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Preparation and Physicochemical Characterization of $(Al_{1-x}Cr_x)_2O_3$ Solid Solutions as Inorganic Green Pigments

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ABSTRACT

An investigation of the reaction products of aluminium hydroxide–chromium nitrate mixtures at 200° and 1000°C with molar ratios 9:1, 8:2, 7:3, 6:4, 5:5 and 4:6 was carried out. The products resulting at 200°C were characterized by XRD, IR and diffuse reflectances spectra (DRS) as mixtures of hexavalent chromium compounds with general formula $Al_2O_3Al_n(OH)_{3n-2}CrO_4$, $Al_2(OH)_4CrO_4$, $Al_2(CrO_4)_2Cr_2O_7$, *and* $Al_2O_3Cr_2(CrO_4)_2Cr_2O_7$.

Upon heating at 1000°C for 12 h transformation into $(Al_{1-x}Cr_x)_2O_3$ *solid solutions took place. The compositions were estimated from plots of lattice parameter values versus compositions of mixed crystals.*

The solid solutions were examined in order to test their suitability as pigments in comparison with the well-known green chromium oxide pigments. They showed a high degree of stability towards water, organic solvents, acids, alkalis, light and heat and had in addition reasonable hiding power.

Their good properties indicate that they can be used as satisfactory pigments for coating applications.

INTRODUCTION

We have previously reported[1-4] the thermal and spectroscopic characterization of the reaction products between some aluminium and chromium

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compounds at different temperatures. The studies demonstrated that the reaction products were composed of mixtures of aluminium chromates and/or dichromates with certain compositions at temperatures lower than *c.* 500°C.

This present investigation is concerned with the reaction of aluminium hydroxide powder with chromium nitrate in different proportions at different temperatures. It was devoted to the characterization of the reaction products at 200°C and 1000°C by different spectroscopic methods. The investigation was extended to pigment evaluation in comparison with the known green chromium oxide pigments.[5]

2 EXPERIMENTAL

2.1 Starting materials

2.1.1 Preparation of $Al(OH)_3$ powder

$Al(OH)_3$ was prepared by the precipitation of $Al(OH)_3$ gel on addition of sodium carbonate (75·6 g/l) to an equivalent amount of aluminium sulphate solution (50%) after complexation of iron (0·62 g Fe_2O_3/l) in it with an equivalent amount of ethylenediaminetetraacetic acid at pH ≈ 2. The gel was washed several times with warm water until the wash was free of sulphate ions. It was dried by heating at $\approx$60°C until the Al_2O_3 content reached 53·1%, which corresponds to $Al(OH)_3 . H_2O$.

2.1.2 The starting material

$Cr(NO_3)_3 . 9H_2O$ was obtained from Merck Chemicals (Darmstadt, FRG).

2.2 Preparation of $Al(OH)_3$–$Cr(NO_3) . 9H_2O$ mixtures

Six mixtures of aluminium hydroxide and chromium nitrate having molar ratios of 9:1(**I**), 8:2(**II**), 7:3(**III**), 6:4(**IV**), 5:5(**V**) and 4:6(**VI**) with respect to Al_2O_3 and Cr_2O_3 were prepared by mixing and homogenizing the appropriate quantities of aluminium hydroxide and chromium nitrate, respectively. They were heated at 250°C for several hours until evolution of nitrogen oxide fumes ceased. The products were thermally treated at 1000°C for 12 h.

2.3 Chemical analysis of starting materials

The percentages of aluminium and chromium oxides in aluminium hydroxide powder and chromium nitrate were determined by igniting known weights of them at 1200°C and 1100°C, respectively, until a constant weight was achieved.

2.4 Techniques

X-ray powder diffraction patterns were obtained at room temperature using a Philips diffractometer (Type PW 1399) employing Ni-filtered CuKα radiation ($\lambda = 1{\cdot}5404$ Å). The X-ray tube was operated at 36 kV and 15 mA. Samples were finely ground and packed in a plastic holder. No adhesive or binder was needed. The diffraction angle 2θ was scanned at a rate of 2°/min. For calculation of the lattice parameters the runs were carried out with a scanning speed of 0·25°/min.

Ligand-field spectra (diffuse reflectance) were obtained with a Shimadzu (Kyoto, Japan) UV-360 automatic spectrophotometer. The finely ground solid samples and MgO reference were lightly compacted into 3 mm-deep wells made in aluminium plates. The powdered sample surfaces were smoothed using a glass slide and the flat surface was mounted directly against the open part of the integrating sphere.

IR spectra were measured on KBr discs using a Perkin-Elmer 577 spectrophotometer.

2.5 Evaluation of $(Al_{1-x}Cr_x)_2O_3$ solid solutions as pigments

The evaluation of $(Al_{1-x}Cr_x)_2O_3$ solid solutions as pigments was carried out by testing them according to the universal standard methods. The tests used were specific gravity,[6] bulking value,[7] oil absorption,[8] hiding power,[9] bleeding,[10] fastness to light and heat[10] and chemical resistance.[10]

3 RESULTS AND DISCUSSION

Before evaluation of the reaction products between aluminium hydroxide and chromium nitrate as pigments, the samples were characterized by means of their IR, XRD and diffuse reflectance spectra (DRS).

3.1 Characterization of reaction products

In this present investigation we hoped to characterize the reaction products between aluminium hydroxide powder and chromium nitrate in molar ratios 9:1, 8:2, 7:3, 6:4, 5:5 and 4:6 at 200°C and 1000°C.

The reaction products show vibrational bands in the regions 600–1000, 1100 and 1600 cm^{-1}. The first of these is characteristic for chromate or

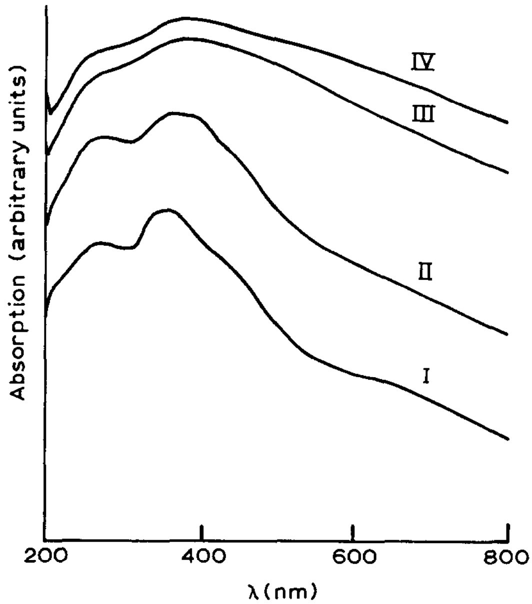

Fig. 1. Electronic absorption spectra of reaction products formed at 200°C.

dichromate groups (CrO stretching), whereas the last two are characteristic for ν_2 of Al–OH groups and ν_2 for water molecules respectively.[1–4]

The electronic absorption spectra of mixtures **I–VI**, showed charge transfer bands at ≈370–380 nm (Fig. 1), characteristic of hexavalent chromium ions.

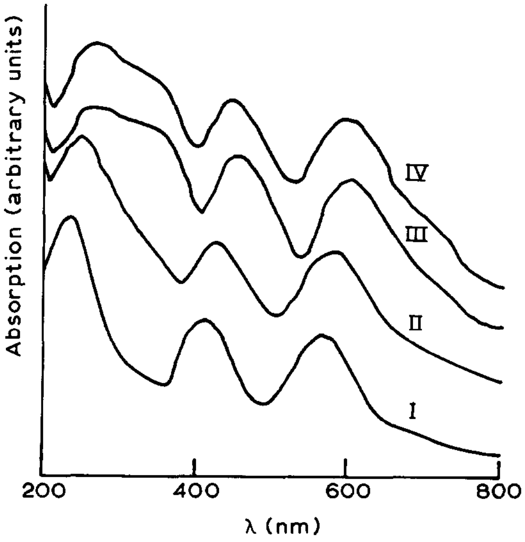

Fig. 2. X-ray diffraction patterns of solid solutions formed at 1000°C.

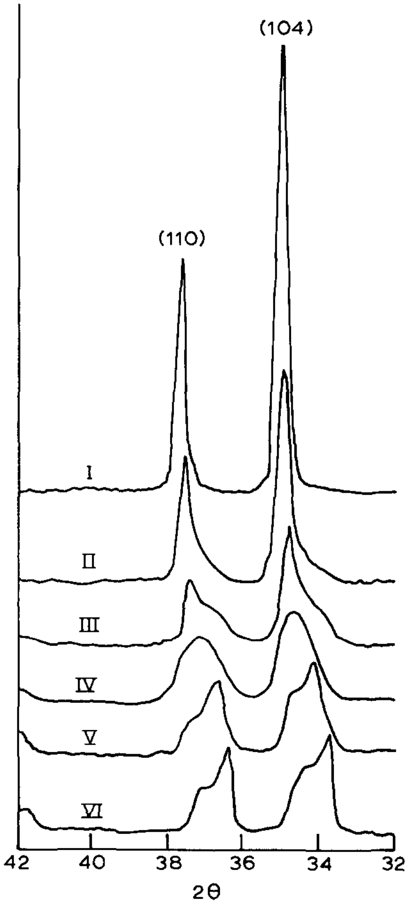

Fig. 3. Electronic absorption spectra of reaction products formed at 1000°C.

Similar observations were made in previous studies on the thermal and spectroscopic characterization of the reaction products between some aluminium and chromium compounds at different temperatures.[1-4]

At temperatures higher than 500°C the hexavalent chromium compounds are transformed into $(Al_{1-x}Cr_x)_2O_3$ solid solutions.[1-4,11-13] An X-ray investigation of the products (Fig. 2) resulting from heating the reaction mixtures at 1000°C showed that they are composed of several solid solutions. The lattice parameters were determined with the aid of line-broadening of their spectra and indicated them to be hexagonal.[14] The compositions were estimated from the plot of linear variation of lattice parameter with mole% Cr_2O_3 in mixed crystals $(Al_{1-x}Cr_x)_2O_2$. Mixtures I and II produced one solid solution from each, where the values of x were 0·1 and 0·2, respectively. On the other hand, the remaining mixtures produced two different solid solutions in each case, as can be seen from Fig. 3. The solid

TABLE 1
Chemical Composition of Products at 200° and 1 000°C

Mixture	*Products at 200°C*	*Products at 1 000°C*
I	$Al_2O_3Al_7(OH)_{19}CrO_4$	$(Al_{0\cdot9}Cr_{0\cdot1})_2O_3$
II	$Al_2O_3Al_2(OH)_4CrO_4$	$(Al_{0\cdot8}Cr_{0\cdot2})_2O_3$
III	$Al_2O_3Al_3(OH)_7CrO_4$ $Al(OH)CrO_4$	$(Al_{0\cdot83}Cr_{0\cdot17})_2O_3$ $(Al_{0\cdot5}Cr_{0\cdot5})_2O_3$
IV	$Al_2(OH)_4CrO_4$ $Al(OH)CrO_4$	$(Al_{0\cdot67}Cr_{0\cdot33})_2O_3$ $(Al_{0\cdot5}Cr_{0\cdot5})_2O_3$
V	$Al_2(OH)_4CrO_4$ $Al_2(CrO_4)_2Cr_2O_7$	$(Al_{0\cdot67}Cr_{0\cdot33})_2O_3$ $(Al_{0\cdot33}Cr_{0\cdot67})_2O_3$
VI	$Al_2(OH)_4CrO_4$ $Al_2O_3Cr_2(CrO_4)_2Cr_2O_7$	$(Al_{0\cdot67}Cr_{0\cdot33})_2O_3$ $(Al_{0\cdot125}Cr_{0\cdot87})_2O_3$

solutions $(Al_{1-x}Cr_x)_2O_3$ which have x values higher than 0·5 were found in chromium-rich mixtures, such as V and VI.

The electronic absorption spectra of the solid solutions showed characteristic absorption bands due to: $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions[14] of trivalent chromium in mixed crystals. The shift in maxima of the absorption peaks in the visible region of the spectra from mixture I–VI may be attributed to the relative increase in the percentages of solid solutions rich in chromium content.[14]

The aluminium chromates and/or dichromates produced at 200°C which correspond to the characterized solid solutions can be formulated as shown in Table 1. The general formulae of them are:

$$Al_2O_3Al_n(OH)_{3n-2} \cdot CrO_4Al_2(OH)CrO_4Al_2(CrO_4)_2Cr_2O_7$$

and

$$AlCrO_3Cr_2(CrO_4)_2Cr_2O_7$$

3.2 Identification of $(Al_{1-x}Cr_x)_2O_3$ solid solutions as green pigments

In order to test the suitability of $(Al_{1-x}Cr_x)_2O_3$ solid solutions as pigments for various coating applications, it was of interest to evaluate them in comparison with the known chrome green pigment, Cr_2O_3.[5]

3.2.1 Specific gravity, bulking value and oil absorption

It can be seen from Table 2 that bulking values (B.V.) decrease with increase in the chromium content of the solid solutions, as a result of increase in their specific gravities (Sp.Gr.) provided that the bulking value equals 12·05/Sp.Gr.[7] It was also found that the oil absorption of solid solutions

TABLE 2

Pigment Characteristics

Pigment (mixture)	*Sp. Gr.*	*Oil absorption (g/100 g)*	*Bulking value (B.V.) (gal/100 lb)*
I	4·12	37·2	2·92
II	4·21	41·9	2·86
III	3·38	65·5	2·75
IV	4·48	51·2	2·69
V	4·56	55·8	2·64
VI	4·67	55·8	2·58
Cr_2O_3	5·18	81·8	2·33

increases with increase in their chromium content but, in general, their absorption values, were better than that of the chromium oxide green pigment.[10]

3.2.2 *Hiding power of the $(Al_{1-x}Cr_x)_2O_3$ solid solutions*

The method used for estimation of the hiding power is the same as that described in the International Standards.[9] The value of hiding power equals the area (in m^2) hidden by one kilogram of the pigment when applied in the form of a paint or lacquer.[7]

From Table 3, it can be concluded that increase in the chromium content in the solid solutions improves their hiding power. On the other hand, the decrease in hiding values of mixtures V and VI in comparison to that of pure chromium oxide can be offset economically.

3.2.3 *Bleeding test, chemical resistance and fastness to light and heat of the $(Al_{1-x}Cr_x)_2O_3$ solid solutions*

The six pigments investigated showed excellent results for bleeding tests in various solvents such as water, ethanol, acetone, chloroform, carbon

TABLE 3

Estimated Hiding Power

Pigment (mixture)	*Hiding power (m^2/kg)*
I	10·20
II	10·78
III	11·40
IV	12·85
V	13·70
VI	14·60
Cr_2O_3	18·62

tetrachloride, toluene, xylene and tetrahydrofuran. They also showed very high resistance towards acids and alkalis. The acidic solutions used in these investigations were 5% HCl and 5% H_2SO_4, and the alkaline solutions were 2% NaOH, 5% Na_2CO_3 and a saturated solution of calcium hydroxide.

Light fastness evaluations were carried out for 7 days, and the tests for heat resistance were carried out for 60 min at 120°C, 45 min at 130°C, 30 min at 150°C, 15 min at 170°C and 10 min at 200°C. The results of the tests indicate that the $(Al_{1-x}Cr_x)_2O_3$ solid solutions have excellent stability to light and heat.

The generally good properties of these materials indicates that they can be used as satisfactory pigments for coating applications, especially taking into consideration the economics in comparison with the relatively high price of green chromium oxide pigments.

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