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THERMAL STUDY OF NAPHTHYLAMMONIUM- AND NAPHTHYLAZONAPHTHYLAMMONIUM-MONTMORILLONITE

XRD and DTA

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The blue organo-clay color pigment (OCCP) naphthylazonaphthylammonium-montmorillonite was synthesized from the white naphthylammonium-montmorillonite by treating with $NaNO_2$, the azo colorant being located in the interlayer space. The following effects on the basal spacing of naphthylazonaphthylammonium- and naphthylammonium-clay were investigated: (1) the amount of naphthylammonium loading the clay, (2) the amount of $NaNO_2$ used for the staining, (3) aging of the preparation suspension and (4) thermal treatment.

Samples were heated at 120, 180, 240, 300 and 360°C and diffracted by X-ray. During aging, some of the dye decomposed. Samples, after one day aging, were investigated by DTA. During the dehydration stage both organo-clays gradually decomposed, the naphthylammonium-clay at 120°C and the OCCP at 180°C. That fraction of organic matter, which did not escape, was air-oxidized at above 200°C and charcoal was obtained. The appearance and size of the DTA exothermic peaks depended on the amount of organic matter, which did not escape and this depended on the total amount of organic matter in the DTA cell. DTA proved that naphthylammonium reacted with $NaNO_2$ to form OCCP.

Keywords: *azo dye clay complexes, montmorillonite, naphthyl-1-ammonium, 4-(1-naphthylazo)-1-naphthylamine, organo-clay, pigments, thermo-XRD-analysis*

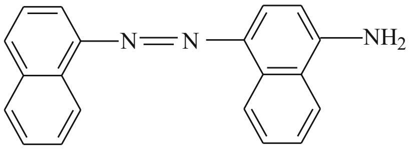
Introduction

An organo-clay color pigment (OCCP) is obtained by the adsorption of organic colorant into the interlayer space of a smectite mineral, or by the synthesis of an intensive colored compound from its source materials, inside the interlayer [1, 2]. Recently we obtained in our laboratory organo-clay color pigments by the synthesis of azo dyes as the coloring agents inside the interlayer space of smectites [3].

Tactoids or oriented aggregates are clusters of parallel layers held by face-to-face interactions (FF associations). In OCCP tactoids layers of the colorant of small thickness, together with water molecules, separate the montmorillonite TOT layers. These organic layers comprise the interlayer space of the clay mineral. According to Bragg's law, particles obtained from FF association of similar layers having similar interlayers, are responsible for X-ray diffraction. Originally the term 'tactoids' was used to describe particles in colloid solutions. In our publications it is also used for solid particles capable to diffract X-rays in powder mixtures [4].

Very often X-ray diffractograms of clay systems contain overlapping peaks. For this reason, curve-fitting calculations are normally applied on the diffractograms [5, 6]. In curve-fitted diffractograms different peak-components result from the presence of different tactoids in the clay mixture. Features associated with a certain peak-component characterize a group of tactoids. The location of its maximum represents the basal spacing of these tactoids. The component width represents the homogeneity of this group. The area of the peak-component relative to the total area of the peak (expressed in percentage) characterizes the amount of tactoids in this group, with certain spacing, relative to the total amount of the clay.

Recently we described the thermo-XRD-analysis of a clay pigment with the azo dye 4-(1-naphthylazo)-1-naphthylamine in the interlayer of montmorillonite (Scheme 1), synthesized from naphthyl-1-ammonium-montmorillonite and sodium nitrite. The



Scheme 1 Chemical structure of 4-(1-naphthylazo)-1-naphthylamine

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samples were heated from room temperature directly at 360°C and diffracted by X-ray in air atmosphere. We showed that naphthyl-1-ammonium-montmorillonite collapsed completely at 360°C whereas only a small fraction of the pigment collapsed under the same thermal treatment. Most of the pigments did not collapse at that temperature due to the formation of charcoal. We expected a correlation between the relative area of the peak-component, which described the charcoal-montmorillonite tactoids and with that of the azo dye, which was synthesized. But the correlation was poor [7].

In the present paper a more advanced thermo-XRD analysis is described [4], the samples are heated at 120, 180, 240, 300 and 360°C, 2 h at each temperature and are diffracted by X-ray after each thermal treatment. The thermo-XRD-analysis is supplemented by DTA of representative samples [8].

The thermal behavior of most N-bearing organo-montmorillonites can be divided into four stages [8–10]. In the first stage from room temperature up to 200 or 250°C (stage A), the dehydration of the clay is the major thermal reaction, shown by a strong DTA endothermic peak at about 100°C [11].

In the second stage between 200/250 and 360/400°C (stage B), the first step of the oxidation of the adsorbed organic matter takes place, shown by a DTA exothermic peak. According to previous MS study of the evolved gases H_2O is the principal product, obtained from the oxidation of the hydrogen component of the organic compound by air-oxygen [12–14]. At this stage the non-oxidized carbon and nitrogen components of the organic compound form charcoal inside the interlayer [12–21].

In the third stage between 360/400 and 590/610°C (stage C), the second oxidation step of the adsorbed organic matter takes place, accompanied by a DTA exothermic peak. At this stage a low-temperature-stable variety of charcoal is air-oxidized [22]. According to previous MS study of the evolved gases CO_2 is the principal product obtained by oxidation of the carbon component of the charcoal. Small amounts of H_2O and NO_2 are also present in the evolved gases, suggesting that charcoal is composed of H, C and N atoms [10, 12, 13].

The thermal reactions of the fourth stage from 590/610°C (stage D) include the third (last) step of the exothermic air-oxidation of the organic matter (the oxidation of a high-temperature-stable variety of charcoal [22]) and the endothermic dehydroxylation of the clay [10, 12, 13]. The two thermal reactions overlap and the recorded DTA peak is the outcome of summation of both reaction-energies.

Experimental

Materials

Na-montmorillonite (Wyoming bentonite) from Upton, Wyoming, purchased from Ward's National Science Establishment, Inc., was manually ground in an agate mortar, passed through an 80-mesh sieve and suspended in distilled water. After 24 h the clay fraction (particle size <1.5 μm) was separated from the impurities by decantation. Distilled water was added to the decanted fraction to obtain a 1 mass% suspension. Sodium nitrite (98.6%) was purchased from Baker A R Chemical Co. and naphthyl-1-ammonium chloride (98%) from Merck. They were used as received.

The preparation of samples for the thermo-XRD analysis [7]

Group A: Four different samples were prepared. In each sample to 25.0 mL of 1% Na-montmorillonite aqueous suspension 2.5 mL of $1.0\cdot10^{-1}$ M naphthyl-1-ammonium chloride aqueous solution was slowly added (100 mmol naphthyl-1-ammonium per 100 g clay). After 2 h 0, 1.25, 2.5 or 3.75 mL $NaNO_2$ aqueous solution ($1.0\cdot10^{-1}$ M) were slowly added to obtain $[NaNO_2]/[C_{10}H_7NH_3]$ molar ratios of 0 (blank, naphthylammonium-montmorillonite with no $NaNO_2$), 0.5, 1.0 and 1.5, being labeled blank-II and pigment-AI, -AII and -AIII, respectively.

Group B: Four different samples were prepared. In each sample to 25.0 mL of 1% Na-montmorillonite aqueous suspension 2.5 (blank-II), 1.5, 2.5 or 4.0 mL naphthylammonium chloride ($1.0\cdot10^{-1}$ M) was slowly added (100, 60, 100 or 160 mmol naphthylammonium per 100 g clay, respectively). No $NaNO_2$ was added to the blank. After 2 h 1.5, 2.5 or 4.0 mL $NaNO_2$ aqueous solution ($1.0\cdot10^{-1}$ M) were added to the other three suspensions, to obtain in all cases a molar ratio $[NaNO_2]/[C_{10}H_7NH_3]$ of 1.0, being labeled pigment-BI, -BII and -BIII, respectively.

Each suspension of groups A and B was treated for ten minutes in an ultrasonic bath (Medenet supersonic cleaner mini DG-1) before and after adding $NaNO_2$. Suspensions were aged for 1 and 7 days and solid fractions with a preferred orientation were settled on glass-slides and air-dried for the thermo-XRD-analysis.

The preparation of samples for the DTA studies

Samples of group B were used for the DTA. Two additional samples of naphthylammonium-montmorillonite were prepared in the same procedure by adding 1.5 and 4.0 mL naphthylammonium chloride ($1.0\cdot10^{-1}$ M) to 25.0 mL of 1% Na-montmorillonite suspensions (blank-I and -III, respectively). Suspensions were aged for 1 day. After the sedimentation of the clay to a volume of about 1.0 mL, the upper supernatant, with most of the non-adsorbed material, was decanted. The 1.0 mL concentrated clay suspensions were air dried for the DTA runs.

Methods

Thermo-XRD analysis

Diffractograms of oriented films of air-dried samples, before and after heating at 120, 180, 240, 300 and 360°C for 2 h at each temperature, were recorded at room temperature and at ambient atmosphere, using a Philips Automatic Diffractometer (PW1710) with a Cu tube anode [4].

Curve-fitting

X-ray diffractograms, obtained before and after the thermal treatment, were fitted by 'PHILIPS' (Automatic Powder Diffraction) software previously described [5, 6]. Gaussian shapes were used for the bands.

Differential thermal analysis (DTA)

Two different instruments were used for this study.

For the temperature range up to 400°C measurements were carried out on a Mettler Toledo DSC822 (Greifensee, Switzerland) differential scanning calorimeter. The instrument was calibrated with indium, lauric acid, water and ethyl acetate. Samples of 5–6 mg were weighed using a Mettler M3 microbalance in standard 40 μL aluminum pans and immediately sealed by press. Thermal behavior was studied under an air purge (50 mL min^{-1}) in the range of 25–400°C at a heating rate of 10°C min^{-1}.

For the temperature range 400–900°C a Stanton-Redcroft model 674 differential thermal analyzer (with Pt crucibles) was used. Heating rate was 10°C min^{-1}. Calcined Al_2O_3 was used as reference and diluent. Samples of 10, 20 or 40 mg analyzed material were gently mixed with 90, 80 or 60 mg diluent, respectively.

Results and discussions

As was described in our previous paper [7], an aqueous solution of naphthylazonaphthylamine obtained from naphthylammonium chloride and sodium nitrite in the absence of clay was first red. After a few hours reddish-brown particles settled. The commercial name of the product is 'Solvent Brown 3' [23]. The particles became blue after acidifying with HCl. The azo dye synthesized in the presence of montmorillonite is blue, suggesting that this staining resulted from the surface acidity of montmorillonite [24, 25]. It seems probable that naphthylazonaphthylammonium and/or naphthylazoniumnaphthylamine cations were present in the interlayer. This is now under further investigation.

Thermo-XRD analysis

Representative curve-fitted X-ray diffractograms, before and after thermal treatments, are depicted in Figs 1A and B. The pigment taken for this demonstration is montmorillonite treated with 100 mmol naphthylammonium chloride and 100 mmol sodium nitrite (pigment-BII), aged one day before the sedimentation of the clay. Locations of the maxima of the different peak-components and their areas (in per-

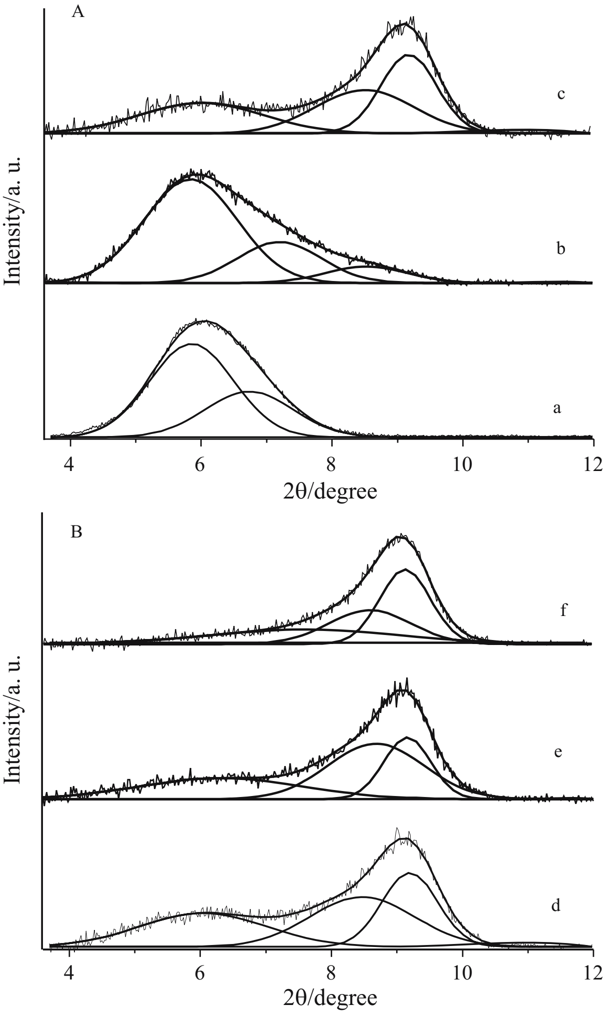

Fig. 1 Curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium chloride and 100 mmol sodium nitrite in aqueous suspension (pigment-BII), aged one day before the sedimentation of the clay, recorded a – before the thermal treatment of the pigment and after thermal treatments at b – 120, c – 180, d – 240, e – 300 and f – 360°C

Table 1 Characteristic features of curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium per 100 g clay and with 0 (blank), 50, 100 and 150 mmol $NaNO_2$ per 100 g clay (molar ratio $[NaNO_2/[C_{10}H_7NH_3]$ of 0, 0.5, 1.0 and 1.5, respectively) before and after gradual heating up to 360°C. The organo-clays were separated from the suspensions 1 day after their preparation

T/°C	Sodium-nitrite:naphthylammonium molar ratio							
	0		0.5		1.0		1.5	
	Blank-II peak components		Pigment-AI peak components		Pigment-AII peak components		Pigment-AIII peak components	
	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%
25	1.35	19	1.28	70	1.28	67	1.29	74
	1.58	81	1.50	30	1.50	33	1.51	26
120	0.97	38	0.98	11	0.98	5	0.98	5
	1.03	46	–	–	–	–	–	–
	–	–	1.18	51	1.18	69	1.18	66
	1.43	16	1.41	38	1.50	26	1.48	29
180	0.98	56	0.97	54	0.97	34	0.96	28
	1.03	44	1.03	46	1.02	44	0.99	45
	–	–	–	–	1.16	22	1.22	27
240	0.97	55	0.98	54	0.97	42	0.96	32
	1.03	45	1.03	46	1.02	36	1.01	44
	–	–	–	–	1.17	22	1.24	26
300	0.98	60	0.98	53	0.96	38	0.97	38
	1.03	40	1.04	47	1.01	41	1.01	35
	–	–	–	–	1.16	21	1.22	27
360	0.98	56	0.98	59	0.96	32	0.97	37
	1.03	44	1.03	41	1.00	45	1.01	40
	–	–	–	–	1.15	23	1.19	23

centage) relative to the total areas of the peaks (in short ‘relative areas’) of blank-II and of pigments A and B are collected in Tables 1–4.

Blank-II

The blank sample for groups A and B, prepared by treating Na-clay with 100 mmol naphthylammonium chloride per 100 g clay, is white. We showed previously that the naphthylammonium-montmorillonite separated from the suspension after one day of aging, and washed thoroughly with distilled water, contained 67.5 mmol naphthylammonium per 100 g clay [7]. In the present thermal analysis experiments the samples are not washed and consequently they contain excess naphthylamine in the form of naphthylammonium-naphthylamine associations [26–29].

The curve-fitted diffractogram of air-dried blank-II separated from the preparation suspension after one aging-day, recorded before the thermal treatment, shows two peak-components with maxima at 1.35 and 1.58 nm and relative areas of ≈20 and ≈80% from the total peak-area, respectively, indicating the presence of two types of tactoids (Tables 1 and 3). The first component characterizes tactoids with monolayers of hydrated naphthylammonium, lying parallel to the TOT clay-layers [27, 30, 31]. The second component characterizes tactoids with naphthylammonium-naphthylamine associations probably tilted relative to the TOT clay-layers [25, 27, 28].

After seven days of aging in the preparation suspension there are changes in the basal spacings (Tables 2 and 4). The curve-fitted diffractogram before the thermal treatment show two components with maxima at 1.42 and 1.67 nm and relative areas of ≈65 and ≈35% from the total peak-areas, respectively, indicating further adsorption of water and dissociation of some naphthylammonium-naphthylamine associations.

The thermal behavior of blank-II after one or seven aging-days is similar. The curve-fitted diffractograms recorded after heating at 120°C, show three components. The first two components with

Table 2 Characteristic features of curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium per 100 g clay and with 0 (blank), 50, 100 and 150 mmol $NaNO_2$ per 100 g clay (molar ratio $[NaNO_2/[C_{10}H_7NH_3]$ of 0, 0.5, 1.0 and 1.5, respectively) before and after gradual heating up to 360°C. The organo-clays were separated from the suspensions 7 days after their preparation

T/°C	Sodium-nitrite:naphthylammonium molar ratio							
	0		0.5		1.0		1.5	
	Blank-II peak components		Pigment-AI peak components		Pigment-AII peak components		Pigment-AIII peak components	
	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%
25	1.42	67	1.28	33	1.28	33	1.28	20
	1.67	33	1.46	67	1.45	67	1.42	80
120	0.97	32	0.97	23	0.97	29	0.97	32
	1.00	47	1.04	48	1.03	44	1.04	46
	1.20	21	1.37	29	1.41	27	1.38	32
180	0.97	55	0.97	47	0.97	32	0.97	27
	1.02	45	1.04	53	1.04	45	1.02	38
	–	–	–	–	1.38	23	1.35	35
240	0.97	49	0.97	47	0.97	30	0.97	33
	1.02	51	1.04	53	1.01	47	1.03	40
	–	–	–	–	1.26	23	1.40	27
300	0.96	49	0.97	49	0.97	23	0.98	27
	1.02	51	1.04	51	1.01	62	1.04	53
	–	–	–	–	1.26	15	1.38	20
360	0.97	59	0.97	50	0.97	43	0.97	31
	1.03	41	1.03	50	1.01	40	1.01	47
	–	–	–	–	1.21	17	1.30	22

spacings ≤1.03 nm and relative areas of about 80% are characteristic for thermally collapsed tactoids, indicating that organic matter has evolved from these tactoids already at 120°C. Melting and boiling points of naphthylamine are 50 and 301°C, respectively, suggesting that naphthylammonium and naphthylammonium-naphthylamine cations have been first deprotonated. This has been followed by evaporation of the amine at temperatures lower than those required for boiling. The spacings of the third component (1.43 and 1.20 nm, respectively) with a relative area of about 20% is characteristic of a swollen clay, suggesting the presence of some tactoids with organic matter in their interlayers (Tables 1–4).

The curve-fitted diffractograms recorded after heating both samples at 180°C show a complete collapse of the clay. Similar diffractograms are obtained after heating at higher temperatures, suggesting that the naphthylammonium cation has been completely deprotonated and evolved at temperatures lower than those required for its transformation into charcoal.

The effect of $NaNO_2$ on the OCCP and its thermal behavior (group A)

Samples separated from the suspensions after one aging-day

By adding $NaNO_2$, the adsorbed naphthylammonium reacts to form an azo dye [32], shown by the blue staining of the clay. Curve-fitted diffractograms of $NaNO_2$-treated clays differ from that of naphthylammonium-montmorillonite. Samples with molar ratios $[NaNO_2]/[C_{10}H_7NH_3]$ of 0.5, 1.0 and 1.5 (pigment-AI, -AII and -AIII) before heating exhibit two peak-components, at 1.28 and 1.50 nm (Table 1) characterizing tactoids with monolayer and bilayer or tilted organic compounds, respectively, in the interlayers [25, 30, 31]. Relative areas of peak-component attributed to tactoids with monolayers, which are small (≈20%) in the diffractogram of naphthylammonium-montmorillonite, increase after $NaNO_2$ treatment (≥65%). Consequently this component is attributed mainly to tactoids with interlayer azo dye. The decrease in basal spacing from 1.35 to 1.28 nm,

Table 3 Characteristic features of curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium per 100 g clay and of montmorillonite treated with 60, 100 and 160 mmol naphthylammonium and sodium nitrite (molar ratio $[NaNO_2]/[C_{10}H_7NH_3]$ of 1.0), before and after heating up to 360°C. The organo-clays were separated from the suspensions 1 day after their preparation

T/°C	Loading (mmol/100 g clay)							
	Naphthylammonium		Sodium-nitrite plus naphthylammonium (molar ratio 1)					
	100		60		100		160	
	Blank-II		Pigment-BI		Pigment-BII		Pigment-BIII	
	peak components		peak components		peak components		peak components	
	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%
25	1.35	19	1.28	83	1.28	67	1.28	65
	1.58	81	1.50	17	1.50	33	1.49	35
120	0.97	38	0.99	11	0.98	5	0.99	8
	1.03	46	–	–	–	–	–	–
	–	–	1.20	87	1.18	69	1.27	55
	1.43	16	1.56	2	1.50	26	1.51	37
180	0.98	56	0.97	52	0.97	34	0.96	36
	1.03	44	1.01	48	1.02	44	1.04	34
	–	–	–	–	1.16	22	1.46	30
240	0.97	55	0.96	51	0.97	42	0.96	30
	1.03	45	1.01	49	1.02	36	1.04	38
	–	–	–	–	1.17	22	1.47	31
300	0.98	60	0.96	53	0.96	38	0.97	25
	1.03	40	1.02	47	1.01	41	1.02	46
	–	–	–	–	1.16	21	1.39	29
360	0.98	56	0.97	54	0.97	32	0.97	41
	1.03	44	1.04	46	1.00	45	1.03	30
	–	–	–	–	1.15	23	1.16	29

as a result of the transformation of the naphthylammonium into the azo dye, indicates stronger surface π interactions between the clay O-plane and the dye than between this plane and naphthylammonium [3, 25]. Tactoids with bilayer or tilted organic compounds in the interlayers contain organic matter, which probably did not react with $NaNO_2$. Additional organic matter may be located in the interparticle space of the flocs.

The $NaNO_2$-treated naphthylammonium-clay with a ratio $[NaNO_2]/[C_{10}H_7NH_3]$ of 0.5 (pigment-AI) is intense blue. Nevertheless its thermal behavior differs only slightly from that of blank-II. The latter collapses almost completely at 120°C, whereas the former collapses at 180°C. The present results indicate that the azo dye is also thermally decomposed to volatile compounds, but at higher temperatures.

The thermal behavior of the $NaNO_2$-treated naphthylammonium-clay with ratios $[NaNO_2]/[C_{10}H_7NH_3]$ of 1.0 and 1.5 (pigment-AII and -AIII) is different and at 180°C the relative area of the peak-components of expanded clay is about 25%. At 360°C the non-collapsed fraction shows peak-component maximum at about 1.17 nm, indicating the presence of tactoids with monolayer charcoal in the interlayers. Charcoal is formed from that fraction of the azo dye, which has not been evolved at 180°C. It should be noted that when the thermal treatment of the pigment was not gradual but directly to 360°C, most of the dye did not escape but became charcoal [7].

Samples separated from the suspensions after seven aging-days

Before the thermal treatment, curve-fitted diffractograms of pigment-AI, -AII and -AIII, separated from the suspension after seven aging-days, show two peak-components, with maxima at 1.28 and ≈1.45 nm, representing two types of tactoids (Table 2). Similar two peak-components have been detected after one aging-day, but with different

Table 4 Characteristic features of curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium per 100 g clay and of montmorillonite treated with 60, 100 and 160 mmol naphthylammonium and sodium nitrite (molar ratio $[NaNO_2]/[C_{10}H_7NH_3]$ of 1.0), before and after heating up to 360°C. The organo-clays were separated from the suspensions 7 days after their preparation

T/°C	Loading (mmol/100 g clay)							
	Naphthylammonium		Sodium-nitrite plus naphthylammonium (molar ratio 1)					
	100		60		100		160	
	Blank-II peak components		Pigment-BI peak components		Pigment-BII peak components		Pigment-BIII peak components	
	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%
25	1.42	67	1.28	33	1.28	33	1.32	36
	1.67	33	1.37	67	1.45	67	1.54	64
120	0.97	32	0.97	32	0.97	29	0.96	18
	1.00	47	1.00	57	1.03	44	1.04	38
	1.20	21	1.21	21	1.41	27	1.51	44
180	0.97	55	0.97	48	0.97	32	0.97	26
	1.02	45	1.03	52	1.04	45	1.04	42
	–	–	–	–	1.38	23	1.52	32
240	0.97	49	0.97	56	0.97	30	0.97	29
	1.02	51	1.04	44	1.01	47	1.04	39
	–	–	–	–	1.26	23	1.52	32
300	0.96	49	0.97	52	0.97	23	0.97	29
	1.02	51	1.03	58	1.01	62	1.03	39
	–	–	–	–	1.26	15	1.52	32
360	0.97	59	0.97	56	0.97	43	0.97	30
	1.03	41	1.03	44	1.01	40	1.03	39
	–	–	–	–	1.21	17	1.52	31

relative areas. The relative area of the 1.28 nm component (the dye in the interlayers) decreases significantly from ≈70% (one day) to ≈25% (seven days). It is therefore concluded that some dye has decomposed during this aging period.

The thermo-XRD analysis of pigments separated after seven aging-days show that their thermal behavior is very similar to that of pigments separated after one aging-day. Namely, pigment-AI, looses its organic matter already at 180°C and collapses, whereas those containing $[NaNO_2]/[C_{10}H_7NH_3]$ in higher ratios keep some of the organic matter at higher temperatures to form charcoal.

The effect of naphthylammonium plus $NaNO_2$ on the OCCP and its thermal behavior (group B)

Samples separated from the suspensions after one aging-day

In this series the ratio $[NaNO_2]/[C_{10}H_7NH_3]$ is always 1. The clay was treated with 60, 100 and 160 mmol naphthylammonium chloride and similar molar amounts of $NaNO_2$ per 100 g clay (pigment-BI, -BII and -BIII). Diffractograms of pigments recorded before heating show the presence of two types of tactoids, with basal spacings 1.28 and 1.50 nm (Table 3), with monolayers and bilayers or tilted organic matter in the interlayers. The thermo-XRD analysis shows that pigment-B1 differs from the other two pigments, as its tactoids are completely collapsed already at 180°C. Diffractograms of pigment-BII and -BIII, at the temperature range 180–360°C show relative areas of peak-components of swollen clays of about 20 and 30%, respectively. At 360°C the non-collapsed tactoids show basal spacing of 1.15 nm, indicating the presence of tactoids with monolayer charcoal in the interlayers.

During the thermal treatment from relative areas of peak-components it appears that the percentage of collapsed tactoids decrease and those with interlayer charcoal increase with the amounts of naphthylammonium and $NaNO_2$. It is therefore assumed that when the ratio [$NaNO_2$]/[$C_{10}H_7NH_3$] is 1, the amount of azo dye molecules increases with the amount of the source materials.

Samples separated from the suspensions after seven aging-days

Before heating, two types of tactoids are identified (Table 4), with basal spacings ≈1.30 nm (≈35%, with monolayer azo dye) and 1.37–1.54 nm (with non-azo organic matter in the interlayers). The percentage of the monolayer component has decreased considerably during aging, suggesting the decomposition of some dye.

Charcoal is not formed during the thermo-XRD-analysis of pigment-BI. Most of the azo dye, which has been formed, decomposes already at 180°C. Only pigment-BII and -BIII, show at temperatures ≥180°C the presence of some organic matter and the formation of charcoal. During the thermal treatment the relative areas of the peak-components show that the percentage of collapsed tactoids decreases and that with interlayer charcoal increases with the amounts of naphthylammonium and $NaNO_2$.

Differential thermal analysis

Wyoming bentonite (montmorillonite)

A DTA curve of 6 mg clay recorded on a METTLER TOLEDO STAR System (25–400°C) shows the dehydration endothermic peak at 115°C (Fig. 2). A curve of 40 mg clay recorded on a Stanton-Redcroft DTA shows the dehydroxylation endothermic peak at 700°C, with the onset and endset at 400 and 735°C, respectively.

Naphthyl-1-ammonium-montmorillonite

Three different types of naphthylammonium-montmorillonite were prepared by treating the clay with 60, 100 and 160 mmol naphthylammonium chloride per 100 g clay, labeled blank-I, -II and -III, respectively.

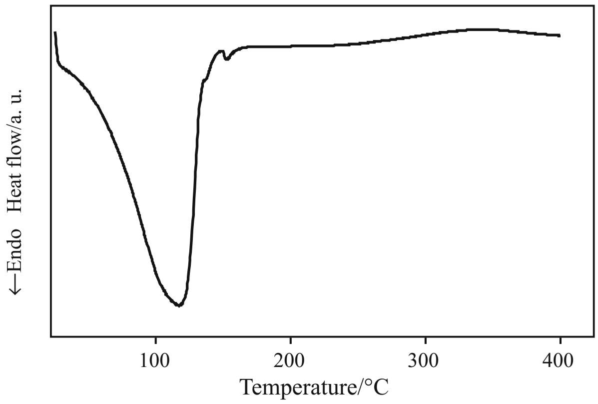

Fig. 2 A DTA curve of 6 mg montmorillonite

The DTA curves of the three samples, recorded on a Metler Toledo Star System in the temperature range 25–400°C are depicted in Fig. 3. Blank-II exhibits five endothermic peaks, of which two are very intense at 85 and 100°C, overlapping the clay-dehydration peak, and three are very weak at 135, 170 and 185°C. Several investigators attributed the appearance of endothermic peaks in the temperature range of the dehydration stage to the evolution of organic matter [17, 33, 34]. In the present study these peaks are attributed to the deprotonation of some naphthylammonium cations and the evolution of the resulted naphthylamine molecules.

A small exothermic peak is traced at 295°C, the first oxidation step of the organic matter, which has not been evolved during the dehydration stage. Following previous simultaneous DTA-EGA studies of different organo-clays [10, 12, 13] it is supposed that at this stage organic H is oxidized into H_2O together with the transformation of C and N into charcoal. This is in agreement with the persistence of few non-collapsed interlayers during the thermo-XRD-analysis after the thermal treatment at 360°C, described in the previous section. Blank-III shows a similar curve.

Blank-I shows the dehydration peak at 115°C in addition to the 85–100°C endotherms. Only the first of the three very weak endothermic peaks observed with blank-II and III is traced here. Blank-I probably looses most of the organic matter already below 150°C and consequently does not show the endothermic peaks at 170 and 185°C and the exothermic peak at 295°C. This observation is in agreement with the

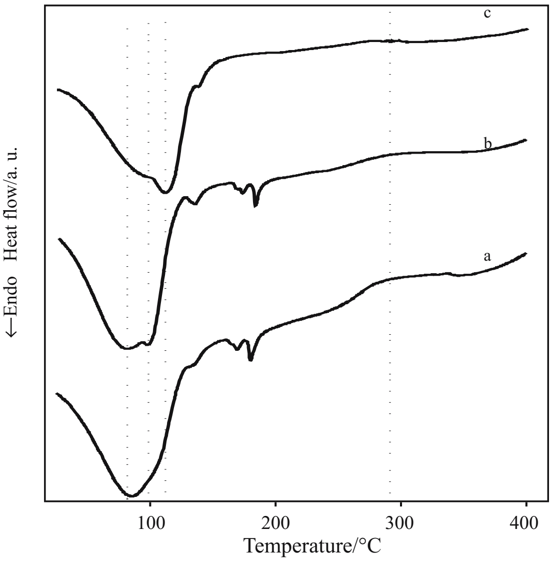

Fig. 3 DTA curves of 6 mg naphthylammonium-montmorillonite, a – blank-III, b – blank-II and c – blank-I

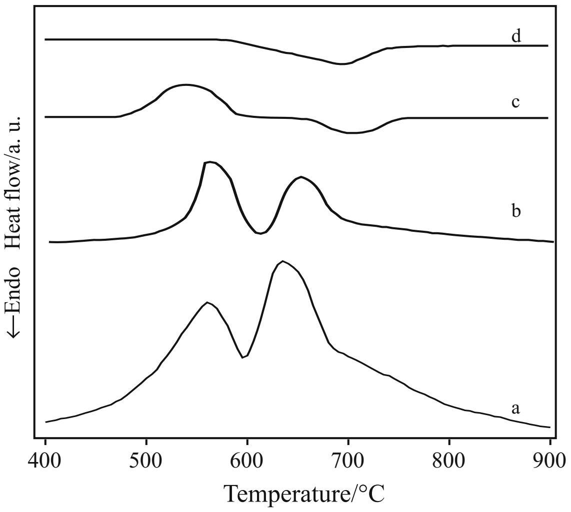

Fig. 4 DTA curves of naphthylammonium-montmorillonite, a – 40 mg of blank-III, b – 40 mg of blank-II, c – 20 mg of blank-II and d – 20 mg of blank-I

complete collapse of blank-I during the thermo-XRD-analysis at 180°C.

Some representative DTA curves recorded on a Stanton-Redcroft Instrument in the temperature range 400–900 °C are depicted in Fig. 4. With 40 mg of blank-III in the DTA cell (Fig. 4a), only part of the organic ammonium cations has evolved with the dehydration of the clay at temperatures up to 200°C. The first oxidation step and charcoal formation is traced in Fig. 3 at 295°C. The oxidation of the low- and high-temperature-stable-charcoal occurs in the range above 400°C, giving rise to two intense exothermic peaks at 560 and 635°C, respectively. The dehydroxylation peak of the clay, expected to occur at 700°C, is not traced in this DTA curve because of the overlapping of this endothermic reaction with the charcoal oxidation steps.

Two different DTA runs were recorded with blank-I. In these runs 10 and 20 mg organo-clay were applied. The latter is depicted in Fig. 4d. The curves do not show any exothermic peak indicating that the organic matter has been evolved together with the dehydration of the clay. The clay dehydroxylation peak is traced at 695°C.

Two different DTA runs were recorded with blank-II. In these runs 20 and 40 mg organo-clay were applied. With 20 mg organo-clay (Fig. 4c), much of the organic matter has been evolved together with the dehydration of the clay at temperatures up to 200°C and only a small amount persisted to the oxidation stages, forming charcoal at 295°C (Fig. 3b). The oxidation of the charcoal occurs with a weak exothermic peak at 540°C and a shoulder at 645°C. The clay dehydroxylation peak is traced at 700°C.

With 40 mg of blank-II (Fig. 4b) the shape of the DTA curve is very similar to that of the curve of blank-III. However, the exothermic peaks, and especially the one representing the oxidation of the high-temperature-stable-charcoal, are weaker than those in the DTA curve of blank-III. Furthermore, this latter peak appears at 650°C, instead of 635°C, in the DTA curve of blank-III.

Naphthylazonaphthylamine-montmorillonite

Three different pigments were prepared by treating the clay with 60, 100 and 160 mmol naphthylammonium chloride plus 60, 100 and 160 mmol $NaNO_2$ per 100 g clay, labeled pigment-BI, -BII and -BIII, respectively.

A DTA curve of pigment-BIII, recorded on a Metler Toledo Star System in the temperature range 25–400°C (Fig. 5a) shows three endothermic peaks, at 80 (intense), 105 (intense) and 135°C (weak) and a weak exothermic peak at 230°C. A similar curve is recorded for pigment-BII (Fig. 5b), whereas pigment-BI shows only the first two endothermic peaks (Fig. 5c). The endothermic peaks are attributed to the thermal decomposition of some naphthylazonaphthylamine and the evolution of the products. The exothermic peak is attributed to the oxidation of organic H into H_2O and the formation of charcoal. By thermo-XRD-analysis we showed that pigment-BI lost all the azo dye at 180°C whereas pigment-BII and -BIII lost only part of it.

Representative DTA curves recorded on a Stanton-Redcroft Instrument in the temperature range 400–900°C are shown in Fig. 6. In addition to the exothermic peak at 230°C depicted in Fig. 5, pigment-BIII (Fig. 6a) shows exothermic peaks at 520 (very intense) and at 660°C (of a medium size) associ-

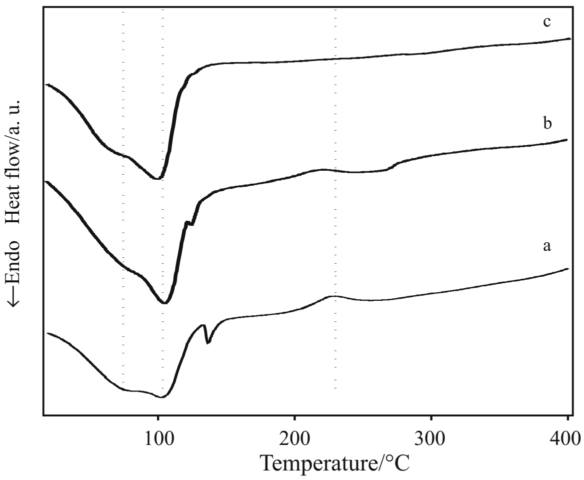

Fig. 5 DTA curves of 5 mg naphthylazonaphthylamine-montmorillonite, a – pigment-BIII, b – pigment-BII and c – pigment-BI

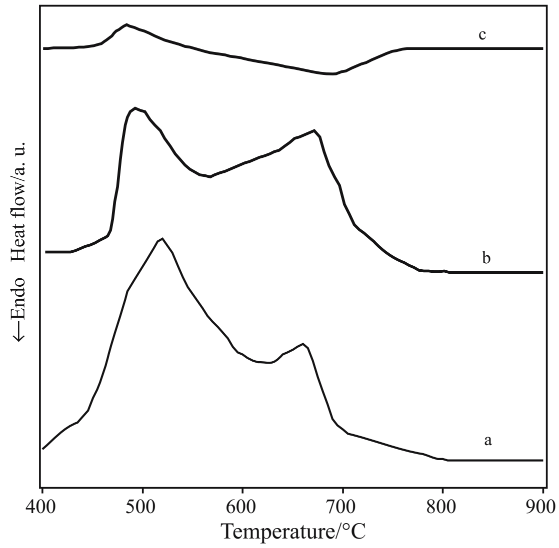

Fig. 6 DTA curves of 40 mg naphthylazonaphthylamine-montmorillonite, a – pigment-BIII, b – pigment-BII and c – pigment-BI

ated with the oxidation of the low- and high-temperature-stable-charcoal, respectively. The dehydroxylation peak of the clay, expected to occur at 700°C, is not traced because of the overlapping of this endothermic reaction with the exothermic charcoal oxidation.

The DTA curve of pigment-BII (Fig. 6b) also shows these exothermic peaks but they are weaker than those of pigment-BIII and their temperatures are slightly different (Fig. 6b). The peak of the oxidation of the low-temperature-stable-charcoal appears at 485°C (instead of 520°C) and that of the high-temperature-stable-charcoal appears at 675°C (instead of 660°C) suggesting that different charcoals are obtained in pigment-BII and -BIII. The last oxidation step overlaps the endothermic dehydroxylation, which is not traced in this DTA curve.

The DTA curve of pigment-BI shows a very weak exothermic peak at 485°C (Fig. 6c). An exothermic peak, which should represent the oxidation of the high-temperature-stable-charcoal, is not traced in this curve. In contrast to the other two pigments, the endothermic clay dehydroxylation peak is traced here at 690°C.

Conclusions

In thermo-XRD-analysis of naphthylammonium-montmorillonite most of the tactoids collapsed after two hours at 120°C. Collapse was complete at 180°C, indicating complete loss of organic matter at a temperature lower than that required for the boiling of naphthylamine or for charcoal formation.

In thermo-XRD-analysis of naphthylazonaphthylamine-montmorillonite different results were obtained when the heating occurred in stages or when the sample was directly heated at 360°C. During heating in stages the azo dye decomposed at 180°C. Some organic matter remained in interlayers of pigments obtained with 100 or 160 mmol naphthylammonium per 100 g clay and charcoal was formed at higher temperatures. When the thermal treatment of the pigment was not gradual but directly to 360°C, most of the dye did not escape but became charcoal [7].

In DTA the samples were gradually heated at a rate of 10°C min^{-1}. It was expected that with considerable amounts of organic matter only part of it would escape and the remaining, from 200°C, be subjected to thermal air-oxidation. When total amount of naphthylammonium in the Stanton-Redcroft DTA cell was $12\cdot10^{-3}$ mmol, exothermic peaks were not recorded. Higher amounts were necessary to obtain exothermic peaks.

DTA curves of naphthylammonium-montmorillonite differ from those of naphthylazonaphthylamine-montmorillonite proving that the adsorbed naphthylammonium reacted with sodium nitrite.

References

1 S. Yariv, in ‘Proc. 2nd Mediterranean Clay Meeting, Aveiro’, (C. S. F. Gomes, Ed.), Portuguese Clay Society, University of Aveiro, 1998 Vol. 1, p. 99.
2 S. Yariv, in ‘Organo-clay complexes and interactions’, (S. Yariv and H. Cross, Eds), Marcel Dekker, New York 2002, p. 463.
3 Patent: WO 2004/000948; Yissum Research Development Company of the Hebrew University of Jerusalem; S. Yariv, I. Lapides, H. Peled and Z. Yermiyahu, 2003.
4 S. Yariv and I. Lapides, J. Therm. Anal. Cal., 80 (2005) 11.
5 Z. Yermiyahu, I. Lapides and S. Yariv, Appl. Clay Sci., 30 (2005) 33.
6 M. Epstein, I. Lapides and S. Yariv, J. Therm. Anal. Cal., 82 (2005) 585.
7 Z. Yermiyahu, I. Lapides and S. Yariv, J. Therm. Anal. Cal., 88 (2007) 795.
8 A. Langier-Kuźniarowa, in ‘Organo-clay Complexes and Interactions’, (S. Yariv and H. Cross, Eds), Marcel Dekker, New York 2002, p. 273.
9 S. Yariv, in ‘Natural and laboratory-simulated thermal geochemical processes’, (R. Ikan, Ed.), Kluwer Academic Publishers, Dordrecht 2003, p. 253.
10 D. Ovadyahu, I. Lapides and S. Yariv, J. Therm. Anal. Cal., 87 (2007) 125.
11 R. Greene-Kelly, in ‘The differential thermal investigation of clays’, R.C. Mackenzie, Ed.), Mineralogical Society, London 1957, p. 140.
12 S. Yariv, M. Mueller-Vonmoos, G. Kahr and A. Rub, J. Thermal Anal., 35 (1989) 1941.
13 S. Yariv, J. Thermal Anal., 36 (1990) 1953.
14 S. Yariv, Appl. Clay Sci., 24 (2004) 225.

15 W. F. Bradley and R. E. Grim, J. Phys. Chem., 52 (1948) 1404.
16 W. H. Allaway, Soil Sci. Soc. Am. Proc., 13 (1949) 183.
17 W. Bodenheimer, L. Heller and S. Yariv, Clay Miner., 6 (1966) 167.
18 N. Sonobe, T. Kyotani, Y. Hishiyama, M. Shiraishi and A. Tomita, J. Phys. Chem., 92 (1988) 7029.
19 N. Sonobe, T. Kyotani and A. Tomita, Carbon, 26 (1988) 573.
20 N. Sonobe, T. Kyotani and A. Tomita, Carbon, 28 (1990) 483.
21 N. Sonobe, T. Kyotani and A. Tomita, Carbon, 29 (1991) 61.
22 Z. Yermiyahu, A. Landau, A. Zaban, I. Lapides and S. Yariv, J. Therm. Anal. Cal., 72 (2003) 431.
23 'Color Index', The Society of Dyes and Colourists, Bradford, Yorkshire, England, The American Association of Textile Chemists and Colorists, Lowell, Mass, USA, 2nd Ed., Vol 3, p. 3020. (1958)
24 M. M. Mortland and K. V. Raman, Clays Clay Miner., 16 (1968) 393.
25 S. Yariv, Intern. Rev. Phys. Chem., 11 (1992) 345.
26 M. M. Mortland, in 9th International Congress of Soil Science Transactions, Vol. 1, p. 691 (1969).
27 V. C. Farmer and M. M. Mortland, J. Chem. Soc. A, 62 (1966) 344.
28 L. Heller and S. Yariv, Israel J. Chem., 8 (1970) 391.
29 S. Yariv and L. Heller-Kallai, Clay Miner., 10 (1975) 479.
30 R. Green-Kelly, Trans. Faraday Soc., 51 (1955) 412.
31 R. Green-Kelly, Trans. Faraday Soc., 51 (1955) 425.
32 H. Zollinger, 'Color chemistry', VCH-Verlag, Weinheim 1987.
33 I. M. Eltantawy, Bull. Groupe Fr. Argiles, 26 (1974) 211.
34 B. L. McNeal, Soil Sci., 97 (1964) 96.

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