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THERMAL AND SPECTROSCOPIC CHARACTERIZATION OF REACTION PRODUCTS OF Al-NITRATE–Cr-NITRATE INTERACTION AT VARIOUS TEMPERATURES

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ABSTRACT

Thermal decomposition of aluminium nitrate and chromium nitrate was carried out. The decomposition products of these salts at 250, 350, 500, 750 and 1000 °C were characterized by means of chemical analysis, IR, diffuse reflectance and X-ray diffraction. The same studies were also carried out on three mixtures of aluminium and chromium nitrates with molar ratios 3 : 1, 1 : 1 and 1 : 3, where two intermediates were produced from each mixture in the temperature range 375–475 °C. These were

$AlCrO_3Al(OH)CrO_4$, $Al_2O_3Al_3(OH)_7CrO_4$
$Al_{0.67}Cr_{1.33}O_3Al_2(CrO_4)_2Cr_2O_7$, $Al_2(OH)_4CrO_4$
$Al_{1.33}Cr_{0.67}O_3Cr_2(CrO_4)_2Cr_2O_7$, $AlCrO_3Al(OH)CrO_4$

The dichromates or chromates with an Al/Cr ratio of less than 1 are transformed to corresponding solid solutions of Al_2O_3 in Cr_2O_3 at about 500 °C, whereas those with an Al/Cr ratio of more than 1 are transformed to solid solutions of Cr_2O_3 in Al_2O_3 at temperatures above 750 °C. The corresponding solid solutions of the above-mentioned dichromates and chromates are

$(Al_{0.5}Cr_{0.5})_2O_3$, $(Al_{0.83}Cr_{0.17})_2O_3$
$(Al_{0.33}Cr_{0.67})_2O_3$, $(Al_{0.67}Cr_{0.33})_2O_3$
$(Al_{0.17}Cr_{0.83})_2O_3$, $(Al_{0.5}Cr_{0.5})_2O_3$

INTRODUCTION

It is well known that a vast number of chromium and aluminium compounds are widely used for many industrial purposes: as refractory materials [1], as pigments [2], in ruby synthesis [3], and in the case of chromium oxide supported on aluminium oxide, as important catalysts for a wide variety of reactions [4–7].

Although most areas of the systematic chemistry of molten nitrates, especially alkali metal nitrates, have been reasonably well explored [8], the reactions of Cr(III) nitrate with Al(III) nitrate in molten states and at

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elevated temperatures has not been extensively studied. The present work is concerned with a detailed investigation of the progressive reactions between mixtures of aluminium and chromium nitrates in molten state, and with the effect of temperature on their reaction products. Thermal and spectroscopic methods of analysis were employed.

EXPERIMENTAL

Materials

The starting materials $Al(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were obtained from Merck Chemicals (West Germany).

Mixtures

Three mixtures of aluminium and chromium nitrates with molar ratios of Al_2O_3 to Cr_2O_3 of 3 : 1 (**I**), 1 : 1 (**II**) and 1 : 3 (**III**) were prepared by mixing the nitrates, homogenizing and grinding. The pure nitrates and their mixtures **I**, **II** and **III** were heated at 250 °C for several hours until cessation of nitrogenous oxide fumes. The products were thermally treated by a gradual increase of temperature up to 500 °C, and kept constant at that temperature for 4 hours. The same heating process was performed with temperatures of 750 and 1000 °C.

Techniques

Thermal analyses by TG, DTG and DTA of the pure and mixed nitrates were carried out using a Netzsch (West Gemany) thermoanalyser with a differential scanning calorimeter cell. The rate of heating was 10 °C min^{-1}.

X-ray powder diffraction patterns were obtained at room temperature using a Philips diffractometer (type PW 1051) employing Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5404$ Å). The X-ray tube was operated at 36 KV and 16 mA. Samples were finely ground and packed in a plastic holder. No adhesive or binder was necessary. The diffraction angle 2θ was scanned at a rate of 2 min^{-1}. For calculation of the lattice parameters the runs were carried out with a scanning speed of 0.25 min^{-1}.

Ligand-field spectra (diffuse reflectance) were obtained with a Schimadzu 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.

TABLE 1

Characterization of TG and DTG curves for $Al(NO_3)_3 \cdot 9H_2O$ and calculation of weight losses

Thermal step	Temp. range	DTG peak (°C)	% loss	
			Actual	Calculated
1	25–36	–	–	–
2	60–96	–	1.75	1.75
3	96–166	160	28.78	28.74
4	166–208	180	45.75	45.59
5	208–285	230	62.25	62.39
6	285–428	330	74.75	73.84
7	428–488	440	76.75	76.84
8	488–628	545	85.45	84.64
9	628–706	666	87.85	87.04

IR–Vibrational spectra were measured using a Perkin–Elmer 577 spectrophotometer. The spectra were obtained by the KBr disc method. The experiments covered the wave number range 4000–400 cm^{-1}.

Chemical analysis

Decomposition products of pure salts

The percentages of aluminium and chromium in intermediate decomposition products of both aluminium nitrate and chromium nitrate were determined by igniting a known weight of the salts at 1200 and 1100 °C, respectively, until a constant weight was achieved (Tables 1 and 2).

Decomposition products of mixtures of aluminium nitrate and chromium nitrate

A known weight of aluminium chromate intermediates or solid solution was fused with an excess of Na_2CO_3. The melt was dissolved in water, after

TABLE 2

Characterization of TG and DTG curves for $Cr(NO_3)_3 \cdot 9H_2O$ and calculation of weight losses

Thermal step	Temp. range (°C)	DTG peak (°C)	% loss	
			Calculated	Actual
1	–	–	–	–
2	75–158	136	31.76	30.20
3	158–185	167	41.89	40.50
4	185–280	206	53.14	52.88
5	280–420	325	75.05	74.19
6	420–480	460	78.90	79.09
7	>480	550	81.15	81.40

cooling, where the pH of the solution was adjusted to approximately 14. The trivalent chromium was oxidized to chromate with H_2O_2. After decomposition of the excess peroxide, the solution was neutralized by nitric acid in the presence of phenolphthalein until the solution became slightly pink. $Al(OH)_3$ was precipitated by passing CO_2 into the hot solution, the precipitate was collected on a filter paper, washed with 1% neutralized ammonium nitrate solution and it was then ignited at 1200 ° C and weighed as Al_2O_3. Chromate was determined in the combined filtrate in the form of barium chromate [9].

RESULTS AND DISCUSSION

In order to study the chemical reaction between aluminium nitrate and chromium nitrate at various temperatures, we will begin by characterizing the compounds produced from each of the salts alone at these temperatures. This will give us a useful guide as to the reactions which probably take place when there is interaction between aluminium nitrate and chromium nitrate.

Aluminium nitrate

Figure 1 presents TG, DTG and DTA plots of $Al(NO_3)_3 \cdot 9H_2O$. The courses of the TG and DTG curves suggest several transformations starting at 36 ° C. These transformations directly follow the melting of the salt. The successive, gradual losses of gases and vapours at higher temperatures are not separated by a period of weight constancy. This can be attributed to instability of the intermediates produced through a particular range of temperatures. Moreover, the DTA curve shows eight endothermic peaks, corresponding to dissolution of salt in its water of crystallization, melting, and losses of water, nitrogen oxides and nitric acid. Therefore, according to

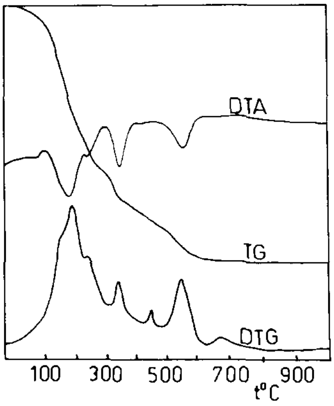


Fig. 1. Thermal analysis of $Al(NO_3)_3 \cdot 9H_2O$.

TG and DTG curves and calculation of weight losses (Table 1), the decomposition of $Al(NO_3)_3 \cdot 9H_2O$ can be represented by the following steps

$$\left.\begin{array}{l} 1.\ Al(NO_3)_3 \cdot 9H_2O \xrightarrow{25-36\,^\circ C} \\ 2.\ Al(NO_3)_3 \cdot 9H_2O \xrightarrow{36-96\,^\circ C} \end{array}\right\} \begin{array}{l}\text{melting and dissolution in water}\\ \text{of crystallization}\end{array}$$

3. $Al(NO_3)_3 \cdot 9H_2O \xrightarrow{96-166\,^\circ C} HNO_3 + 2.5H_2O + Al(OH)(NO_3)_2 \cdot 5.5H_2O$

4. $Al(OH)(NO_3)_2 \cdot 5.5H_2O \xrightarrow{166-208\,^\circ C} HNO_3 + Al(OH)_2(NO_3) \cdot 4.5H_2O$

5. $Al(OH)_2(NO_3) \cdot 4.5H_2O \xrightarrow{208-285\,^\circ C} HNO_3 + Al(OH)_3 \cdot 3.5H_2O$ (**I-A**)

6. (**I-A**) $\xrightarrow{285-428\,^\circ C} 3.5H_2O + \frac{1}{2}(Al_2O_3 \cdot 6H_2O)$ (**II-A**)

7. (**II-A**) $\xrightarrow{428-488\,^\circ C} 1.5H_2O + Al_2O_3 \cdot 2H_2O$ (**III-A**)

8. (**III-A**) $\xrightarrow{488-628\,^\circ C} 1.5H_2O + Al_2O_3 \cdot 0.5H_2O$ (**IV-A**)

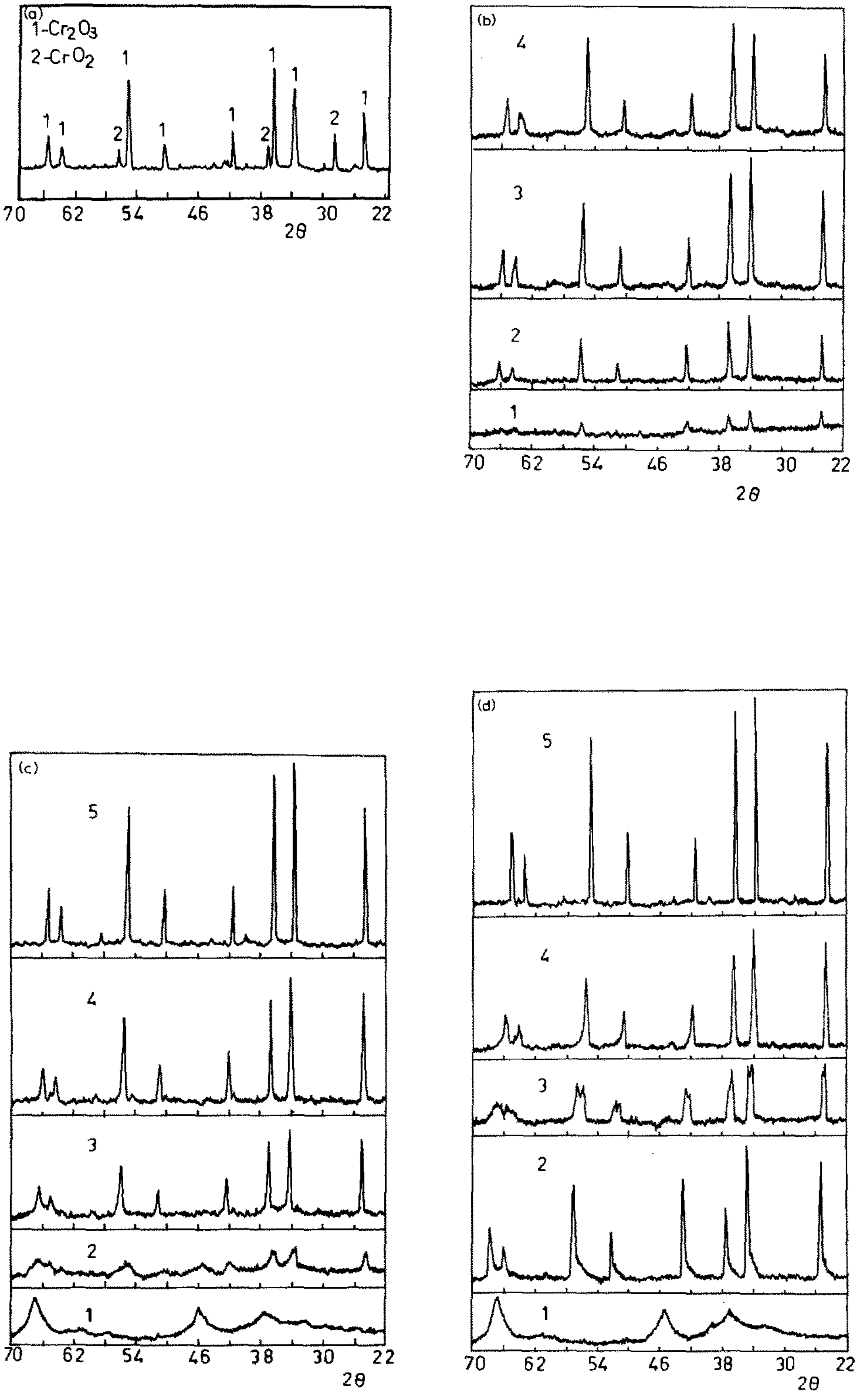
9. (**IV-A**) $\xrightarrow{628-706\,^\circ C} 0.5H_2O + \gamma\text{-}Al_2O_3$ (**V-A**)

The intermediates **I-A**, **II-A**, **IV-A** and **V-A** were obtained by heating $Al(NO_3)_3 \cdot 9H_2O$ at 250, 350, 500 and 750 °C, respectively, for 4 hours. Subjecting them to chemical analysis (Table 3) revealed that the percentage of aluminium in each agreed well with the theoretical value. X-ray analysis revealed that intermediates **I-A**–**IV-A** are not crystalline. On the other hand, their IR spectra showed that they contain OH groups or water molecules. The intensity of characteristic bending and stretching OH bands at 1650 and 3300 cm^{-1}, respectively, decreased with increase of temperature of treatment along the compounds **I-A**–**IV-A**. Compound **V-A** [10] was found to be crystalline (Fig. 2c) and gave X-ray diffraction *d*-spacings of 2.39, 2.276, 1.98, 1.519 and 1.397 Å. (ASTM Index for $\gamma\text{-}Al_2O_3$ is as follows: 2.39, 2.28, 1.977, 1.52 and 1.395 Å.)

TABLE 3

Chemical analysis of the thermal decomposition intermediates of $Al(NO_3)_3 \cdot 9H_2O$

Temp. of decomposition (°C)	Intermediate	Suggested formula	%Al	
			Experimental	Calculated
250	**I-A**	$Al(OH)_3 \cdot 3.5H_2O$	19.23	19.09
350	**II-A**	$Al_2O_3 \cdot 6H_2O$	40.10	39.63
500	**IV-A**	$Al_2O_3 \cdot 0.5H_2O$	48.22	48.57
750	**V-A**	$\gamma\text{-}Al_2O_3$	53.35	53.77


(a)
1-Cr_2O_3
2-CrO_2
1 1 2 1 1 1 2 1 1 2 1
70 62 54 46 38 30 22
2θ
(b)
4
3
2
1
70 62 54 46 38 30 22
2θ
(c)
5
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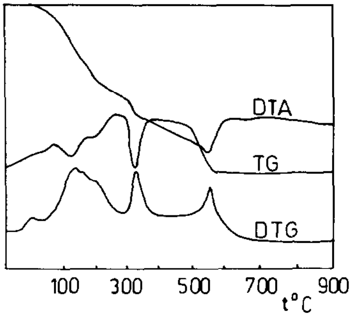

Fig. 3. Thermal analysis of $Cr(NO_3)_3 \cdot 9H_2O$.

Chromium nitrate

From Fig. 3 and Table 2 it can be seen that the courses of the TG and DTG curves for chromium nitrate decomposition have almost the same features as those observed for aluminium nitrate and proceed through seven stages leading to intermediates with chromium valencies Cr^{3+}, Cr^{4+} and Cr^{6+}. (Decomposition equations are given later.) From the results of chemical analysis of decomposition products of chromium nitrate heated for 4 h at 250, 350, and 500 °C (Table 4), together with the calculated weight losses found at the ends of DTG peaks, i.e. at 158, 206, 280, 420, 480 and 550 °C (Fig. 3), it seems that the decomposition process of chromium nitrate involves two parallel reactions. The first of these proceeds via evolution of nitric acid leading to the formation of chromic hydroxide, while the second proceeds via evolution of nitrogen dioxide gas leading to chromic trioxide. The steps of the decomposition can be represented as follows

1. $Cr(NO_3)_3 \cdot 9H_2O \xrightarrow{< 75\,^{\circ}C}$ melting and dissolution in water of crystallization

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Fig. 2a. X-ray diffraction patterns of thermal products from $Cr(NO_3)_3 \cdot 9H_2O$ at 350 °C.

Fig. 2b. X-ray diffraction patterns of thermal products from individual and mixed $Cr(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ at 500 °C (1, mixture **I**; 2, mixture **II**; 3, mixture **III**; 4, Cr-oxide).

Fig. 2c. X-ray diffraction patterns of thermal products from individual and mixed $Cr(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ at 750 °C (1, Al-oxide; 2, mixture **I**; 3, mixture **II**; 4, mixture **III**; 5, Cr-oxide).

Fig. 2d. X-ray diffraction patterns of thermal products from individual and mixed $Cr(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ at 1000 °C (1, Al-oxide; 2, mixture **I**; 3, mixture **II**; 4, mixture **III**; 5, Cr-oxide).

TABLE 4

Chemical analysis of thermal decomposition intermediates of $Cr(NO_3)_3 \cdot 9H_2O$

Temp. of decomposition (°C)	Inter-mediate	Suggested formula	% Cr	
			Experimental	Actual
250	**III-C**	$[1/2CrOOH \cdot 1/4Cr_2O_3 \cdot CrO_3 \cdot 10H_2O]$	26.33	26.17
350	**IV-C**	$[1/2CrO_2 \cdot 1/8Cr_8O_{21} \cdot 1/4Cr_2O_3]$	60.10	59.77
500	**VI-C**	Cr_2O_3	68.20	68.42

$$2.\ 2Cr(NO_3)_3 \cdot 9H_2O \xrightarrow{75\text{–}158\,^\circ C} [Cr(OH)_2(NO_3) \cdot CrO_2(NO_3) \cdot 14H_2O] + 2HNO_3 + 2NO_2 + 2H_2O\ (\textbf{I-C})$$

$$3.\ (\textbf{I-C}) \xrightarrow{158\text{–}206\,^\circ C} [Cr(OH)_3 \cdot CrO_3 \cdot 13H_2O] + HNO_3 + NO_2\ (\textbf{II-C})$$

$$4.\ (\textbf{II-C}) \xrightarrow{206\text{–}280\,^\circ C} [\tfrac{1}{2}CrOOH \cdot \tfrac{1}{4}Cr_2O_3 \cdot CrO_3 \cdot 10H_2O] + 4.25H_2O\ (\textbf{III-C})$$

$$5.\ (\textbf{III}\cdot\textbf{C}) \xrightarrow{280\text{–}420\,^\circ C} [\tfrac{1}{2}CrO_2 \cdot \tfrac{1}{8}Cr_8O_{21} \cdot \tfrac{1}{4}Cr_2O_3] + \tfrac{3}{16}O_2 + H_2O\ (\textbf{IV-C})$$

$$6.\ (\textbf{IV-C}) \xrightarrow{420\text{–}480\,^\circ C} [\tfrac{1}{4}Cr_2O_3 \cdot \tfrac{1}{8}Cr_8O_{19.48} \cdot \tfrac{1}{4}Cr_2O_3] + 0.545O_2\ (\textbf{V-C})$$

$$7.\ (\textbf{V-C}) \xrightarrow{>480\,^\circ C} Cr_2O_3 + 0.48O_2\ (\textbf{VI-C})$$

Additional evidence for the proposed decomposition scheme is gained from characterization of the products **III-C**, **IV-C** and **VI-C**, which were obtained by heating chromium nitrate for 4 h at 250 °C, 350 °C and 500 °C respectively, using IR, X-ray and electronic absorption spectra.

Product **III-C** ($1/2CrOOH \cdot 1/4Cr_2O_3 \cdot CrO_3 \cdot 10H_2O$) was found to be amorphous and has three IR bands located at 650, 1650 and 3400 cm^{-1} (Fig. 4), which are characteristic for OH groups attached to chromium atoms in Cr^{3+} and Cr^{6+} compounds. The electronic absorption spectrum of this product showed broad bands with maxima at 594, 456, 360 and 250 nm, which are related to absorption bands of both Cr^{3+} and Cr^{6+} (Fig. 5).

X-ray diffraction patterns of product **IV-C** ($1/2CrO_2 \cdot 1/8Cr_8O_{12} \cdot 1/4Cr_2O_3$) showed the characteristic *d*-spacings of both Cr_2O_3 and CrO_2 (Fig. 2a). The latter oxide may be formed as a result of oxidation of CrOOH by CrO_3 leading to formation of CrO_2 as well as chromium dichromate, according to the equation

$$2CrOOH + 8CrO_3 \rightarrow 2CrO_2 + Cr_2(Cr_2O_7)_3 + 3H_2O + O_2$$

The existence of amorphous chromium dichromate was indicated by the presence of a charge transfer absorption band located at 340 nm, whereas the characteristic vibrational band of dichromate at 335 cm^{-1} was overshadowed by Cr_2O_3 vibration bands at 410, 440, 575 and 625 cm^{-1}.

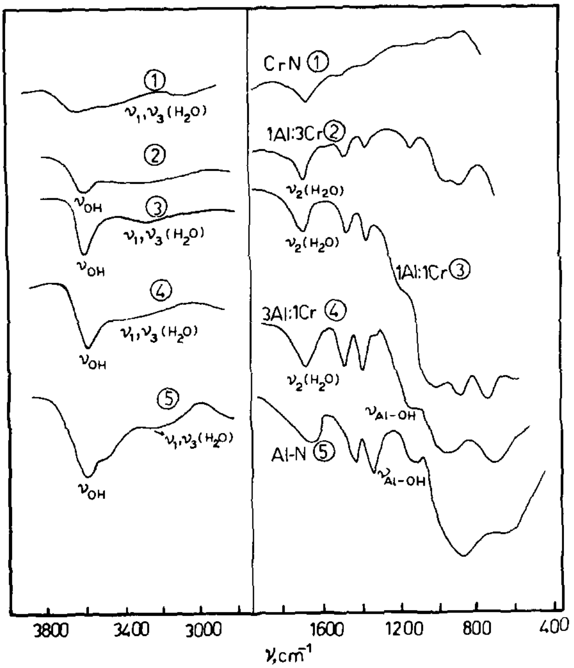


Fig. 4. IR spectra of Al-nitrate, Cr-nitrate and their mixtures **I**, **II** and **III**, thermally treated at 350 °C.

At temperatures of 420–480 °C species of CrO_2 and $Cr_2(Cr_2O_7)_3$ (product **IV-C**) are transformed to Cr_2O_3 and oxygen deficient chromium dichromate $Cr_8O_{19.48}$ [11], whereas at higher temperatures the latter compound produces chromium oxide (**IV-C**, see eqn. (7)) which is the final product of chromium nitrate decomposition [9] as identified by various spectroscopic methods (Figs. 4 and 5).

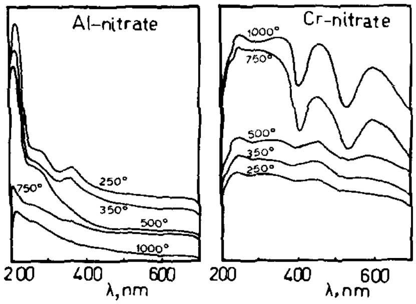
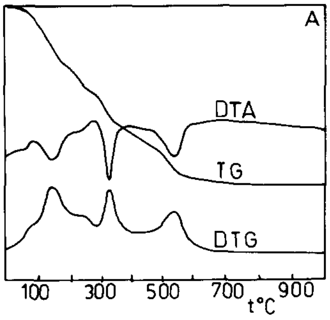


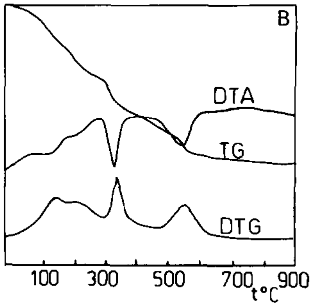
Fig. 5. Diffuse reflectance spectra of individual Al- and Cr-nitrates thermally treated at varying temperatures.

Interaction between aluminium nitrate and chromium nitrate

In this section we describe the reaction between aluminium nitrate and chromium nitrate in molar ratios 3 : 1, 1 : 1 and 1 : 3 at various temperatures up to 1000 °C, hoping to establish the interactions which may be occurring between their decomposition products.

From the values of weight losses (Fig. 6) and results of chemical analysis of both aluminium and chromium in decomposition products at 280 °C (Table 5), it can be concluded that the mixed nitrates **I**, **II** and **III** produced mixtures of [$Al(OH)_3 \cdot 3.5H_2O$] and [$CrOOH \cdot Cr_2O_3 \cdot CrO_3 \cdot xH_xO$] in quantities proportional to the ratios of the reactants. These mixtures are amorphous and show the same electronic absorption peaks as those observed when heating the nitrates individually (Figs. 5 and 7). These peaks correspond to tri- and hexavalent chromium in addition to those of aluminium hydroxide which cause some broadening and shifting of charge transfer bands of chromium compounds in the UV region to shorter wavelength.





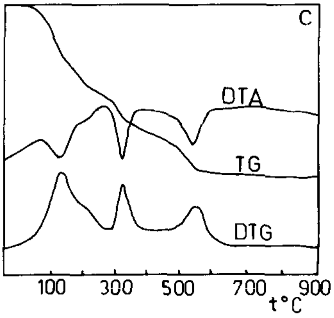


Fig. 6A. Thermal analysis of mixture **I** (3Al : 1Cr).

Fig. 6B. Thermal analysis of mixture **II** (1Al : 1Cr).

Fig. 6C. Thermal analysis of mixture **III** (1Al : 3Cr).

TABLE 5

Lattice parameter (α) of thermal decomposition products of Al-nitrate–Cr-nitrate mixtures at different temperatures

Temp. of treatment (° C)	Lattice parameter (Å)		
	3 Al : 1 Cr	1 Al : 1Cr	1 Al : 3 Cr
500	4.8964	4.8911	4.9234
750	4.8879	4.8815	4.9234
1000	4.8522	4.885	4.9234
	4.7918	4.827	4.853

At temperatures of 375–475° C aluminium hydroxide seems to interact with chromium oxides, forming mixtures of amorphous chromates and dichromates depending on the Al/Cr ratio. The same phenomenon has also been observed in the cases of interaction between $NaNO_3$ and Cr_2O_3 [12] and between $Al(OH)_3$ and $Cr(OH)_3$ or Cr^{6+}-compounds [13–16]. Chromates and dichromates were identified spectrally from their IR spectra (Fig. 4), where they show characteristic bands in the region 600–1000 cm^{-1}. The existence of Al–OH groups, in compounds containing both OH^- and CrO_4^{2+} groups, are identified by vibration bands at about 1100 and 1600 cm^{-1}.

An X-ray investigation of products resulting from the interaction between Al-nitrate and Cr-nitrate in molar ratios 3 : 1 (**I**), 1 : 1 (**II**) and 1 : 3 (**III**) when heated at 500° C for four hours showed an amorphous matrix and a single crystalline phase, in each mixture, with lattice parameters 4.9234, 4.8911 and 4.8964 Å (Table 5 and Fig. 8), assuming that this crystalline phase is hexagonal. The electronic spectra of these products showed absorption bands in the UV region characteristic of hexavalent chromium, in addition

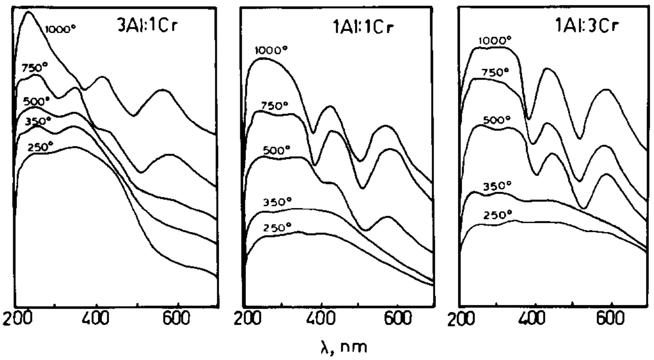


Fig. 7. Diffuse reflectance spectra of Al- and Cr-nitrate mixtures **I**, **II** and **III**.

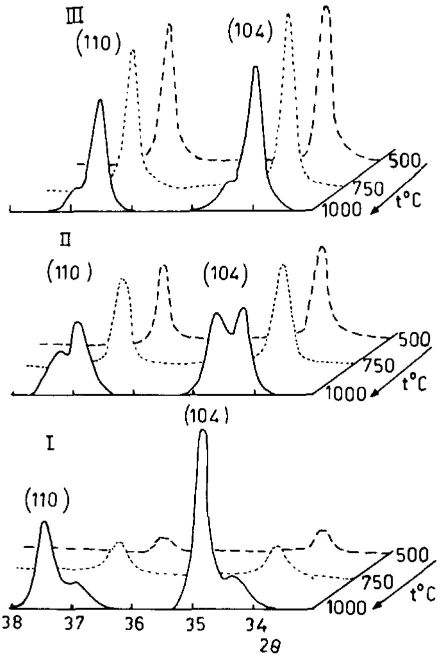


Fig. 8. Line-broadening of (104) and (110) lines of mixtures I, II and III, calcined at varying temperatures.

to those of trivalent chromium in the visible region, but with shifting to a lower wavelength. These phenomena are characteristic of $Al_{2-x}Cr_xO_3$ solid solutions [17].

Increasing the temperature of the treatment up to 750 °C increased the degree of crystallinity of the solid solutions. This was accompanied by a slight decrease in lattice parameters, especially for the solid solutions produced from mixtures **I** and **II** (Table 5 and Fig. 8). The spectral features of these compounds were found to be almost the same as those observed for

TABLE 6

Chemical composition of products obtained at 1000 ° C, calculated from Fig. 11

Molar ratio AlN : CrN	Lattice parameter (Å)	Composition of solid solution
3 : 1	4.8522	$(Al_{0.5}Cr_{0.5})_2O_3$
	4.7918	$(Al_{0.83}Cr_{0.17})_2O_3$
1 : 1	4.885	$(Al_{0.33}Cr_{0.67})_2O_3$
	4.827	$(Al_{0.67}Cr_{0.33})_2O_3$
1 : 3	4.9234	$(Al_{0.17}Cr_{0.83})_2O_3$
	4.853	$(Al_{0.5}Cr_{0.5})_2O_3$

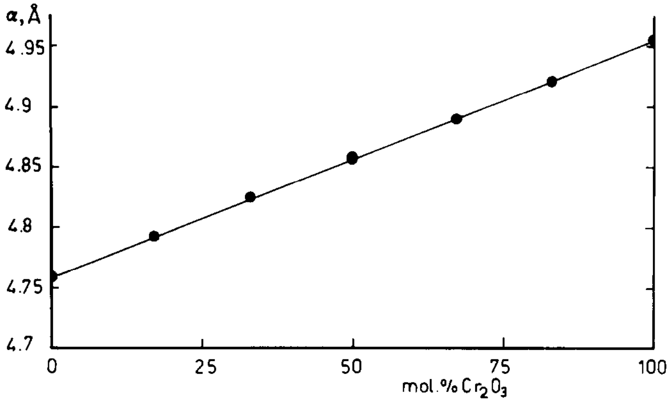


Fig. 9. Dependence of lattice parameters on Cr content in the solid solution $Al_{2-x}Cr_xO_3$.

mixtures heated at 500 °C, but with a slight shift of absorption maxima towards shorter wavelengths (Fig. 7).

At 1000 °C an additional crystalline phase was observed (Fig. 8), with lattice parameters 4.7918, 4.827 and 4.853 Å (Table 5), characteristic of products resulting from mixtures **I**, **II** and **III**, respectively.

The compositions of the two solid solutions with known lattice parameters (Table 6) produced by heating mixtures **I**, **II** and **III** at 1000 °C for four hours were estimated from the plot of lattice parameter values vs. composition of $Al_{2-x}Cr_xO_3$ mixed crystals (Fig. 9) as reported by Schimitz-DuMont and Reinen [17]. The compositions of these solid solutions were formulated as follows

$AlCrO_3$ and $Al_{1.67}Cr_{0.33}O_3$ (from mixture **I**)

$Al_{0.67}Cr_{1.33}O_3$ and $Al_{1.33}Cr_{0.67}O_3$ (from mixture **II**)

$Al_{0.33}Cr_{1.67}O_3$ and $AlCrO_3$ (from mixture **III**)

It was found that percentages of both aluminium and chromium, as determined by chemical analysis, were in good agreement with their calculated values from the suggested formulae (Table 7).

Cudennec and Bonnin [16] found that some chromates and dichromates of aluminium such as $Al_2(OH)_4CrO_4$ and $Al_2(CrO_4)_2Cr_2O_7$ are transformed to solid solutions of chromium oxide in aluminium oxide and vice versa above 600 °C. Our own observations from IR and electronic absorption spectra (Figs. 4, 5, 7, and 9) indicate that some hexavalent chromium compounds of aluminium are formed above 375 °C. These decompose, leading to the formation of a crystalline solid solution of Al_2O_3 in Cr_2O_3 below 500 °C, and Cr_2O_3 in Al_2O_3 above 750 °C, as can be seen from X-ray diffraction patterns (Fig. 8). From this set of findings we can formulate the

TABLE 7

Chemical analysis and suggested formulae of the intermediates produced between 375 and 475 ° C

Molar ratio Al : Cr	No. of Al atoms	No. of Cr atoms	Al/Cr ratio	Suggested formula
3 : 1	2	2	1.00	$\mathrm{AlCrO_3Al(OH)CrO_4}$
	5.00	1.00	5.00	$\mathrm{Al_2O_3Al_3(OH)_2CrO_4}$
1 : 1	2.67	5.33	0.50	$\mathrm{Al_{0.67}Cr_{1.33}O_3Al_2(CrO_4)_2Cr_2O_7}$
	2.00	1.00	2.00	$\mathrm{Al_2(OH)_4CrO_4}$
1 : 3	1.33	6.67	0.20	$\mathrm{Al_{1.33}Cr_{0.67}O_3Cr_2(CrO_4)_2Cr_2O_7}$
	2	2	1.00	$\mathrm{AlCrO_3Al(OH)CrO_4}$

chromates and dichromates of aluminium which are transformed to solid solutions, as follows

$\mathrm{AlCrO_3Al(OH)CrO_4}$ and $\mathrm{Al_2O_3Al_3(OH)_7CrO_4}$ (from mixture **I**)

$\mathrm{Al_{0.67}Cr_{1.33}O_3Al_2(CrO_4)_2Cr_2O_7}$ and $\mathrm{Al_2(OH)_4CrO_4}$ (from mixture **II**)

$\mathrm{Al_{1.33}Cr_{0.67}O_3Cr_2(CrO_4)_2Cr_2O_7}$ and $\mathrm{AlCrO_3Al(OH)_7CrO_4}$
(from mixture **III**)

It is noteworthy that the temperatures of transformation of chromates and dichromates to solid solutions was found to depend essentially on their Cr/Al ratio. Chromates or dichromates with a ratio higher than 1 were transformed to solid solutions of $\mathrm{Al_2O_3}$ in $\mathrm{Cr_2O_3}$ at the relatively low temperature of 500 ° C, whereas those with Cr/Al < 1 were transformed to solid solutions of $\mathrm{Cr_2O_3}$ in $\mathrm{Al_2O_3}$ at temperatures higher than 750 ° C.

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