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THERMAL AND SPECTROSCOPIC CHARACTERIZATION OF REACTION PRODUCTS OF ALUMINIUM HYDROXYACETATE–CHROMIUM NITRATE INTERACTION AT DIFFERENT TEMPERATURES

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ABSTRACT

The present study on the interaction between aluminium hydroxyacetate (AlA) and chromium nitrate (CrN) is considered as a continuation of our preceding studies on the interaction between aluminium nitrate and both chromium nitrate and chromium carbonate at different temperatures up to 1000 °C. The products of interaction (200–480 °C) between AlA and CrN with molar ratio of AlA/CrN higher than 1 are amorphous and composed of two different chromates having $AlCrO_3Al(OH)CrO_4$ and $Al_2O_3Al_{3-x}Cr_x(OH)_7CrO_4$, whereas those produced from reactants with molar ratio equal to 1 are mixture of chromate and dichromate namely, $Al_2(OH)_4CrO_4$ and $Al_{2-x}Cr_xO_3Al_2(CrO_4)_2Cr_2O_7$ respectively. On other hand, the reactants with higher AlA/CrN ratio give the same species of chromate ($AlCrO_3Al(OH)CrO_4$) in addition to chromate dichromate species with formula $Al_{2-x}Cr_xO_3Al_{2-x}Cr_x(CrO_4)_2Cr_2O_7$. The presence of these hexavalent chromium compounds was verified by the presence of a charge transfer band in the UV region in addition to the presence of characteristic vibrational bands in the IR region.

The chromates and dichromates are converted into definite solid solutions of Cr_2O_3 in Al_2O_3 and vice versa on heating above ca. 480 °C. The composition of such crystalline solid solutions is estimated from the plot of lattice parameter values versus composition of $Al_xCr_{2-x}O_3$ mixed crystals.

INTRODUCTION

The chemical interactions of aluminium nitrate with chromium nitrate were studied and reported in a previous article [1]. The reaction products at different temperatures were characterized by different thermal and spectral methods. The studies clarify that aluminium chromate and/or dichromate with certain compositions were produced at temperatures lower than ca. 500 °C as a result of interaction between oxides (or hydroxides) produced

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from aluminium and chromium salts after their decomposition at relatively high temperatures. The present study is devoted to the investigation of the chemical reactions which take place between chromium nitrate and aluminium hydroxyacetate with different molar ratios at 250, 350, 500, 750 and 1000 °C.

EXPERIMENTAL

Materials

The starting materials $Al(OH)(OOCH_3C)_2 \cdot \frac{1}{2}H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were obtained from Merck Chemicals (F.R.G.).

Mixtures

Six mixtures of molar ratios 3 : 1 (I), 2 : 1 (II), 1 : 1 (III), 1 : 2 (IV), 1 : 3 (V) and 1 : 4 (VI) with respect to Al_2O_3 and Cr_2O_3 were prepared according to the procedure described earlier [1].

Techniques

The thermal analysis, IR, X-ray diffraction and electronic absorption spectra were carried out as previously described [1].

Chemical analysis

Decomposition products of pure salts

The percentages of aluminium and chromium in decomposition intermediate products of aluminium hydroxyacetate and chromium nitrate [1] were determined by ignition of a sample at 1200 °C and 1100 °C, respectively, until constant weight was obtained. The results are given in Table 1.

Decomposition products of aluminium hydroxyacetate–chromium nitrate mixtures

Both aluminium and chromium in intermediates or solid solutions were determined according to the method described elsewhere [1].

RESULTS AND DISCUSSION

The chemical interaction between aluminium hydroxyacetate and chromium nitrate depends essentially on the chemical composition and molar ratios of their decomposition products at different temperatures. It therefore

TABLE 1

Characterization of TG and DTG curves for $Al(OOCH_3C)_2OH \cdot \frac{1}{2}H_2O$ and calculation of weight losses

Thermal step	Temp. range (° C)	DTG peak (° C)	Loss (%)	
			Actual	Calculated
1	0–120	65, 80	5.20	5.26
2	200–370	300	52.30	54.38
3	370–430	395	62.20	64.91
4	430–900	–	69.77	70.17
5	> 900			

seems reasonable to investigate their thermal behaviour accompanied by characterization of decomposition products by means of chemical and spectral analysis.

Aluminium hydroxyacetate $Al(OH)(OOCH_3C)_2 \cdot \frac{1}{2}H_2O$

An examination of the TG curve (Fig. 1) of aluminium hydroxyacetate indicates that the compound begins its decomposition at ca. 50 ° C without formation of any stable isolable intermediate giving γ-Al_2O_3 as a final

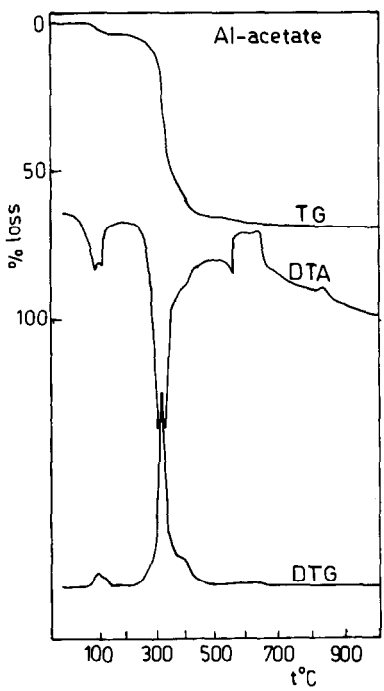

Fig. 1. Thermal analysis of aluminium hydroxyacetate.

product at 910 °C. However, the TG curve shows four discontinuities corresponding to the formation of $Al(OH)(OOCH_3)_2$, $Al(OH)_3$, $Al_2O_3 \cdot \frac{1}{2}H_2O$ and γ-Al_2O_3 (Table 1).

In the DTA curve the dehydration and deacetation of salt is indicated by the presence of endothermic peaks at 70, 100 and 300 °C respectively. The first exothermic peak between 400 and 560 °C corresponds to loss of hydroxyl group from aluminium hydroxide which converts to $Al_2O_3 \cdot \frac{1}{2}H_2O$. The second endothermic peak which splits into two bands at 560 and 650 °C corresponds to dehydration of $Al_2O_3 \cdot \frac{1}{2}H_2O$ leading to formation of amorphous Al_2O_3 whereas the last exothermic peak at 840 °C may correspond to the process of crystallization of amorphous alumina which produces γ-alumina. According to weight losses calculated from TG and DTG curves (Fig. 1 and Table 1), the thermal decomposition steps of aluminium hydroxyacetate may be expressed as

$$Al(OH)(OOCH_3C)_2 \cdot \tfrac{1}{2}H_2O \xrightarrow{50-120\,^\circ C} Al(OH)(OOCH_3C)\ (\text{I-A}) + \tfrac{1}{2}H_2O \quad (1)$$

$$\text{I-A} \xrightarrow{200-370\,^\circ C} Al(OH)_3\ (\text{II-A}) + \text{gaseous products} \quad (2)$$

$$\text{II-A} \xrightarrow{370-430\,^\circ C} \tfrac{1}{2}Al_2O_3 \cdot \tfrac{1}{2}H_2O\ (\text{III-A}) + H_2O \quad (3)$$

$$\text{III-A} \xrightarrow{430-890\,^\circ C} \tfrac{1}{2}Al_2O_3\ (\text{IV-A}) + \tfrac{1}{2}H_2O \quad (4)$$

$$\text{IV-A} \xrightarrow{> 890\,^\circ C} \tfrac{1}{2}\gamma\text{-}Al_2O_3\ (\text{V}) \quad (5)$$

Samples of intermediates II-A, IV-A and V-A were obtained by heating $Al(OH)(OOCH_3C)_2 \cdot \frac{1}{2}H_2O$ at 350, 750 and 1000 °C respectively for 4 h. They were subjected to chemical analysis for determination of percentages of aluminium in them. The results obtained (Table 2) show that the estimated values of aluminium agree well with corresponding theoretical values. X-ray investigation of intermediates III-A and IV-A revealed that both are amorphous whereas intermediate V-A is crystalline (Fig. 2).

TABLE 2

Chemical analysis of the thermal decomposition intermediates of $Al(OOCH_3C)_2OH \cdot \frac{1}{2}H_2O$

Temp. of decomposition (°C)	Intermediate	Suggested formula	Al (%)	
			Experimental	Calculated
350	II-A	$Al(OH)_3$	34.86	34.51
900	IV-A	Al_2O_3	52.10	52.93
1000	V-A	γ-Al_2O_3	53.48	52.93

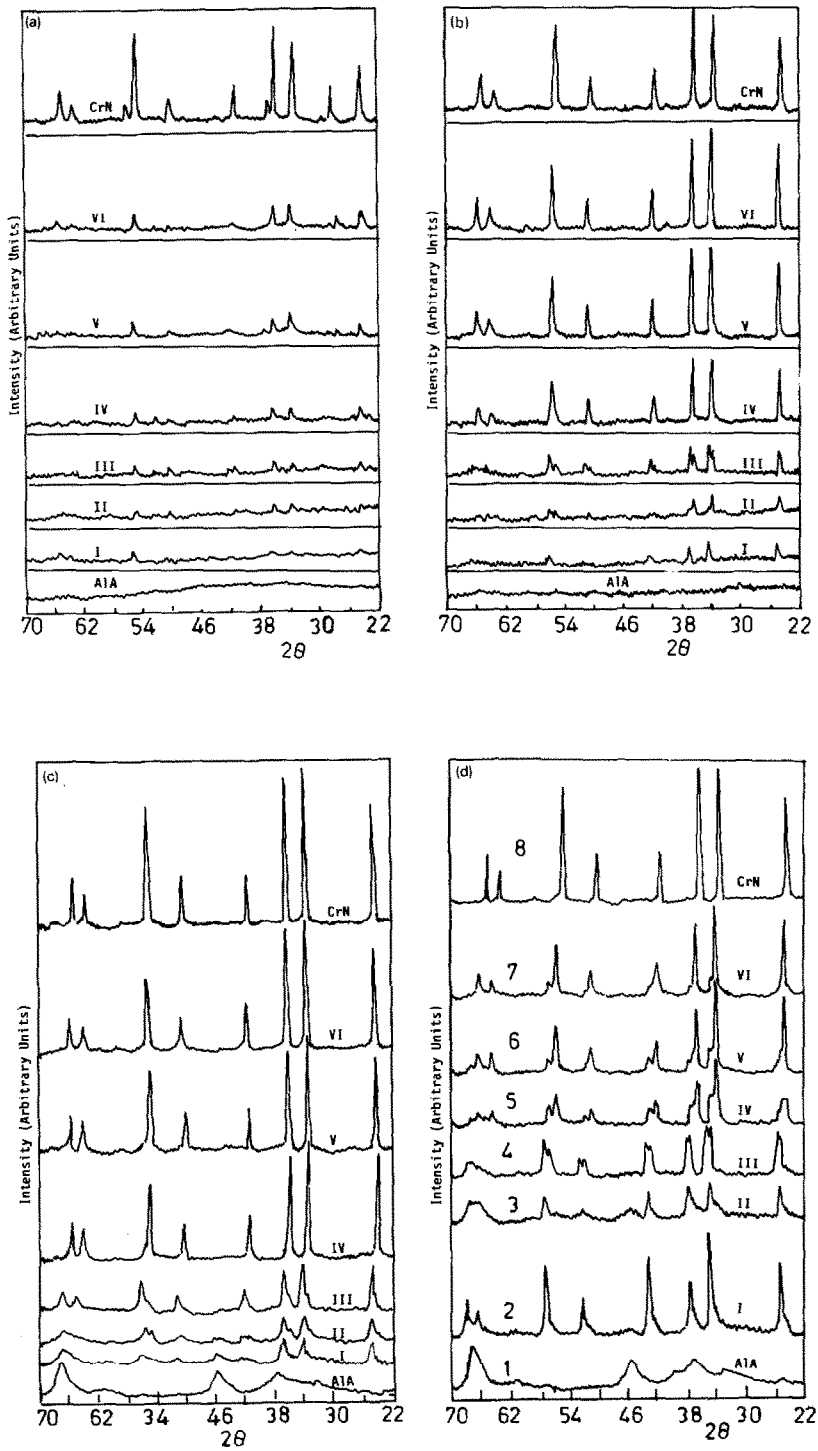

Fig. 2. X-ray diffraction patterns of thermal products from aluminium hydroxyacetate, chromium nitrate and their mixtures I–VI at (a) 350, (b) 500, (c) 750 and (d) 1000 °C.

Chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$

The effect of temperature on chromium nitrate was studied in detail by means of thermal analysis, IR, X-ray, and electronic absorption spectra for characterization of its decomposition products at different temperatures [1]. The decomposition steps are summarized as

$$Cr(NO_3)_3 \cdot 9H_2O \xrightarrow{< 75\,^\circ C} \text{melting and dissolution in water of crystallization} \quad (6)$$

$$2Cr(NO_3)_3 \cdot 9H_2O \xrightarrow{75\text{–}158\,^\circ C} [Cr(OH)_2(NO_3) \cdot CrO_2(NO_3) \cdot 14H_2O]\,(\text{I-C}) + 2HNO_3 + 2NO_2 + 2H_2O \quad (7)$$

$$(\text{I-C}) \xrightarrow{158\text{–}206\,^\circ C} [Cr(OH)_3 \cdot CrO_3 \cdot 13H_2O]\,(\text{II-C}) + HNO_3 + NO_2 \quad (8)$$

$$(\text{II-C}) \xrightarrow{206\text{–}280\,^\circ C} [\tfrac{1}{2}CrOOH \cdot \tfrac{1}{4}Cr_2O_3 \cdot CrO_3 \cdot 10H_2O]\,(\text{III-C}) + 4.25H_2O \quad (9)$$

$$(\text{III-C}) \xrightarrow{280\text{–}420\,^\circ C} [\tfrac{1}{2}CrO_2 \cdot \tfrac{1}{8}Cr_8O_{21} \cdot \tfrac{1}{4}Cr_2O_3]\,(\text{IV-C}) \quad (10)$$

$$(\text{IV-C}) \xrightarrow{420\text{–}480\,^\circ C} [\tfrac{1}{4}Cr_2O_3 \cdot \tfrac{1}{8}Cr_8O_{19.48} \cdot \tfrac{1}{4}Cr_2O_3]\,(\text{V-C}) \quad (11)$$

$$(\text{V-C}) \xrightarrow{> 480\,^\circ C} Cr_2O_3\ (\text{VI-C}) + 0.48O_2 \quad (12)$$

Chemical interaction between aluminium hydroxyacetate and chromium nitrate

The interaction between the two salts in any proportion in the range 200–370 °C produce mixtures of amorphous chromates and dichromates as a result of chemical reaction between aluminium hydroxide and both $Cr(OH)_3$ and CrO_3 which are the decomposition products of aluminium hydroxyacetate and chromium nitrate, respectively. The presence of hydroxychromates and dichromates was confirmed spectrally from their characteristic IR bands between 600 and 1000 cm^{-1}, in addition to characteristic Al–OH vibration bands between 1100 and 1600 cm^{-1} [1,3].

Additional support for the presence of the hexavalent chromium was gained from the presence of charge transfer bands (ca. 375 nm) as shown from diffuse reflectance spectra (Fig. 3). At temperatures higher than 500 °C, as calculated from the previous studies [1], the hexavalent chromium compounds are decomposed and changed into $Al_{2-x}Cr_xO_3$ solid solutions with liberation of oxygen. The lattice parameters of solid solutions were determined with the aid of their line broadening (Fig. 4, Table 3) provided that they are hexagonal.

Their compositions were determined from the plot of their lattice parameter versus the composition of $Al_{2-x}Cr_xO_3$ [2] as shown in Fig. 5.

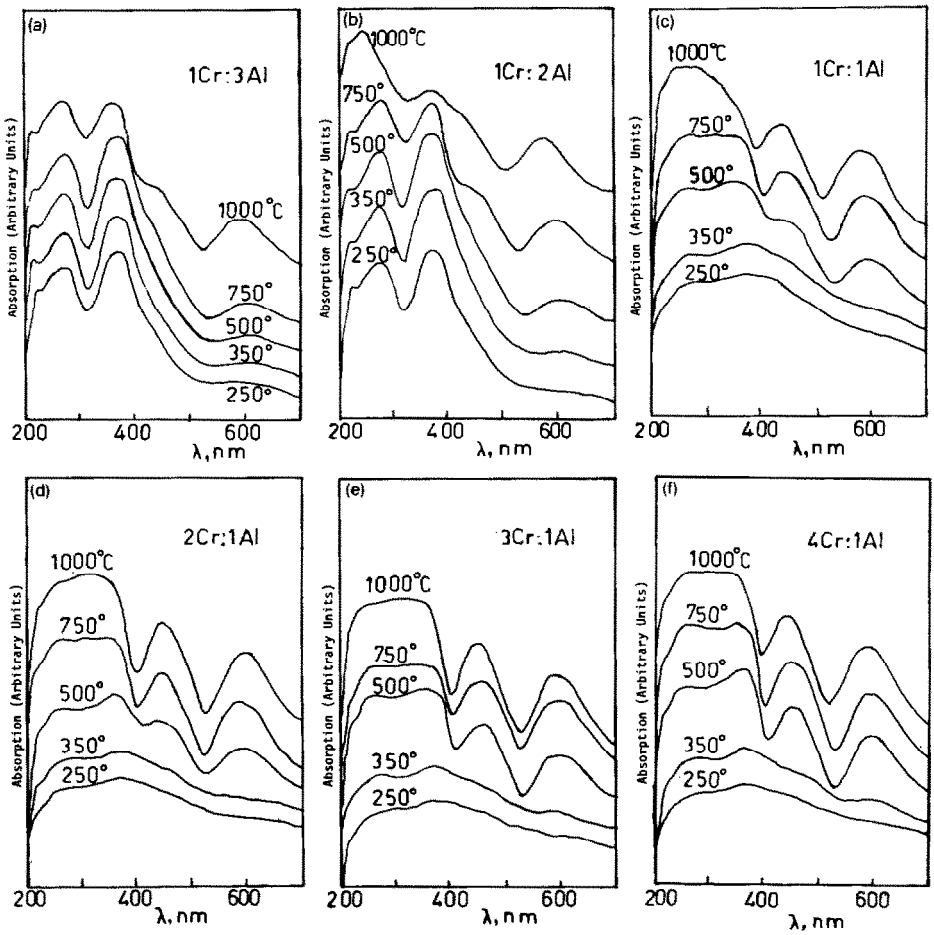

Fig. 3. Diffuse reflectance spectra of thermal products of mixtures I–VI at different temperatures.

The electronic absorption spectra of such solid solutions show the characteristic absorption bands which are due to: $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions [4] of Cr^{3+} in $Al_{2-x}Cr_xO_3$ mixed crystals (2) as shown in Fig. 3 where they are located at 17120–16850 and 23250–22730 cm^{-1} respectively.

TABLE 3

Lattice parameters a of thermal decomposition products of aluminium oxyacetate–chromium nitrate mixtures (I–VI)

Temp. of treatment (°C)	Lattice parameter					
	I	II	III	IV	V	VI
1000	4.86	4.856	4.872	4.9137	4.92998	4.93324
1000	4.79	4.810	4.812	4.8465	4.8592	4.8592

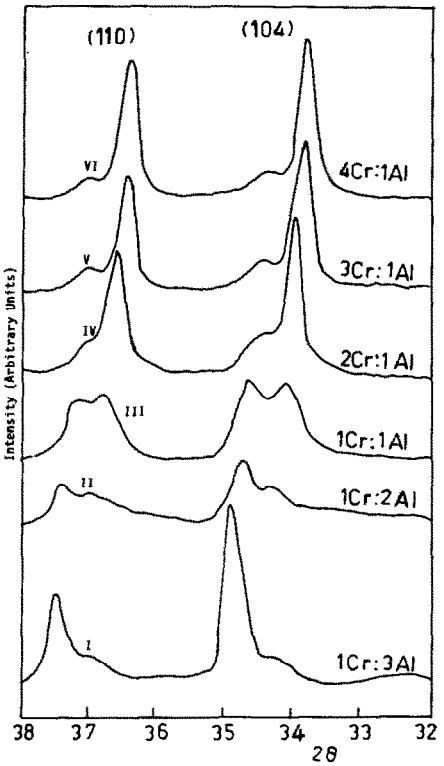

Fig. 4. Line broadening of (104) and (101) of mixtures I–VI heated at 1000 °C for 4 h.

According to the findings of Cuddennic and Bonnin [3], which were previously confirmed by us [1], aluminium chromate and/or dichromate are transformed into $Al_{2-x}Cr_xO_3$ solid solutions at temperatures higher than

TABLE 4

Composition of chromates and corresponding solid solutions

Mixture	Chemical formula of chromates	Corresponding solid solution	Al : Cr
I	$AlCrO_3Al(OH)CrO_4$	$AlCrO_3$	1 : 1
	$Al_2O_3Al_3(OH)_7CrO_4$	$Al_{1.67}Cr_{0.33}O_3$	5 : 1
II	$AlCrO_3Al(OH)CrO_4$	$AlCrO_3$	1 : 1
	$Al_2O_3Al_{2.5}Cr_{0.5}(OH)_7CrO_4$	$Al_{1.5}Cr_{0.5}O_3$	3 : 1
III	$Al_{0.67}Cr_{1.33}O_3Al_2(CrO_4)_2Cr_2O_7$	$Al_{0.66}Cr_{1.34}O_3$	1 : 2
	$Al_2(OH)_4CrO_4$	$Al_{1.34}Cr_{0.66}O_3$	2 : 1
IV	$AlCrO_3Al(OH)CrO_4$	$AlCrO_3$	1 : 1
	$AlCrO_3AlCr(CrO_4)_2Cr_2O_7$	$Al_{0.5}Cr_{1.5}O_3$	1 : 3
V	$AlCrO_3Al(OH)CrO_4$	$AlCrO_3$	1 : 1
	$Al_{1.33}Cr_{0.67}O_3Cr_2(CrO_4)_2Cr_2O_7$	$Al_{0.33}Cr_{1.67}O_3$	1 : 5
VI	$AlCrO_3Al(OH)CrO_4$	$AlCrO_3$	1 : 1
	$AlCrO_3Cr_2(CrO_4)_2Cr_2O_7$	$Al_{0.25}Cr_{1.75}O_3$	1 : 7

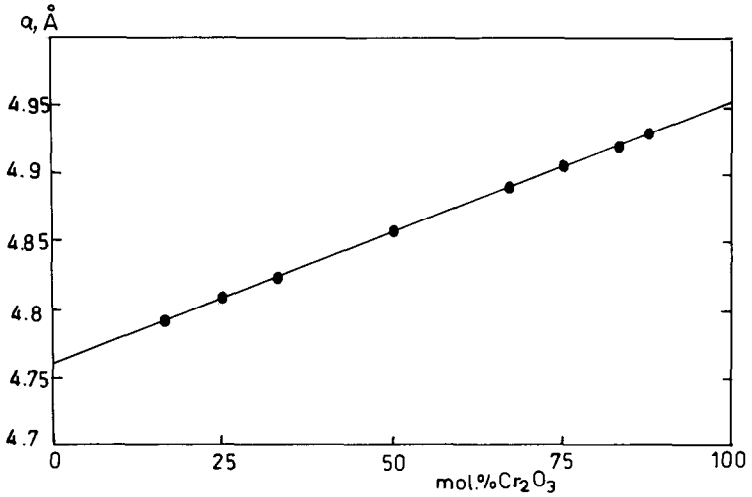

Fig. 5. Dependence of lattice parameters on chromium content in the solid solution $Al_{2-x}Cr_xO_3$.

TABLE 5

Chemical analysis of reaction mixture heated at 400 °C for 4 h

Mixture	Al (wt.% (found))	Cr (wt.% (found))	Al (atom) Cr (atom)
I	28.85	18.53	3
II	26.62	25.65	2
III	16.97	32.69	1
IV	11.47	44.21	1/2
V	8.35	48.26	1/3
VI	6.56	50.58	1/4

600 °C. The composition of chromates which correspond to solid solutions can be represented as shown in Table 4.

According to the values of weight losses resulting from heating the reaction mixtures I–VI at 400 °C for 4 h together with the weight percentage of both aluminium and chromium in the reaction products (Table 5) the following equations are proposed for formation of different aluminium chromium chromate and/or dichromate compounds.

Mixture I (3AlA : 1CrN)

$$6Al(OH)(OOCH_3C)_2 \cdot \tfrac{1}{2}H_2O + 2Cr(NO_3)_3 \cdot 9H_2O$$

$$\xrightarrow[\text{wt. loss (calc.} = 69.27)]{\text{wt. loss (found} = 70.10)} 0.5AlCrO_3Al(OH)CrO_4 + Al_2O_3Al_3(OH)_7CrO_4$$

$$+ 3HNO_3 + 3NO_2 + 18H_2O + \text{gaseous products}$$

Mixture II (2AlA : 1CrN)

$$4Al(OH)(OOCH_3C)\cdot\tfrac{1}{2}H_2O + 2Cr(NO_3)_3\cdot 9H_2O \xrightarrow[\text{wt. loss (calc.} = 72.69)]{\text{wt. loss (found} = 73.70)} 0.5AlCrO_3Al(OH)CrO_4 + Al_2O_3Al(OH)CrO_4 + 3HNO_3 + 3NO_2 + 17H_2O + \text{gaseous products}$$

Mixture III (1AlA : 1CrN)

$$Al(OH)(OOCH_3C)_2\cdot\tfrac{1}{2}H_2O + Cr(NO_3)_2\cdot 9H_2O \xrightarrow[\text{wt. loss (calc.} = 72.16)]{\text{wt. loss (found} = 73.00)} 1/8Al_{0.67}Cr_{1.33}O_3Al_2(CrO_4)_2Cr_2O_7 + 1/3Al_2(OH)_4CrO_4 + 1.5HNO_3 + 1.5NO_2 + 8H_2O + \text{gaseous products}$$

Mixture IV (1AlA : 2CrN)

$$Al(OH)(OOCH_3C)_2\cdot\tfrac{1}{2}H_2O + 2Cr(NO_3)_3\cdot 9H_2O \xrightarrow[\text{wt. loss (calc.} = 75.01)]{\text{wt. loss (found} = 75.35)} \tfrac{1}{4}AlCrO_3Al(OH)CrO_4 + \tfrac{1}{4}AlCrO_3AlCr(CrO_4)_2Cr_2O_7 + 15.5H_2O + 3HNO_3 + 3NO_2 + \text{gaseous products}$$

Mixture V (1AlN : 3CrN)

$$Al(OH)(OOCH_3C)_2\cdot\tfrac{1}{2}H_2O + 3Cr(NO_3)_3\cdot 9H_2O \xrightarrow[\text{wt. loss (calc.} = 75.85)]{\text{wt. loss (found} = 76.20)} 3/8Al_{1.33}CrO_{0.67}O_3Cr_2(CrO_4)_2Cr_2O_7 + \tfrac{1}{4}AlCrO_3Al(OH)CrO_4 + 23.0H_2O + 4.5HNO_3 + 4.5NO_2 + \text{gaseous products}$$

Mixture VI (1AlN : 4CrN)

$$Al(OH)(OOCH_3C)_2\cdot\tfrac{1}{2}H_2O + 4Cr(NO_3)_3\cdot 9H_2O \xrightarrow[\text{wt. loss (calc.} = 76.77)]{\text{wt. loss (found} = 77.10)} \tfrac{1}{2}AlCrO_3Cr_2(CrO_4)_2Cr_2O_7 + \tfrac{1}{4}AlCrO_3Al(OH)CrO_4 + 6NO_2 + 6HNO_3 + 30.5H_2O + \text{gaseous products}$$

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