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Bangladesh J. Sci. Ind. Res. **48(3)**, 213-216, 2013

Short Communication

BANGLADESH JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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Production and characterization of iron-chromium-zinc pigment based ceramic stain colour of red-brown shade

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Abstract

Considering the demand of ceramic stain colours in Bangladesh, an attempt has been taken to develop iron-chromium-zinc pigment based ceramic stain colour of red-brown shade which could be used as an import substitute material in the local ceramic industries. The desired shade of red-brown stain was synthesized from an equimolar mixture of pure chromium oxide (Cr_2O_3), iron oxide (Fe_2O_3) and zinc oxide (ZnO). The developed stain was characterized by X-ray diffraction (XRD) technique. The characteristic of the stain complied with the chemical durability. Moreover, chromium leaching was below the permissible exposure limit which makes it as a promising ceramic stain to be used in our ceramic industries.

Keywords: Pigment; Glaze; Spinel; Colour

Introduction

Ceramic stain colours play an imperative role in decorating the ceramic wares and potteries. According to Bill Jones "*Commercially prepared ceramic pigments, commonly referred to as ceramic stains, expand the potter's palette with infinite color options*" (Jones, 2010). However, ceramic stains are usually the synthesized products which comprise a mixture of fired inorganic oxides in fine powder form. The most significant aspect of the stain is its' stability over any individual inorganic oxide. Moreover, ceramic stains produce much more consistent and repeatable color than that of inorganic oxide colors. Another key advantage of stains which has led it to become top scorer over the inorganic oxide is its' ability to produce a targeted definite color.

Ceramic stains are widely used in the ceramic industries to colour ceramic glazes (Eppler and Eppler, 2000; Bondiolini *et al*., 1997). Most of the pigments contained crystals of mixed oxides, such as silicates, spinels and zircon oxides (Azevedo *et al.*, 2002).

Ceramic stains must be thermally and chemically stable at high temperature as well as resistant against chemical agents (acids and alkalis). Moreover, it should not make any gas /bubble to produce a faulty glaze. The most common stains are black and brown shades, which are the amalgamated products of iron oxide and chromium oxide.

In Bangladesh, ceramic industries have emerged as one of leading foreign exchange earning sectors. Its ever increasing demand in domestic and particularly in foreign market indicates its prospective future throughout the world (Abdullah *et al.*, 2012). Bangladesh annually produces more than 40 thousand tons of ceramic products (Writuparna, 2008). A considerable portion of these ceramic products are decorated with various ceramic stains to make it attractive as well as to increase the market value. Total demands of ceramic stains in Bangladesh are met by importing it from abroad. Hence, in this present research work an attempt has been taken to develop iron-chromium zinc pigment based ceramic stain colour of red-brown shade which could be used as an import substitute material in the local ceramic industries.

Materials and methods

Materials

Ferric (III) oxide, chromic oxide, zinc oxide, sodium carbonate, sulphuric acid and acetic acid used were from Merck, Germany. Bijoypur clay and calcite were collected from the local market. All the solutions were prepared using distilled water.

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Method

A requisite amount of ferric oxide, chromic oxide and zinc oxide were thoroughly mixed. The mixture was then ball milled in aqueous medium for three hours which facilitated homogeneous slurry. Prior to calcination at 1150°C in an electric furnace, the extra water of the slurry was removed by oven drying at 100°C. Calcination was continued for one hour fixing the rate of temperature increment at 3°C/min. The calcined product was left at ambient temperature and a ball milling operation was followed in aqueous medium for another hour. At this stage the product was washed with plenty of water to remove any trace of unwanted soluble salts which might effect in achieving the desired shade of the stain. The final product (red-brown stain powder) was obtained by drying in an oven at 110°C which was then applied on biscuit-fired ceramicware with a ready transparent glaze (previously prepared). The ratio of red-brown stain and transparent glaze powder was maintained at 7:93. The mixture of stain and transparent glaze was ground with water in a ball mill for 4 hours. The biscuit-fired ceramic ware was then dipped well into this resultant slurry and dried at room temperature. Finally this stain coated ceramicware was calcined at 1250°C for 30 minutes. A flow diagram of the preparation of iron-chromium zinc stain is given in Fig. 1.

Characterization

The desired phases present in the developed red-brown stain was analyzed by X-ray diffractometer (PANalytical X´Pert PRO XRD PW 3040). The intensity data was collected in 0.02° steps fixing the scanning range at 2 = 10° to 70° using CuK$_\alpha$ (λ = 1.54178 Å) radiation source. The observed data was compared with the standard data.

Chemical durability and chromium leaching out tests of the stain were carried out according to ASTM (ASTM Designation: C 724-91) methods. Briefly, for chemical durability test, the ceramicware coated with the red-brown stain was dipped into (i) 3.7% HCl solution; (ii) 10% CH_3COOH; and (iii) 1% Na_2CO_3 solution at room temperature. The soaking times were 3 hours and 24 hours for the acid solu-

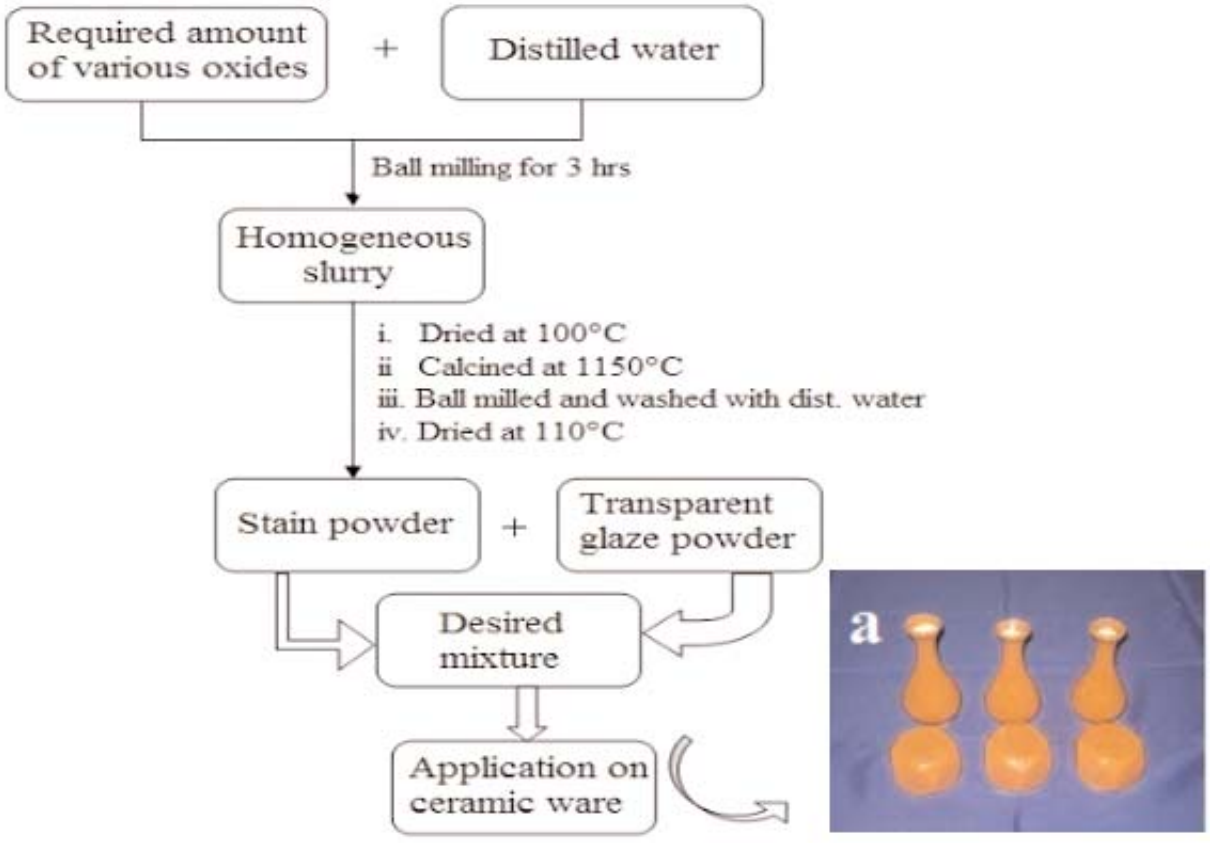

Fig. 1. Flow diagram of the preparation process of red-brown ceramic stain. (a) Red-brown stain applied on ceramicware

tions while for later case the ceramicware was boiled in 1% Na_2CO_3 solution for 1 hour. The result of chemical durability is tabulated in Table I. In order to monitor the leaching of chromium ion from the developed stain, the ceramic ware was soaked into 4% acetic acid solution. After the interval of 24 hours, the concentration of chromium was determined at the wavelength 357.9 nm using Atomic Absorption Spectrophotometer (AAS, PERKIN ELMER USA; Model - A Analyst 800).

fairly consistent with that observed by Emel and Servet, 2003; where the authors prepared iron-chromium based black pigment using a mixture of Cr_2O_3 and Fe_2O_3. This spinel is formed due to calcination and it is a combination of the oxide forms of the compounds present in the raw materials. The general formula of spinel group is expressed as AB_2O_4 where A symbolizes divalent metal ions such as Mg, Fe and Ni; B signifies the trivalent metal ions such as Al, Fe and Cr.

Table I. Chemical durability test of the developed red-brown stain

Ceramic stain	Solution	Condition	Result
	3.7% HCl solution	Room temperature, 3 hours	Not affected
Red brown	10% CH_3COOH	Room temperature, 24 hours	Not affected
	1% Na_2CO_3 solution	Boiling, 1 hour	Not affected

Result and discussion

The XRD pattern of the prepared stain of red-brown shade is shown in Fig. 2. The diffractogram clearly revealed the expected peaks of spinel group as this red-brown coloured stain was calcined at 1150°C. The formation of this spinel is

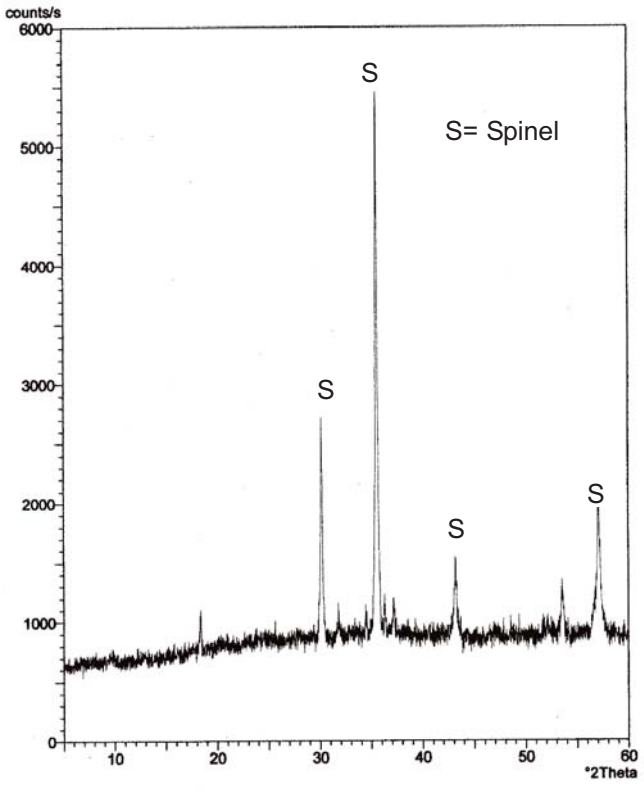

Fig. 2. XRD of iron-chromium based stain colour

Fig. 3 shows the XRD spectrum (a) of the prepared red-brown stain interacted with transparent glaze. Since the mixture of iron-chromium based stain (7%) and the zinc oxide based transparent glaze (93%) was calcined at 1250° C, it formed the expected zinc-iron-chromite based red-brown spinel pigment. Clearly the experimental result (Fig. 3a) matched very well with the standard JCPDS data Ref. code:

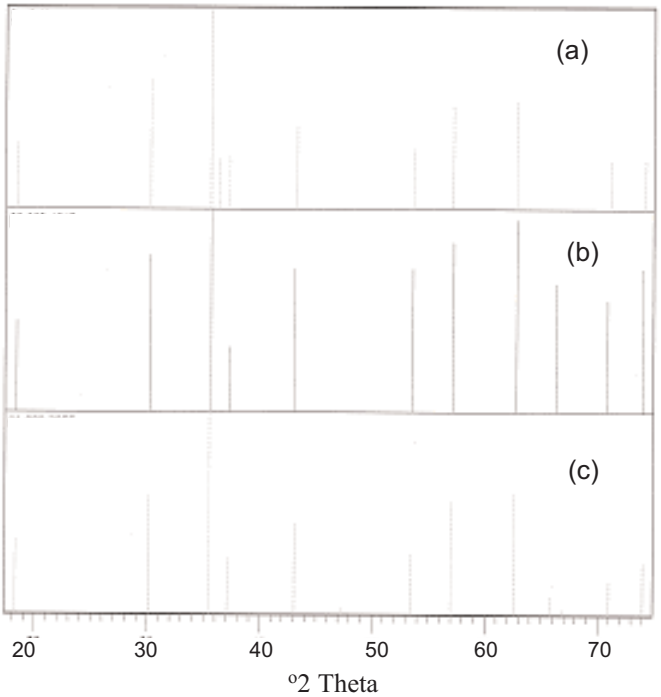

Fig. 3. XRD spectra of (a) prepared red-brown stain interacted with transparent glaze; (b) Ref. code: 00-002-1043 and (c) Ref. code: 01-089-3855

00-002-1043 (Fig. 3b) and Ref. code: 01-089-3855 (Fig 3c). Such observation has already been reported (Emel *et al.*, 2003) that the interaction of the iron-chromium pigment or stain with the zinc oxide based transparent glaze forms zinc-iron-chromite based brown spinel pigment.

However, since chromium is regarded as toxic and hazardous, so it was obviously a vital issue to examine the chemical durability and chromium leaching out of the developed red-brown stain. The data in Table I shows the chemical durability of the developed red-brown stain under three different conditions. It is clearly evident from Table I that under the present experimental protocol as carried out according to ASTM (ASTM Designation: C 724-91) methods, there is no effect of either acid or alkaline solution on the red-brown pigment. Such an observation obviously conform the chemical durability of the developed red-brown stain. On the other hand the level of chromium was below the permissible exposure limit, *i.e*. no leaching of chromium ion occurred which was fairly promising.

Conclusion

Iron-chromium-zinc pigment based red-brown coloured ceramic stain was synthesized from a mixture of pure iron oxide (Fe_2O_3), chromium oxide (Cr_2O_3) and zinc oxide (ZnO). The XRD of the developed red-brown stain revealed the presence of desired phase. The characteristic of the stain comply with the chemical durability. Moreover, chromium leaching was below the permissible exposure limit which makes it as a promising ceramic stain to be used in our ceramic industries.

Acknowledgement

We are grateful to BCSIR authority for funding and we particularly acknowledge the support of Dr. Husna Parvin Nur, Director, IGCRT for her continuous care for the R&D projects.

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ASTM, Designation: C 724-91 standard test method for acid resistance of ceramic Decoration.

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Received: 27 January 2013; Revised: 13 June 2013; Accepted: 08 July 2013.