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EVALUATION OF CHROMITE CONCENTRATE AS AN UNDERGLAZE COLORANT

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ABSTRACT

Chromium oxide of technical purity serves as a green colorant in the mixed metal oxides system. Chromite concentrate processed at Antalya Ferrochromium plant has been studied as a potential underglaze colorant of ceramic materials. The green colour expected from the chromite concentrate was damped by the $Fe_2 O_3$ content resulting in a brown colour. Cobalt oxide addition to the concentrate leads to commercial quality blue colours.

Key Words : Chromite Concentrate, Ceramic colorants, Green colorant

KROMİT KONSANTRESİNİN SIRALTI BOYA HAMMADDESİ OLARAK DEĞERLENDİRİLMESİ

ÖZET

Teknik saflıktaki krom oksit karışık metal oksitler sisteminde yeşil renk verici olarak kullanılmaktadır. Antalya Ferrokrom tesislerinde işlem görmekte olan kromit konsantresinin sıraltı boya hammaddesi olarak kullanılıp kullanılamayacağı incelenmiştir. Kromit konsantresinden beklenen yeşil rengin konsantredeki $Fe_2 O_3$ tarafından bastırılıp kahverengi renge dönüştürüldüğü gözlenmiştir. Konsantreye kobalt oksit ilavesi ile ticari kalitede mavi renk elde edilmiştir.

Anahtar Kelimeler : Kromit konsantresi, Seramik boyalar, Yeşil boya

1. INTRODUCTION

Colouring constituents in ceramic systems are the transition elements characterised by an incompleted shell, particularly V, Cr, Mn, Co, Ni, Cu and a lesser extent the rare earth elements characterised by an incomplete f shell. In addition to the individual ion and its oxidation state, absorbtion phenomena are markedly affected by the ionic environment. Ions absorb light in characteristic ranges of wavelength. Electron energy levels contribute to colour formation in the transition elements. The colours of these materials are subject to changes in coordination numbers and the nature of adjacent ions. These changes give rise to the description of colours as resulting from specific chromophores (Kingeryet et al., 1976).

In order to be used in ceramics, stability at elevated temperatures is required and this limits the palette of available colours. As the temperature level is increased, the number of stable colours diminishes. Underglaze colours for high-temperature porcelains are limited whereas overglaze colours and colours for low temperature glazes are numerous.

Basic classification of ceramic colorants is made by Dry Colour Manufacturers Association. Coloured constituents are classified into metal oxides, mixed colour oxides, metal salts, natural compounds and others. White constituents are either opaque or nonopaque. 14 Basic crystal structures and 51 materials are defined by American DCMA for mixed metal oxides (Anon., 1982). DCMA code is made up of three groups of numbers. The first number defines the crystal structure of the pigment. The second number is a subgroup number. The third number defines the resultant colour of the pigments:

1. Violet,
2. Blue,
3. Green,
4. Yellow,
5. Pink
6. Camel,
7. Brown,
8. Grey,
9. Black.

The colour ranges and main oxides of some of the mixed metal oxides are given below (Colorobbia and Bitossi, 1985):

Vanadium-Turqoise Blue: (Zr-Si-V)
Cobalt Blue : (Al-Zn-Co), Zn-Si-Co)
Dark Brown : (Fe-Cr-Mn)
Grey and Black : (Co-Cr-Zr-Si),(Co-Cr-Fe)
Yellow-brown : (Fe-Cr-Zn-Al)
Sn-Cr Red : (Ca-Cr-Sn-Si)
Sn-Cr Violet : (Ca-Cr-Co-Sn-Si)
Zr-Fe Pink : (Fe-Zr-Si), (Fe-Zr-Si-V)
Pb-Sb Yellow : (Pb-Sn-Sb), (Pb-Sb-Fe)
Pb-Sb Orange : (Pb-Sb-Al-Ti)
Sb-Ti Yellow : (Sb-Cr-Ti)
Sb-Ti Orange : (Sb-Fe-Ti)
V-Sn Yellow : (Sn-V)
Cr Green : (Ca-Cr-Si), (Cr-Si-Al)
Cr-Co Green : (Cr-Co), (Cr-Co-Al-Zn)
V-Sn Green : (Sn-Zr-Si-V)
V-Zr Green : (Zr-Si-V)

Chromium oxide green is used mainly as a colouring agent in ceramics, glaze making of ceramics, coatings, polishing, construction and refractory materials. Other uses are smelting of metal chrome, colouring agent of chrome carbide , enamel, glass, artificial leather and building material, organic synthetic catalyst, sunlight fast coating, special printing ink for paper money, making of polishing ointment and abrasives, cosmetics. Basic properties are green crystal powder, metal luster, magnetic, good covering strength, high temperature resistance and sunlight fastness. It is not soluble in water, barely soluble in acids, comparatively stable in air, unaffected by acids and alkalis of common density. Tinting strength, oil absorbtion, fineness (residue through 320 mesh), water soluble matter, moisture, Cr_2O_3 content affect the colour and the shade.

Prolonged expensive processes are employed to produce ceramic colorants in pure oxide states (Ozel et al., 2001).

The aim of this research is to try to produce chrome oxide green from less expensive and less pure chromite concentrate of Antalya Ferrochrome plant.

2. EXPERIMENTAL PROCEDURE

Production of ceramic colorants is accomplished by either dry mixing or wet grinding method. The procedure for production consists of mixing, calcination (700-1400 ºC) and grinding. The maximum temperature of calcination is limited with the materials which disintegrate at such temperatures. The green colours are based on chromite green.The colour may vary to blue with cobalt oxide additions and to pale green with addition of combinations of Pb-Sb , V-Si-Sn and V-Si-Zr.

Experiments were conducted in three phases and on three recipes (Dündar and Çakı,1987).

- 1st phase: Application of chrome-oxide of technical purity to various recipes
- 2nd phase: Addition of various metal oxide colorants to chromite concentrate
- 3rd phase: Application of chromite concentrate without any colorant addition
- Recipe1, named as chromium green, was made up of 33.3 % chrome oxide and 66.7 % kaolin.
- Recipe 2, named as green blue, was made up of 5.6 % chrome oxide, 27.7 % cobalt oxide and 66.7 % kaolin.
- Recipe 3, named as blue green , was made up of 13.7 % chrome oxide, 19.7 % cobalt oxide and 66.6 % kaolin.

The chromite concentrate, used in the experimental procedure against chrome oxide of technical purity, had Cr/Fe ratio of max.3.

The mixtures of the recipes were wet ground in ball mills, dried and calcined at 1210 ºC. The colorants produced at furnaces were applied in three forms:

1. With no additive
2. With additive (20 gr colorant + 50gr kaolin + 30 gr quartz) but without any frit
3. With additive (20 gr colorant + 45 gr kaolin +25 gr quartz) and with frit (5 gr)

These colorants were applied on plates and glazed with leadless and lead-containing glazes. The glaze in powder form was mixed with water in 1/3 ratio and the glazing was accomplished by dipping in the suspension. The plates were then fired at 960 ºC.

3. RESULTS

Experiments on phase 1 consisted of leadless (Table 1) and lead-containing (Table 2) glazing of recipes of technical purity chrome oxide.

Table 1. Colours Produced After Leadless Glazing

	No Additive	Additive	Add. +Frit
Recipe1	Green-Black	Green-Brown	Dark Green
Recipe2	Green-Black	Green-Blue	Green-Black
Recipe3	Green-Black	Blue-Green	Dark Green

Table 2. Colours Produced With Lead-Containing Glazing

	No Additive	Additive	Add. +Frit
Recipe1	Olive Green	Pale Brown	Green Brown
Recipe2	Green-Black	Blue Green	Green-Black
Recipe3	Matte Green	Grey-Green	Green Black

In phase 2 only lead-containing glazing was applied to recipes when chromite oxide was replaced with chromite concentrate. Colour palettes of brown and blue colours were obtained (Table 3).

Table 3. Colours Produced With Lead-containing Glazing of Chromite Concentrate Recipes

	No Additive	Additive	Add. +Frit
Recipe1	Brown	Pale Brown	Pale Brown
Recipe2	Blue-Black	Matte Blue	Dark Blue
Recipe3	Blue-Black	Grey Blue	Grey Blue

In phase 3, in place of recipes, chromite concentrate was ground, dried, calcined and applied on plates which were then glazed (lead-containing). Only brown and black colours could be obtained (Table 4).

Table 4. Colours Produced With Chromite Concentrate

	No Additive	Additive	Add. +Frit
Chromite			
Concent.	Brown	Green-Brown	Black

Note: Coloured pictures could not be included in this paper due to the unavailability of coloured printing. They can be obtained on request from drsdundar@hotmail.com.

4. DISCUSSION

The green colour produced by technical quality chrome oxide is generally damped by the blue colour of cobalt oxide. In other words cobalt oxide is the more dominant colour.

The Fe_2O_3 constituent of chromite concentrate affects adversely the production of green colour. In the absence of cobalt oxide, it leads to brown-black colours. However in the presence of cobalt oxide it remains passive and the blue colour is dominant.

Kaolin and quartz, in the absence of cobalt oxide, makes the green colour pale and leads to brown-green colours. In the presence of cobalt oxide, the blue colour is dominant once more.

5. CONCLUSION

Green colour cannot be obtained by using chromite in place of chrome oxide in recipes of colorants. The Fe_2O_3 impurity destroys the green colour and makes its brown colour more dominant.

Cobalt oxide addition to chromite concentrate leads to commercial quality blue colours. Thus by avoiding an expensive procedure of removing impurities of Fe_2O_3, a blue colorant can be obtained with some addition of cobalt oxide.

6. REFERENCES

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