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CERAMIC COLOURS

Part V. Brown Stains

M. AYUB, FAZALUR REHMAN, M.A. BEG and F.A. FARUQI

PCSIR Laboratories, Lahore 16

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Abstract. Ten families of the brown stains are discussed: (i) chrome–iron, (ii) chrome–iron–zinc, (iii) chrome–iron–alumina, (iv) chrome–iron–lime, (v) chrome–iron–manganese, (vi) iron–zinc–manganese, (vii) iron–chrome–tin, (viii) chrome–manganese, (ix) manganese–alumina, and (x) iron–chromium–zinc with the addition of alumina or tin. Typical glazes were used as base for each stain. Optimum composition of the stains, conditions such as calcination temperature, grinding, composition of the base glazes and that of the flux used for underglaze and onglaze are investigated. Maturing temperature in the range of cone 02–10 were employed. Brown ceramic stain generally changes its shade when used as inglaze. Stability of brown stain with the incorporation of Al_2O_3, SnO_2 zircon and Sb_2O_3 into the calcined chrome–iron–zinc brown stain, mostly used in the industry, have been investigated.

This investigation, a continuation of earlier work[1–4] on ceramic colour, deals with brown ceramic stains development, its application as underglaze onglaze and inglaze stain. Many families of brown ceramic stains can be made. This work contains the following types of brown: (i) Fe_2O_3–Cr_2O_3, (ii) Fe_2O_3–Cr_2O_3–ZnO, (iii) Fe_2O_3–Cr_2O_3–Al_2O_3, (iv) Fe_2O_3–Cr_2O_3–$CaCO_3$, (v) Fe_2O_3–Cr_2O_3–MnO, (vi) Fe_2O_3–ZnO–MnO_2, (vii) Fe_2O_3–Cr_2O_3–SnO_2, (viii) Cr_2O_3–Mn_2O_3, (ix) Al_2O_3–MnO, and (x) Fe_2O_3–Cr_2O_3–ZnO with the addition of Al_2O_3 or SnO_2 and Sb_2O_3. These stains have been developed, keeping in view the increasing demand of ceramic colours by the local pottery industry, at present by importing almost all of its colour requirements. The effect of glaze composition for inglaze stain and that of the flux for underglaze and onglaze colours have been studied. Imported colours are selling at very high price in the market. We have tried to lower the cost as far as possible by using the indigenous raw materials.

The study of the brown stain comprises of the four variables namely composition of stain, calcination temperature, fineness of the stain, i.e. uniform texture, and adjustment of the glaze composition for inglaze and that of the flux for underglaze and onglaze colour.

Experimental

Raw Materials. Indigenous raw materials have been used as far as possible. Imported materials used were of technical grade. Chemical analysis of the indigenous materials are given in Table 1.

Composition. The following families of the brown stains have been studied, (1) chrome–iron: (2) chrome–iron–zinc, (3) chrome-iron–alumina, (4) chrome–iron–lime, (5) chrome–iron–manganese, (6) iron–zinc–manganese, (7) chrome–iron–tin, (8) chrome–manganese, (9) alumina–manganese, (10) chrome–iron–zinc–tin oxide, (11) chrome–iron–zinc–alumina.

Other combinations of metallic oxide when calcined at different temperatures also give brown colour. They are costly, therefore, not dealt herewith. They are: (i) titanatungstum–chrome, (ii) manganese–alumina–zircon–vanadium and (iii) uranium.

Chromium and iron are taken from chromite ore or from $K_2Cr_2O_7$ and $FeSO_4$, manganese from manganese ore, calcium from lime, zinc, tin, as oxides, zirconium as microzone and antimony as Sb_2O_3.

Calcination Temperature. Exact firing temperatures for different compositions were located by trial firing; temperatures selected for each composition was such that if overfired, it would change into clinker. Temperature range studied lies between 900–1300°C in oxidizing atmosphere. Addition of 5–10% boric acid helps the formation of stains at lower temperature.

Colour Preparation. The ingredients were weighed in batches of 100 g mixed thoroughly in an agate mortar and placed in grog-fire-clay crucibles. The firing was done in a globar type electric furnace and after firing the product washed with water if necessary. Water washing helps in eliminating the scummy spotted appearance by removing the soluble materials. Washed stains were milled for 30–36 hr to pass through 300 B.S. Mesh. Sieve in order to secure uniform texture of the finished product. Finer particles give orange to yellowish tinge to the colour.

Application. Finely ground stain 5–10%, were added in mill batch of the selected glaze and applied to experimental pieces by spraying or dipping. Glaze composition sometimes, changes the stain composition during firing as some of the stain ingredients are dissolved into the glazes. According to Marquis and Carpenter,[5] and Hawks[6] and Hurd,[7] the composition of the glaze is as important as that of stain itself in determining the colour. Some of the colours, i.e. chrome–iron–zinc–stains usually change their original tinge, thus losing brightness. Different glaze compositions due to variation in oxides produce different shades with the same stain.

Various glaze compositions were tried and those found successful (1–6) are given in Table 2. Composition of the flux for underglaze and onglaze colour is also mentioned (Table 2). Different percentages of the stain and fluxes were tried. Best results were obtained by the colour–flux ratio ranging 1:1, 1:2 and 2:3 according to the shade required. Addition of the opacifier zirconium silicate into the glaze brightens the colour shades, 2.5–10% of zirconium silicate gives best brown colour of the tan shade.

Results and Discussion

1. *Chrome–Iron Brown.* Brown stain of this type were prepared either by the calcination of chromite ore with NaCl or by the calcination of the mixture of $K_2Cr_2O_7$ and $FeSO_4$. Composition studied are given in Table 3. Chromite ore when calcined with NaCl gives a brown colour depending upon the composition of chromite, i.e. the percentage of iron oxide and chrome oxide present. Reddish brown colour increases as the amount of iron oxide increases. All the colours have greyish or blackish tinge. They are not true brown colour.

2. *Chrome–Iron–Zinc Brown.* The chrome–iron–zinc stain, one of the most widely used in industry, was prepared by the calcination of $K_2Cr_2O_7$, $FeSO_4$ and ZnO, $K_2Cr_2O_7$ and $FeSO_4$ provide Cr_2O_3 and Fe_2O_3 for the reaction. The study of this series showed that the presence of ZnO played a very important and prominent role in the formation of reddish brown colour. Zinc oxide supplies the necessary oxygen to change Cr_2O_3 to a higher form and it also reacts with Cr_2O_3 to form zinc chromate. Both these reactions are responsible for the formation of chrome–iron-zinc brown stains. Bryan[8] concludes that ZnO acts as an agent supplying the necessary oxygen to change the Cr_2O_3 to a higher form; it remains as such, unless it is given a violent reducing atmosphere. The colouring power of chromium is merely a question of oxidation, and when zinc is present the chromium is oxidized hence a red brown colour. Pence[9] infers that the colour effect of zinc upon chromium in underglaze stain is similar to the action of the same inglazes; the tint or quality of the colour is determined by the composition of the stain. This indicates that the change in colour is the result of the formation of one or more compounds into which zinc and chromium enter and that the different compounds have their characteristic tints. Oxidation plays a leading part

TABLE 1

Oxide given	Clay (%)	Quartz (%)	Chromite ore (%)	$K_2Cr_2O_7$ (%)	$FeSO_4$(%)
Loss on ignition	12.16	0.25	—	—	—
Al_2O_3	39.85	1.92	16.2	—	—
SiO_2	45.8	97.8	23.2	—	—
Fe_2O_3	0.35	0.22	13.2	—	28.0 (after calcination)
CaO	0.13	—	—	—	—
MgO	0.18	0.07	6.9	—	—
Cr_2O_3	—	—	40.3	48.3	—

TABLE 2. MOLECULAR FORMULAE OF THE GLAZES.

No.	(Na_2O+ K_2O)	CaO	MgO	PbO	B_2O_3	Al_2O_3	SiO_2	ZnO	BaO
1	0.3	0.4	—	0.3	1.2	0.25	2.8	—	—
2	0.45	0.55	—	—	1.2	0.5	3.5	—	—
3	—	—	—	1.0	—	0.15	1.75	—	—
4	0.3	0.2	0.1	0.4	0.5	0.2	2.5	—	—
5	0.22	0.31	0.19	—	—	0.37	3.04	0.28	—
6	0.33	0.40	0.12	—	—	0.41	4.06	—	0.14
Flux	0.182	—	—	0.456	0.362	—	0.578	—	—

TABLE 3

Composition No.	Composition (%) Fe_2O_3	Cr_2O_3	Colour	Composition (%) Cr_2O_3	Mn_2O_3	Colour	Composition (%) Al_2O_3	MnO_2	Colour
1	90	10	Greyish red	90	10	Blackish green	90	10	Light grey
2	80	20	Blackish red	80	20	Blackish green	80	20	Grey
3	70	30	Blackish red	70	30	Greenish brown	70	30	Brownish grey
4	60	40	Reddish brown	60	40	Brown	60	40	Brown
5	50	50	Brown	50	50	Dark brown	50	50	Dark brown
6	40	60	Greenish brown	40	60	Dark brown	40	60	Dark brown
7	30	70	Greenish brown	30	70	Greenish black	30	70	Blackish brown
8	20	80	Brownish green	20	80	Greenish black	20	80	Blackish grey
9	10	90	Greyish dark green	10	90	Black	10	90	Dark blackish grey

TABLE 4

Composition No.	Cr_2O_3 (%)	Fe_2O_3 (%)	ZnO (%)	Colour after calcination	Colour in underglaze: Glaze No. 1	Glaze No. 2	Glaze No. 3	Colour in inglaze No. 4	Colour in onglaze 5 or 6
1	100	—	—	Dark green	Green	Green	Green	Green	Olive green
2	80	20	—	Dark brown	Brownish	Brownish	Brownish grey	Pea green	Blackish brown
3	80	—	20	Greyish green	Olive green	Olive green	Olive green	Green	Light olive green
4	60	40	—	Very dark black	Brownish black	Brownish black	Brownish black very dark	Greyish green	Dark blackish grey
5	60	20	20	Brown	Dark brown	Dark brown	Dark brown	Dark grey green	Brown
6	60	—	40	Dark grey	Light greyish green	Light greyish green	Yellowish green dark	Yellowish green	Yellowish grey
7	40	60	—	Black	Light chocolate brown	Chocolate brown light	Black	Pale yellowish grey green	Very dark black (brownish)
8	40	40	20	Brown	Yellowish brown	Yellowish brown	Brown yellowish	Pale yellowish green	Light red brown
9	40	20	40	Light brown	Yellowish brown	Reddish brown	Reddish brown	Yellowish green with brown tinge	Dark orange
10	40	—	60	Grey	Yellowish brown dark	Yellowish brown	Yellowish brown light	Yellowish green	Pale green
11	20	80	—	Black	Greyish brown	Grey brown	Greyish brown	Pale green	Dark brown
12	20	60	20	Bright brown	Pinkish brown	Brownish pink	Brown	Pale green dark	Red brown
13	20	40	40	Light brown	Pinkish brown	Pinkish brown	Brownish pink	Pale green brown tinge	Reddish brown
14	20	20	60	Light brown	Light red brown	Red brown	Brown	Yellowish green	Dark orange
15	20	—	80	Grey	Yellowish brown light	Yellowish brown light	Yellowish brown	Yellowish green	Pale yellow
16	—	100	—	Red brown	Yellowish brown	Yellowish brown	Yellowish brown	Light yellow	Very good pinkish brown
17	—	80	20	Choccolate	Yellowish brown	Yellowish brown	Reddish brown	Light yellow	Very good chocolate
18	—	60	40	Yellowish brown	Yellowish brown light	Yellowish brown dark	Light reddish brown	Light yellow	Reddish orange
19	—	40	60	Yellowish brown	Light yellow	Light yellow	Light brown	Faint yellow	Dark orange
20	—	20	80	Light yellow brownish	Faint yellow	Faint yellow	Light yellow	Very faint yellow	Light brownish yellow
21	—	—	100	Light yellow	White	White	White	White	White

in the action of chromium in glazes containing zinc.[10] While oxidation and reduction play a great part, the formation of chrome brown in the presence of zinc is not due to the formation of higher forms of chromium through oxidation by zinc oxide, but by the formation of zinc chromates. Zinc chromate is, however, influenced by kiln condition. Chromium oxide in presence of zinc produces colours other than green through the formation of chromate, rather than through the oxidation of Cr_2O_3 to higher forms.

Compositions of this type of brown colours are shown in the well-known triangular system (Fig. 1, Table 4). It is obvious from the Table 1 that compositions having higher percentage of Cr_2O_3 gave green or greenish shades. As the amount of iron oxide increases the shade changes to reddish brown and finally to iron oxide red. Best reddish brown colours are obtained when compositions range runs as Cr_2O_3 30–35%, Fe_2O_3 30–35% and ZnO 30–35%.

From the comparison of chrome–iron brown and chrome–iron–zinc brown stains, it is concluded that chrome–iron brown give blackish brown shades while chrome–iron–zinc brown impart beautiful brown shades; a true brown tinge of the chrome–iron–zinc brown stain, depends upon the formation of different compounds containing zinc and chromium.

3. Chrome–Iron–Alumina. Composition of chrome–iron–alumina are given in Fig. 2 and their shades in Table 5. It is obvious from the Table that as the chromium decreases the greenish tinge of the stain changes to greyish and then to red with the increase of iron. Maximum Al_2O_3 gives maximum greyish shade and maximum iron oxide impart maximum reddish tinge. Percentage composition of the best reddish brown and dark brown colours are as follows:

	Reddish brown (%)	*Dark brown* (%)
Cr_2O_3	10–20	20–25
Fe_2O_3	60–80	18–25
Al_2O_3	10–20	50–60

Calcination temperature was 1200°C.

4. Chrome–Iron–Lime. Compositions of this series are shown in Fig. 3 and their shades after calcination in Table 5 which reveals that the shade of the stain so formed are yellowish or orange. Maximum chromium and minimum of iron impart greenish and a maximum of iron and minimum of chromium gave reddish or reddish brown through orange and yellowish shades. As the amount of $CaCO_3$ increases the tinge of the stain changes to orange red through

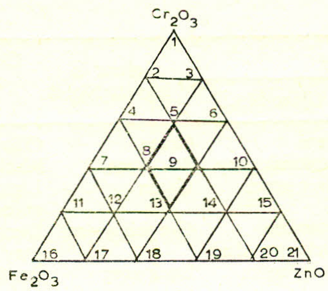

Fig. 1.

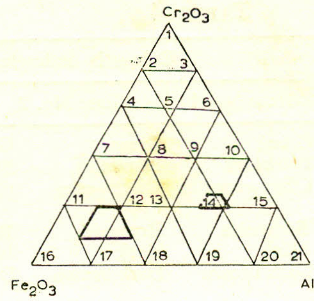

Fig. 2.

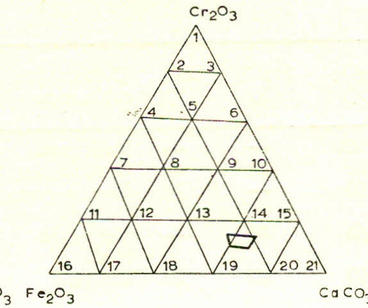

Fig. 3.

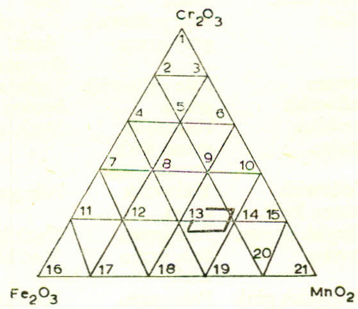

Fig. 4.

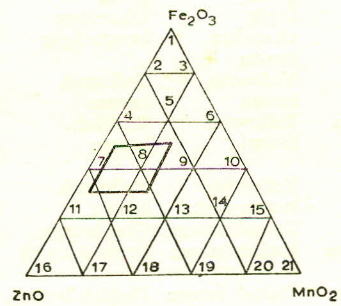

Fig. 5.

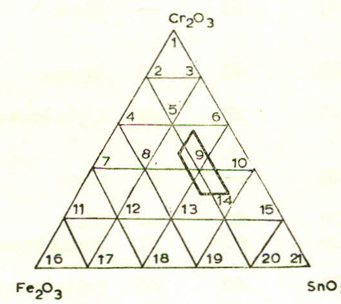

Fig. 6.

TABLE 5

Composition No.	Fig. 2	Fig. 3	Fig. 4	Fig. 5	Fig. 6
1	Green	Green	Green	Red	Dark green
2	Greenish brown	Greenish brown	Reddish green	Chocolate	Dark greenish brown
3	Greenish grey	Green	Blackish green	Black red	Greenish grey
4	Black	Black	Black	Yellowish brown	Dark black
5	Greenish brown	Reddish green	Blackish grey	Dark reddish brown	Greyish green
6	Greenish grey	Green	Blackish green	Brown blackish	Green
7	Blackish red	Brownish black	Black (reddish)	Yellowish brown	Black
8	Dark reddish brown	Orange	Greenish brown	Reddish brown	Reddish grey
9	Dark brown	Reddish brown	Blackish brown	Dark reddish brown	Greyish brown
10	Greenish grey	Greenish grey	Blackish green	Blackish red	Greenish grey
11	Blackish red	Blackish red	Blackish red	Light yellow brownish	Reddish black
12	Reddish brown	Reddish orange	Reddish brown	Brown	Reddish brown
13	Dark reddish brown	Brownish red	Reddish brown	Dark brown	Reddish brown
14	Dark brown	Bright red	Dark brown	Brown	Reddish brown
15	Greenish grey	Grey	Greenish black	Blackish red	Grey greenish
16	Red	Red	Red	White	Red
17	Greenish red	Orange red	Blackish red	Blackish grey	Red
18	Greenish red	Orange red	Reddish black	Blackish grey	Greyish red
19	Greenish red	Orange	Reddish black	Blackish grey	Greyish red
20	Brownish grey	Orange	Blackish red	Light blackish grey	Light grey
21	White	White	Black	Black	White

yellowish brown. The different shades with their compositions are given below:

	Greenish brown(%)	*Light brown*(%)	*Bright brown*(%)
Cr_2O_3	40–50	8–15	10–15
Fe_2O_3	20–30	8–15	20–30
$CaCO_3$	20–30	80–95	60–70

Calcination temperature being 1100–1200°C for 3 hr.

5. Iron–Chromium–Manganese. Compositions of this type of brown colour are shown in Fig. 4 and their shades in Table 3. It is obvious from the table that dark brown shades are produced by this series colour changes from greenish to reddish as Cr_2O_3 decreases and Fe_2O_3 increases. With the increase of Mn_2O_3 colour tinge is darkened. Best dark brown colour is formed by the composition ranging between Fe_2O_3 (20–25%); Cr_2O_3 (20–25%) and MnO_2 (45–55%). Calcination temperature being 1150–1200°C.

6. Iron–Zinc–MnO_2;. The compositions of the stains and shades of the calcined stains are shown in Fig. 5 and Table 5 respectively. Reddish brown to blackish brown shades are produced by this type of stain family. Reddish shades with maximum of Fe_2O_3 and black with maximum of MnO_2 are formed and the shade changes to dark reddish grey with the increase of ZnO. Best reddish brown shades are

TABLE 6

No.	Cr_2O_3	Fe_2O_3	ZnO	Al_2O_3/ SnO_2	Colour with Al_2O_3	Colour with SnO_2
5 (a)	60	20	20	5	Greenish brown Tint decreases as Al_2O_3 increases, though greyish less reddish then 8. More then 9,13,14.	Greenish grey tint in the grey greenish tint decrease as SnO_2 increases. Less reddish then 8,9,13, 14 series.
(b)	60	20	20	10		
(c)	60	20	20	15		
(d)	60	20	20	20		
(e)	60	20	20	25		
(f)	60	20	20	25		
8 (a)	40	40	20	5	Brown with greenish grey tint, decreasing as Al_2O_3 increases. More reddish then 5, 9 and less then 13,14.	More reddish than 5. Less greenish then 5 and reddish increases as SnO_2 increases.
(b)	40	40	20	10		
(c)	40	40	20	15		
(d)	40	40	20	20		
(e)	40	40	20	25		
(f)	40	40	20	30		
9 (a)	40	20	40	5	Greenish grey having brown tint. Greenish tint decreases as Al_2O_3 increases.	Reddish tint increases as SnO_2 increases more reddish than 5,8,13,14 series
(b)	40	20	40	10		
(c)	40	20	40	15		
(d)	40	20	40	20		
(e)	40	20	40	25		
(f)	40	20	40	30		
13 (a)	20	40	40	5	Reddish brown tint increases as Al_2O_3 increases. More reddish then 5,8,9 less than 14..	Red brown increases as SnO_2 increases.
(b)	20	40	40	10		
(c)	20	40	40	15		
(d)	20	40	40	20		
(e)	20	40	40	25		
(f)	20	40	40	25		
14 (a)	20	20	60	5	Reddish brown tint increases as Al_2O_3 increases. Less reddish then 5,8,4,13.	Yellowish brown tint. Brownish colour increases as SnO_2 increases. Less reddish then 5,8,9,13 series.
(b)	20	20	60	10		
(c)	20	20	60	15		
(d)	20	20	60	20		
(e)	20	20	60	25		
(f)	20	20	60	30		

given by the compositions ranging between Fe_2O_3, (40–50%); MnO_2, (5–30%) and ZnO (30–45%). Calcination temperature being 1200°C.

7. *Chrome–Iron–Tin Brown.* These stains were made by calcination of chromite ore and tin oxide or by the calcination of $K_2Cr_2O_7$, Fe_2SO_4 and SnO_2. Compositions are shown in Fig. 6 and shades are given in Table 5. As tin oxide increases, the stain colour changes towards the greyish brown, tin oxide helps in stabilising the tint of the colour.

8. *Chrome–Manganese.* When Cr_2O_3 and Mn_2O_3 calcined at 1100–1200°C beautiful brown shades are produced. Their compositions and shades are given in Table 3. Study of the table shows that the colour changes from green to black through dark brown. 10% boric acid helps the formation of brown colour at a little lower temperature. Best dark brown colour has a molecular formula Cr_2O_3–Mn_2O_3. Percentage composition being Cr_2O_3 (50%)–Mn_2O_3 (50%), calcination temperature 1150°C.

9. *Alumina–Manganese.* Alumina and manganese dioxide with boric acid produce brown colour. Compositions studied are given in Table 3. Best brown colour has the composition Al_2O_3–MnO_2 a composition of a spinel structure. Thus best brown shades are formed between the composition range MnO_2 (40–50%)–Al_2O_3 (50–60%).

10. *Chrome–Iron–Zinc–Alumina Brown.* Addition of Al_2O_3 to basic chrome-iron-zinc brown were made. Compositions studied are arranged in Table 6, alongwith their shades. 5,10,15,20,25 and 30% Al_2O_3 was added into the composition No. 5,8,9,13 and 14 respectively (Table 3). From Table 5 it is clear that this series of brown colour produces yellowish brown rather than reddish brown as compared with chrome–iron–zinc brown. But the shades did not change when applied inglaze, underglaze and onglaze. Thus Al_2O_3 increases the stability of the tan so produced.

11. *Chrome–Iron–Zinc–Tin Brown.* This type of brown colours were made by calcining exactly the same compositions as are given in Table 6 with a difference, i.e. Al_2O_3 was substituted by SnO_2. Compositions and shades are given in Table 5, 20% addition of tin oxide gave best brown shade. This series produces greyish shades as compared to chrome–iron–zinc brown and chrome–iron–zinc–alumina brown.

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