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Chromium–Zircon Pigment

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Abstract: Zircon sand dissociated with fluoride salts was used as a host for Cr_2O_3 to produce green chromophores. Recrystallization of zircon after addition of Cr_2O_3 was followed semi-quantitatively by change in the peak area. The different bonds were detected by IR. CaF_2 + 6% Cr_2O_3 gave maximum zircon formation, yet free ZrO_2 was still present. LiF + NaF, on the other hand, gave the deepest colour and complete recrystallization of zircon. The following formulae were suggested:

$[Na.Cr]_x\ Zr_{1-x}\ SiO_4$

$[Na.Li.Cr]_x\ Zr_{1-x}\ SiO_4$

$[Ca.Cr]_x\ Zr_{1-x}\ SiO_4$.

INTRODUCTION

Chromium oxide may be used to produce green colours in glazes in amounts of about 1–5%. Cr_2O_3 has a tendency to fume or volatilize in firing, so it is usually calcined with silica and alumina to completely react the chromium oxide.[1] The substitution of Al_2O_3 by Cr_2O_3 in the celsian structure when chromium is incorporated as Cr_2O_3 is complete up to 0·25 M.[2] The chromium in stains of the chrome–alumina type is present as Cr^{+3}, the mixed crystal is red or green according to the percentage of alumina and chromium, and the red form is due to the alumina distorting the chromium crystal lattice.[3]

Victoria green is prepared by calcining silica and a dichromite with calcium compounds.[1,4] The pigment has the formula $3CaO.Cr_2O_3.3SiO_2$ and a garnet structure.[4]

The inorganic zircon pigments have an important technological significance, having a high thermal and chemical stability as they are relatively inert in conventional glazes. The use of zircon ($ZrSiO_4$) as a host crystal has continued to increase and the range of colour is widened.[5–7]

According to Eppler's[5] proposition, $ZrSiO_4$ is formed from SiO_2, ZrO_2 in the presence of a mineralizer such as LiF. The transport of silicon through the product layer occurs by either diffusion or vapour transport.[8] The diffusion mechanism involves the SiF_4 decomposition on the surface of the product layer. Then follows the electrons and silicon ion combined with ZrO_2.

Assuming the validity of the vapour transport mechanism, the SiF_4 and oxygen pass through the pores into the product layer leading to the formation of $ZrSiO_4$. The presence of a liquid phase of Li_2SiO_3 results in the rearrangement of zircon particles that grow by a solution and precipitation mechanism. The following equations summarize the reaction sequence taking place:[9]

$$3SiO_2 + 4LiF \rightarrow SiF_4\uparrow + 2Li_2SiO_3$$
$$SiF_4\uparrow + ZrO_2 + O_2\uparrow \rightarrow ZrSiO_4 + 2F_2\uparrow$$
$$2F_2\uparrow + SiO_2 \rightarrow SiF_4\uparrow + O_2\uparrow$$

In zircon based-pigments, colours are formed by inserting the colouring ions into the zircon lattice. This reaction takes place in stains rich in silica,[3,7,10,11] as is the case with vanadium blue, or by dispersion of coloured particles in the matrix. In such stains of zirconia, the dominant phase in the least proportion of SiO_2 appears to act as a mordant for the inorganic chromophore.[3,7]

In heteromorphic pigments nominated by Lavilla and Lopez[9] in Cd pigments, the crystals responsible for the colour are small crystals that are occluded during the sintering process of zircon grains.

Chrome zircon pigments show colours from green to red (up to an oxidation indicator of +6);[10] when Co_2O_3 and CaO are added, a dark violet colour is obtained.

Cuadrado and Alamo[12] studied the formation of $NaZr_2(PO_4)_3$ and $Ca_{0\cdot5}Zr_2(PO_4)_3$ with substituting Cr for Zr + Na or Zr + 0·5 Ca, respectively. They postulated the following formulae:

$Na_{1+x}Cr_xZr_{2-x}(PO_4)_3$ and $Ca_{0\cdot5+x/2}Cr_xZr_{2-x}(PO_4)_3$, where x varies in the range 0·06–1 Cr moles. These formulae can be written in a general form as $(M_1)_1$ $(M_2)_3$ A_2 $(XO_4)_3$, in which M_1 and M_2 are octahedral sites, A are ions in the octa-hedral environment, and (XO_4) is tetrahedral.

In a previous study[13] the dissociation of zircon was attempted using different fluoride salts, mainly AlF_3, LiF, NaF, CaF_2 and NaF + LiF. NaF and CaF showed the maximum degree of dissociation. Making use of these products in the production of stains was attempted by incorporating different chromophores. Chromium salts are introduced to dissociated zircon to produce a green colour. The incorporation of chromium oxide in the crystallized zircon is followed by X-ray diffraction (XRD) and infrared spectroscopy.

EXPERIMENTAL PROCEDURE

Pure zircon sand, and chemical reagents (BDH) NaF, LiF and CaF_2 were mixed in the proportions given in Table 1. Mixes were thoroughly dry mixed in an agate mortar, fabricated in the form of discs, dried and fried at 1200°C with a soaking time of one hour. Then, the discs were crushed, ground and incorporated with a different percentage of chromium oxide in the form of ammonium dichromate. The batch compositions were intimately mixed, pressed and heated up to 1100°C and 1200°C for 10 h. Standard mixes[8] [SCF] were prepared for comparison.

Cr_2O_3 was added to the CF group in the following proportions: 6, 10, 20 and 45% represented by CF_7, CF_1, CF_2 and CF_4. 6% Cr_2O_3 was added to the other two groups N_8C and NLC, respectively, represented by N_8C_6 and NLC_6.

Table 1. Composition of different standard mixes, wt%.

Symbol	Zircon	CaF_2	NaF	LiF
CF	94	6	—	—
N_3C	92	—	8	—
NLC	88	—	6	6

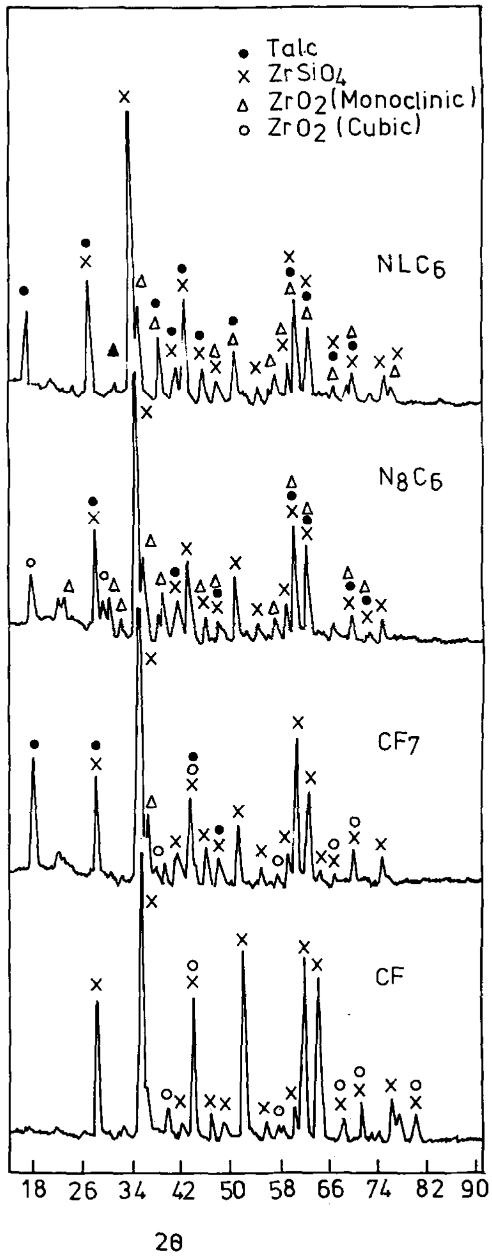

Fig. 1. X-ray diffraction patterns of studied samples.

X-ray diffraction

The conventional powder technique of XRD with a Cu target and Ni filter was used. 10% talc was added as an internal standard at all mixes. Selected peaks of zircon and Cr_2O_3 and talc are at 2θ = 20·05, d = 4·43, hkl = 101; 2θ = 33·62, d = 2·666, hkl = 104 and 2θ = 9·47, d = 9·34, hkl = 002, respectively. Change in the ratio of these peaks was taken as an indication for consummation of Cr_2O_3. Also, the change in the d spacing of zircon was monitored.

Infrared study

The structure of the chosen samples was studied by IR spectroscopy in the range between 4000 and 200 cm^{-1}.

Table 2. Zircon peak area before and after Cr_2O_3 addition

Mineralizer	Cr_2O_3 %	Remaining $ZrSiO_4$ peak area in standard mixes before Cr_2O_3 addition	Remaining $ZrSiO_4$ peak area after Cr_2O_3 addition
8 % NaF	6	4·23	6·73
6 % LiF + 6 % NaF	6	5·68	7·76
6 % CaF_2	6	9·90	18·16
	10	—	9·36
	20	—	7·36
	45	—	5·32

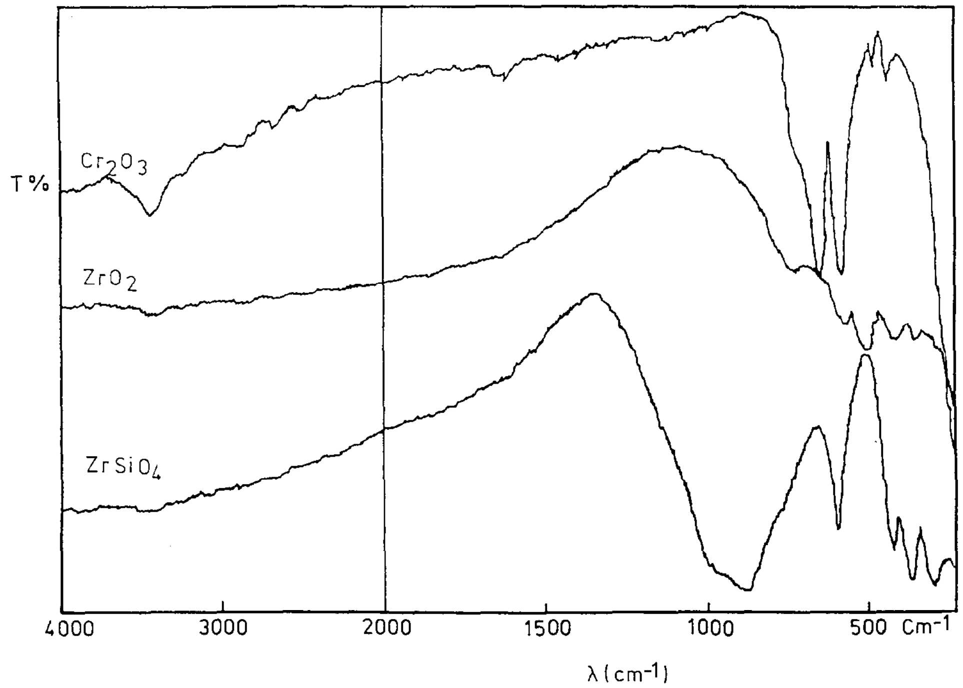

Fig. 2. IR spectra: ZrO_2, $ZrSiO_4$ and CrO_3.

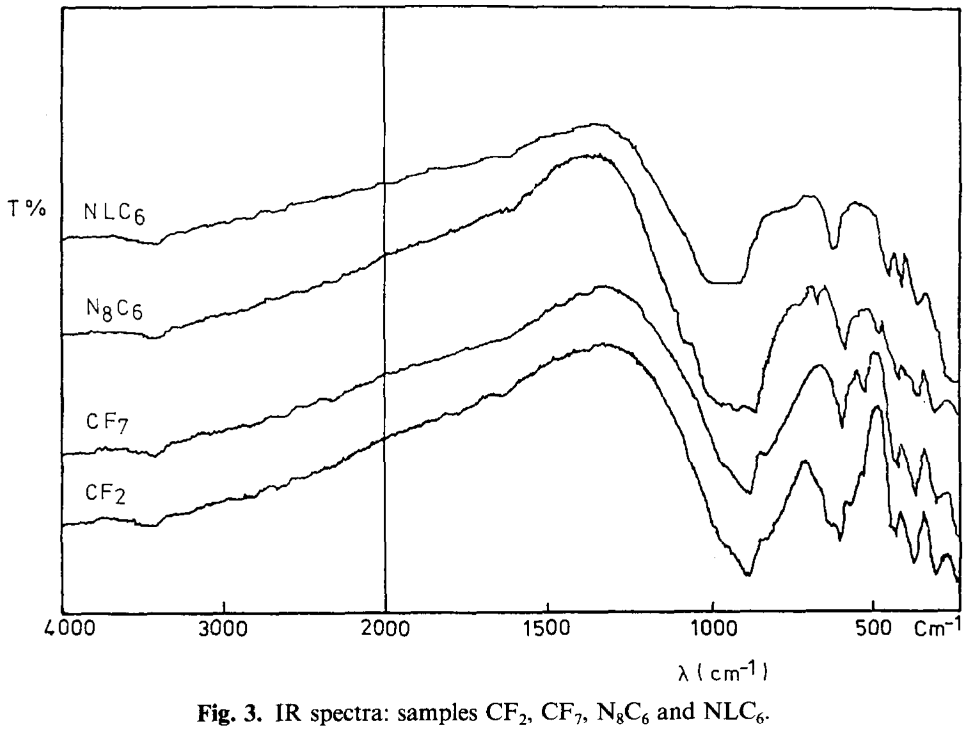

Fig. 3. IR spectra: samples CF_2, CF_7, N_8C_6 and NLC_6.

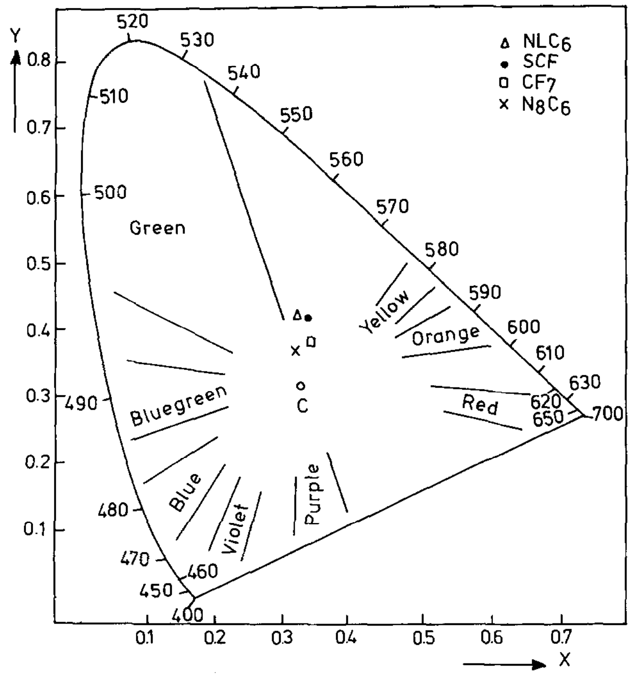

Fig. 4. CLE chromaticity diagram of different prepared pigments.

Scanning electron microscopy (SEM)

A fractured specimen from each of the pigment discs was subjected to thermal etching at 1000°C for 1 h then covered with a gold layer to be examined under SEM.† The different grains were analysed by an energy-dispersive X-ray analyzing spectrum (EDAX) attached to the SEM.

Application of the pigment to glazes

The obtained pigments were added in the proportion of 4 wt% to high temperature tile glaze used in the Chini company. The glazes were applied by brushing to biscuit fried tiles, drying, then firing at 1100°C.

RESULTS AND DISCUSSION

The XRD patterns of the CaF_2 mixes reveal the presence of zircon and zirconia phases (Fig. 1). The addition of Cr_2O_3, on the other hand, gave rise to the detection of the following unidentified d spacing; 6·2154 and 2·8847 occurring at 2θ = 14·25 and 31·0, respectively. Meanwhile, a change in 2θ accompanied by a shift in d spacing took place in zircon main peaks, corresponding to, $2\theta = 27{\cdot}02$, $d = 3{\cdot}30$, hkl = 200, with the introduction of Cr_2O_3.

Comparing the zircon peak before and after addition of Cr_2O_3, an increase in the peak area was recorded in all mixes, as shown in Table 2. It was doubled by the addition of 6% Cr_2O_3 to CaF_2 6% mix. However, with an increase in Cr_2O_3 percentage, the same peak area was reduced and characteristic peaks of Ca chromite, as well as Cr_2O_3, appeared.

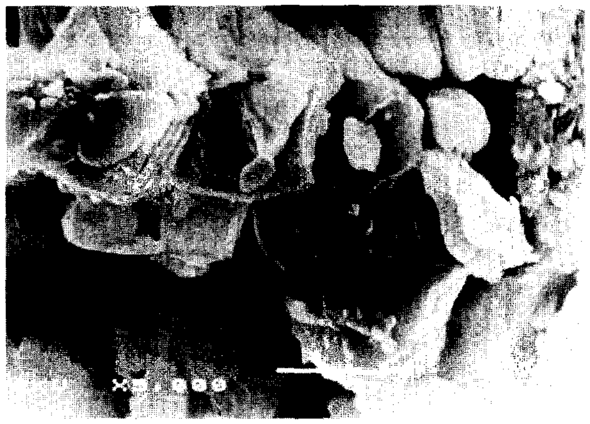

Fig. 5. SEM micrograph of CF_7 pigment, chromaphore large prismatic shaped crystal.

Therefore, it was suggested that the treating of zircon with alkali fluoride salt will cause its partial dissociation leading to the presence of the respective alkali silicate. As suggested by Eppler,[5] this is responsible for the enhancement of the reaction of the chromophore with zircon in the presence of the liquid phase produced. Accordingly, Cr_2O_3 together with the respective alkali will enter into the lattice of zircon during heating up to 1200°C for long periods of time up to 10 h.

To confirm this view, the peak area of zircon formed from its components ZrO_2 and SiO_2 in the presence of CaF_2 and Cr_2O_3 was compared with that of the respective peak in the dissociated zircon mix and Cr_2O_3. It is evident that the latter was always greater than the former, i.e. the dissociated zircon was more reactive.

On comparing the results of semi-quantitative determination of content of zircon from the relative peak areas before and after the addition of different proportions of Cr_2O_3, a correlation between both results was found (Table 2). It was also noticed that the CaF_2 mix with the least percentage of Cr_2O_3 gave the largest zircon area, which represents the maximum percent of Cr_2O_3 going into the lattice. That is, with increase in the Cr_2O_3 percent added, the percent of zircon formed is less and Cr_2O_3 goes into the formation of Ca chromite phase.

The IR absorption bands of Cr_2O_3 were absent in all mixes. Zircon and zirconia bands were detected in all mixes except in mix NLC_6, where zirconia was absent. Zirconia bands were always shifted. New bands were detected in all mixes, namely 1091, 1149, 1082 and 905 in CaF_2 containing samples, and 690, 1087 and 1139 in alkali fluoride mixes, as shown in Figs 2 and 3.

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† Jeol-U3

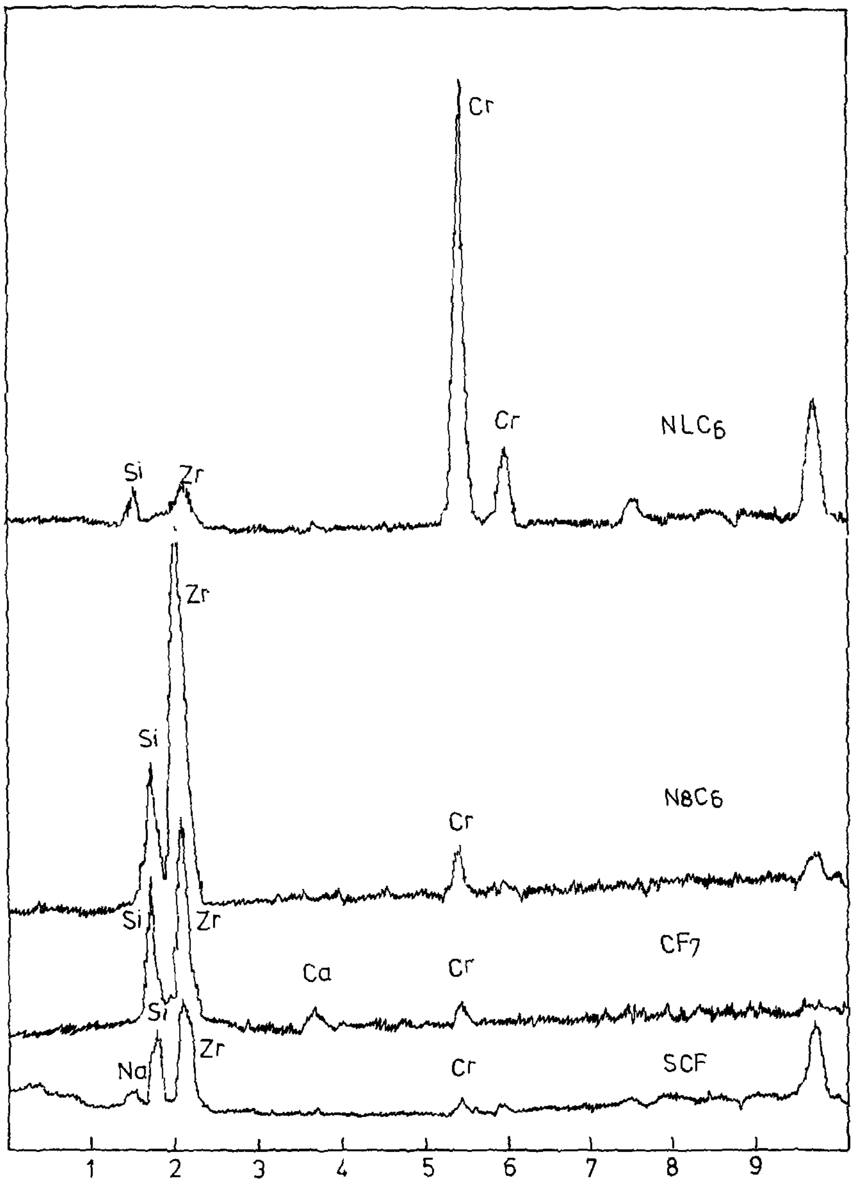

Fig. 6. EDAX of different pigments grains.

Fig. 7. SEM micrograph of N_8C_6 pigment, small size prismatic crystals inseggregate.

Fig. 8. Micrograph of standard pigment SCF, prismatic crystals relatively large in size.

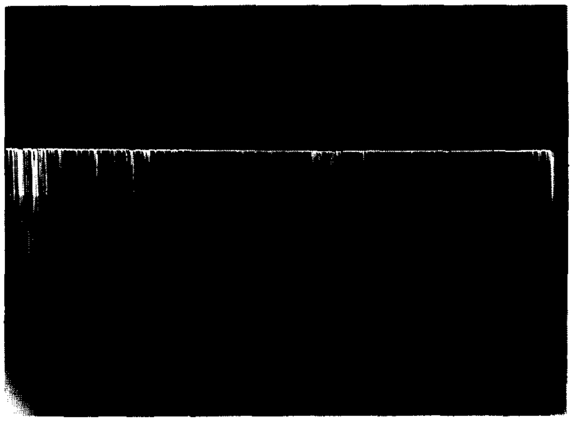

Fig. 9. Line profile of chromium for the above micrograph.

The produced pigments positions on the CIE chromaticity diagram are given in Fig. 4.

The colours of the glazes prepared with pigments containing CaF_2 as a mineralizer were light green. The colour intensity increases with the increase in the percentage of Cr_2O_3. Mix N_8C_6 gave a light grayish green colour, while NLC_6 gave the darkest green colour. Control mix, ZrO_2, SiO_2, Cr_2O_3 and NaF produced a faint green colour.

The SEM micrograph of CF_7 pigment, Fig. 5, show that the chromophore is found in large prismatic shaped crystals. The composition as given by EDAX, Fig. 6, shows the formation of zirconium silicate ($ZrSiO_4$) with relatively small amounts of Ca and Cr.

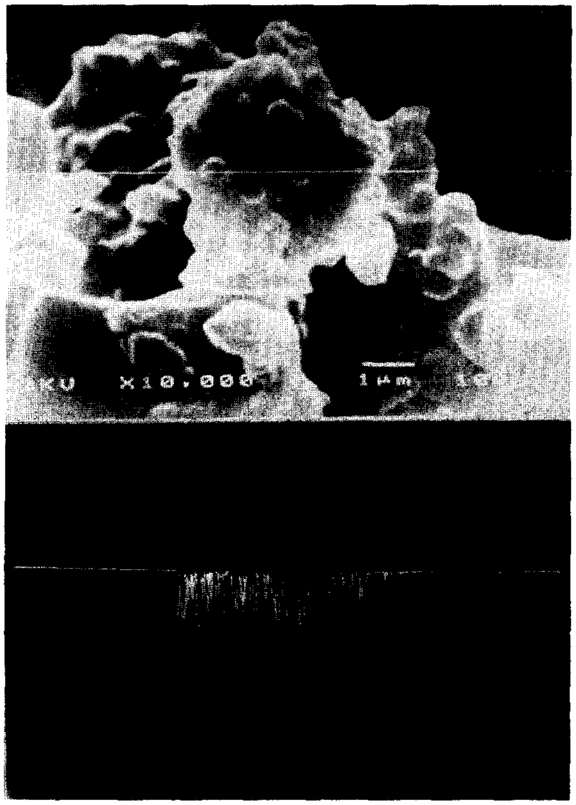

Fig. 10. Micrograph and line profile of NLC_6 pigment, chromophore crystal enriched with Cr.

Pigment N_8C_6 shows smaller size crystals seggregated, also prismatic in shape, Fig. 7.

Standard pigment SCF formed from the constituting oxides also showed prismatic crystals, relatively large in size (about 5 μm), with unreacted grains of ZrO_2, Fig. 8. This is clear from the line profile, Fig. 9. Unreacted grains proved to be free from Cr_2O_3. Additionally, the EDAX of the prisms, Fig. 6, showed that the incorporation of Cr with zircon lattice is relatively small.

NLC_6 pigment, on the other hand, showed an enrichment of Cr in the zircon crystal, as is evident from the line profile of the aggregate, Fig. 10. The chromophores are made of tiny crystals seggregated together indicating a recrystallization reaction.

CONCLUSIONS

1. Cr_2O_3 has a limited role in the formation of zircon chromophore. 6% addition to CaF_2 gave the maximum zircon content. Increasing the percentage of Cr_2O_3 lead to the formation of Ca chromite.
2. Alkali fluoride (NaF + LiF) favoured zircon chromophore formation as indicated by the absence of dissociated ZrO_2 and the presence of a new unidentified XRD *d* spacing.
3. Cr_2O_3 enters in the lattice of zircon during its formation from its components, in the treated zircon. This is indicated by the decrease in the XRD peak of zircon with the increase in Cr_2O_3 content.
4. It was difficult to form zircon chromophore containing Cr_2O_3 from its components.
5. Colours were developed deeply in the compositions containing $ZrSiO_4$ (NLC_6).

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