide and chromium oxide calcined at 1000°C forms a very beautiful green colour. As chromium oxide is increased the colour of the stain formed changes, from greenish black to chrome green through a very beautiful dark green. As shown from Table 4, stain so formed is supposed to have a formula NiO. Cr_2O_3; a spinel.[7] Spinel formation is increased by the addition of KCl or boric acid. Best results are obtained at 1000°C for 1 hr. Flux and glazes are shown in Table 6.

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