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CERAMIC COLOURS

Part II.—Pink Stains

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The formation and application of chrome-alumina and chrome-tin pinks were studied. Various compositions were calcined at different temperatures from 1150° to 1350°C. The stains developing good colour were selected and tested in different glaze compositions. Some commercially exploitable stains alonwgith suitable glazes were developed.

Introduction

In an earlier paper,[1] we had dealt with yellow stains. In the present investigation we have selected the development of chrome–alumina and chrome–tin pinks which may be used as inglaze, underglaze and overglaze stains in ceramic industry.

Among all the pink stains known in the ceramic industry, the chrome–alumina and chrome–tin stains are the best. Chrome–alumina stains are used to produce pastel pink glazes. Chrome–tin pinks are used extensively as inglaze and underglaze stains, and as enamel colours. These are pink with a bluish cast. Much deeper colours can be produced with them and this accounts for their popularity. Chrome–tin underglaze colours have exceptional lustre and brilliance.

Experimental

The study of the pink stains comprised three variables, namely, composition of the stains, temperature of calcination and adjustment of the glaze composition.

Composition.—Composition of chrome–alumina pinks studied ranged from 0–100% Al_2O_3, 0–100% ZnO and 0–100% Cr_2O_3. The exact compositions are indicated in Fig. 1. The shades of different compositions are described in Table 1. Chrome–tin pinks were composed of 0–100% SnO_2, 0–100% SiO_2, 0–100% CaO and 1–3% Cr_2O_3. Calcium oxide was added in the form of $CaCO_3$, and Cr_2O_3 in the form of $K_2Cr_2O_7$ Exact compositions are plotted in Fig. 2 and various shades produced are given in Table 1.

Ingredients of the stains were weighed in batches of 50 g each. After thorough hand mixing, these batches were placed in alumina–fire clay crucibles and calcined at the required temperature in a globar type electric furnace (Pereny) in which the atmosphere is slightly oxidising or neutral at 1250°C.

Calcination.—To study the effect of temperature variation and to find out the optimum temperature of calcination, various compositions were fired at temperatures ranging from 1150°C to 1300°C. The optimum temperature was found to be 1250°C as there was no marked change in the shades of the stains at higher temperatures.

Application of the Stains and Glaze Composition.—After calcination, the stains were ground in a mortar and then in a potmill to an average particle size of 2.5 microns. Five to ten percent of finely ground stain was added in the mill batch of the selected glaze and the glaze was applied to experimental pieces, by means of spraying or dipping. According to Hawks[2] and Hurd,[3] the composition of glaze is as important as that of the stain itself in determining the resulting colour because different glaze compositions, due to variation in oxides, produce different shades with the same stain. Various glaze compositions have been tried and those found successful (A,B,C,D,E) are given in Table 2.

Results and Discussion

Figure 1 shows the compositions of chrome–alumina stains studied. The shades of the stains calcined at 1250°C are described in Table 1. Chrome–alumina pinks produced here are rosy pink. Compositions containing no ZnO produce green colour which means that Cr_2O_3 or Cr^{+3} has not undergone any such change which is essential for the production of $Al^{3+}_{2-x}Cr^{3+}_{x}O^{2-}_{3}$ (x=2–4%), the synthetic counterpart of natural ruby in which Cr^{3+} must undergo drastic changes when Cr_2O_3 is sufficiently diluted with Al_2O_3[4]. The minimum amount of Cr_2O_3 added when no ZnO was present is 5% and since ZnO-free compositions give pure green shades, it means that no fraction of Cr_2O_3 has been used to form $Al^{3+}_{2-x}Cr^{3+}_{x}O^{2-}_{3}$. Pink colour is formed only when ZnO is present and the intensity of pink colour increases with increasing amount of ZnO, up to a certain percentage after which the shade begins to change. For example, in those compositions which contain 5% Cr_2O_3 the intensity is maximum in composition No. 23 and 27, in case of compositions having 10% Cr_2O_3, No. 28 is at the

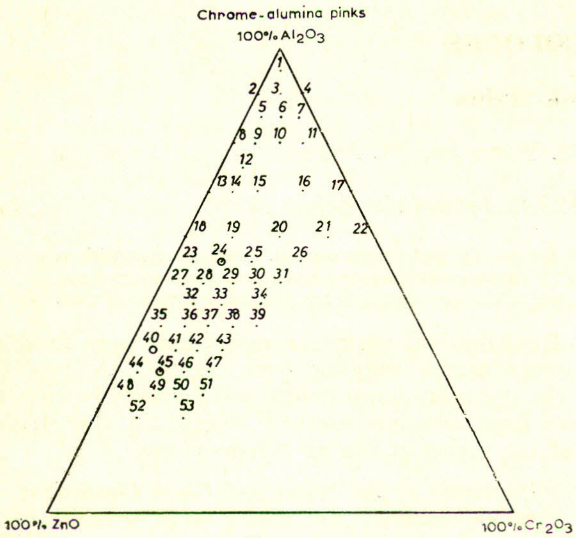

Fig. 1.

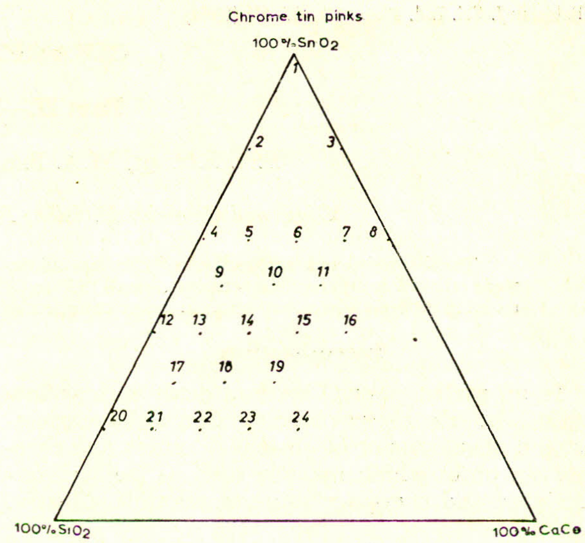

Fig. 2.

TABLE 1.—CHROME–ALUMINA AND CHROME–TIN PINKS TEMPERATURE OF CALCINATION 1250°C.

Chrome-alumina pinks				Chrome–tin pinks	
No.	Colour	No.	Colour	No.	Colour
1	Dirty light pink	28	Pink with violet tinge	1	White
2	White	29	Violet pink	2	Very light violet pink
3	Dirty light pink	30	Pinkish violet	3	Light violet pink
4	Green	31	Violet	4	Very light violet pink
5	Pink	32	Pinkish violet	5	Light violet pink
6	Dirty pink	33	Pinkish violet	6	Violet pink >1 to 4
7	Dirty light pink	34	Pinkish violet	7	Violet pink>3
8	White	35	Light violet	8	Violet pink>6
9	Pink>5	36	Light violet	9	Light violet pink=3
10	Dirty light pink	37	Brownish violet	10	Good violet pink
11	Green	38	Grey violet	11	Good violet pink>10
12	Pink >9	39	Greyish violet	12	Dirty white
13	White	40	Light pink with violet tinge	13	Light violet pink
14	Pink>12	41	Pinkish violet	14	Light violet pink=2,3,4
15	Dirty light pink>1	42	Greyish violet	15	Good violet pink
16	Dirty light green	43	Brownish violet	16	Violet pink>8,6,4,3,2
17	Green	44	Light pink violet tinge	17	Light pink=3
18	White	45	Greyish light violet	18	Violet pink>3<10
19	Dirty light pink>15	46	Greenish violet	19	Good violet pink
20	Dirty light pink>19	47	Grey (violet tinge)	20	Dirty violet
21	Dirty light green	48	Light pink	21	Light pink=3
22	Green	49	Greyish violet	22	Grey
23	Pink >1 to 22	50	Grey (violet tinge)	23	Good violet pink
24	Pink>23	51	Grey (violet tinge)	24	Grey violet
25	Pink>24	52	Light grey		
26	Dirty green	53	Grey		
27	Pink with violet tinge				

*The symbol>means "better than".

TABLE 2.—MOLAR COMPOSITION OF GLAZES.

Glaze	Na_2O	K_2O	ZnO	PbO	CaO	BaO	MgO	Al_2O_3	B_2O_3	SnO_2	ZrO	SiO_2
A	0.18	0.07	0.32	0.14	0.29	—	—	0.32	0.26	—	—	2.66
B	—	0.20	0.30	—	0.25	0.10	0.15	0.22	0.375	—	—	2.50
C	0.0718	—	0.4191	0.4603	0.0488	—	—	0.0739	—	0.0320	—	1.2977
D	0.0509	0.1895	0.3239	0.1449	0.2908	—	—	0.1425	0.078	—	0.054	0.840
E	0.0715	0.2015	0.1848	0.2999	0.2423	—	—	0.2574	0.1429	0.1393	—	2.4422

top and in case of those compositions which have 15% Cr_2O_3, No. 33 is the best.

The study of the stain compositions reveals that the best colour is developed when the amounts of Al_2O_3 and ZnO are near about 50% and 40% respectively. And the proportions of ZnO and Al_2O_3 required to form the spinel ZnO, Al_2O_3 are 81:102. This spinel begins to form at 800°C and the reaction is complete at about 1200°C.[5] Pink colour developed in the stains seems to be linked with the formation of the spinel because, as shown by Table 1, pink colour increases with the increased formation of spinel and is maximum when the amount of ZnO,Al_2O_3 spinel formed is maximum.

Pink colour begins to take up greyish tinge in such compositions (Nos. 37, 38, 42, 43, 46, 47, 50, 51) in which the amount of Cr_2O_3 exceeds the limit up to which the spinel ZnO, Al_2O_3 formed can take up Cr_2O_3. The grey tinge is thus a mixture of green and pink colours.

According to Hedvall-effect,[6] mixtures of solids in which one component undergoes a phase transformation at a certain temperature exhibit maximum chemical reactivity at that particular temperature. Here, in the formation of pink stains from Al_2O_3–ZnO–Cr_2O_3, the spinel $ZnOAl_2O_3$ begins to form at 800°C and is complete at about 1200°C. The rearrangement of the crystal lattices during the formation of the spinel helps in the take up of Cr^{3+} ions into the lattice ZnO $(AlCr)_2O_3$.

According to Hurd[3] and Mellor[7] chrome–tin stains are actually a deposit of finely divided particles of chromic oxide on that of tin oxide. But change of colour with simple deposition of finely divided particles of Cr_2O_3 does not seem probable because for producing a change in colour, Cr^{3+} must undergo some electronic changes to alter its light absorption characteristics. According to Weyl and Techeichvili,[4] Cr^{3+} replaces some of the Sn^{4+} ions in SnO_2 lattice or calcium stannate lattice, producing $Sn^{4+}_{1-2x}\,Cr^{3+}_{2x}\,(An.\ Vac)_3O^{2-}_{2-x}$

The charge difference between the two ions is compensated for by anion vacancies. This change in the electronic environment of Cr_3 is responsible for colour change.

The colour of the stains depends to a great extent, upon the ratio of Cr_2O_3 to SnO_2. According to Hurd[3] pink colour is produced when this ratio is 1:25 or greater. After trial experiments the compositions were selected in which 2g $K_2Cr_3O_7$ was added per 100 g mixture of SnO_2, $CaCO_3$ and SiO_2. Figure 2 represents the compositions of stains and Table 1 gives the shades of the stains. All the stains are pink except Nos. 20, 22, 24 which are grey or grey violet. The grey tinge is possibly due to the excess of Cr_2O_3 which has not been incorporated into the SnO_2 lattice. The pink colour of the stains deepens as the percentage of $CaCO_3$ increases which means that the formation of calcium stannate helps in the take up of Cr^{3+} ions by the SnO_2 part of the calcium stannate lattice. Compositions Nos. 10, 11, 15, 16, 18 and 19 and 23 have good pink colours. Thirty percent calcium carbonate seems to be optimum concentration. Addition of silica helps to make the stains more stable.

Stains having good shades were tested in different glazes. The glazes were fired between 1100°C and 1150°C and soaked at the peak temperature for 1 hr. For chrome–alumina pinks glaze D was found to be the best. There was no change in the shades of the stains and the glaze had good lustre. For chrome–tin pinks glaze E was the best glaze as there was no change in the shade of the stain and the lustre of the glaze was good. Glazes A,B and C were found to be suitable for these stains.

Conclusion

Best chrome-alumina pinks were obtained from compositions, fired at 1250°C for 1 hr, having ZnO 35–40%, Al_2O_3 45–50% and Cr_2O_3 10–15%. These stains when applied in the glaze D gave the best results.

In case of chrome–tin pinks compositions in the range of $CaCO_3$ 25–35%, SnO_2 30–50% and SiO_2, 20–50% plus 3% Cr_2O_3, gave good colours. Glaze E was found to be suitable for these stains.

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