

SYNTHESIS AND THERMO-XRD-ANALYSIS OF THE ORGANO-CLAY COLOR PIGMENT

Naphthylazonaphthylamine-montmorillonite

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An intense blue organo-clay color pigment was obtained by adding naphthyl-1-ammonium chloride to a Na-montmorillonite aqueous suspension followed by treatment with sodium nitrite. This treatment resulted in the synthesis of the azo dye 4-(1-naphthylazo)-1-naphthylamine adsorbed onto the clay. The pigment was subjected to thermo-XRD-analysis and the diffractograms were curve-fitted. Heating naphthylammonium-montmorillonite at 360°C resulted in the evolution of the amine at temperatures lower than those required for the formation of charcoal and consequently the clay collapsed. On the other hand, heating the pigment at 360°C resulted in the conversion of the adsorbed azo dye into charcoal. The clay did not collapse, thus proving that the azo dye was located inside the interlayer space. Before the thermal treatment a short basal spacing in the pigment compared with that in the ammonium clay (1.28 and 1.35 nm, respectively) indicated stronger surface π interactions between the clayey O-plane and the azo dye than between this plane and naphthylammonium cation. The amount of dye after one aging-day of the synthesis-suspension increased with $[\text{NaNO}_2]/[\text{C}_{10}\text{H}_7\text{NH}_3]$ ratio but did not increase with naphthylammonium when the $[\text{NaNO}_2]/[\text{C}_{10}\text{H}_7\text{NH}_3]$ ratio remained 1. After 7 and 56 aging days it decreased, indicating that some of the dye decomposed during aging.

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

Introduction

Dyes and pigments are coloring materials used for different purposes in different applications. In order for a colored chemical to serve as a useful dye or pigment, it should have the following features: intense color, solubility or dispersability in water or another solvent, substantivity to the material being colored, having the ability of coating surfaces, durability to further treatments, safe and easy to handle [1].

Coloring materials are classified according to their solubility in water or other solvents into three groups: soluble dyes, disperse dyes and pigments, the latter being insoluble in solvents but are dispersible and are used as surface coaters in the form of extremely fine particles in the range of one micron. In one particle there are tens to thousands molecules grouped together [1, 2]. An organo-clay color pigment (OCCP) is obtained by the adsorption of organic colorant into the interlayer space of a smectite mineral, for example pigments are obtained by the adsorption of cationic dyes [3, 4]. 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.

Azo dyes are characterized by the presence of one or more azo groups, $-\text{N}=\text{N}-$, as chromophores, obtained from aniline or its derivative and nitrous

acid, bridging its aromatic relic to a secondary aromatic compound, which contains powerful electron-releasing groups, such as $-\text{OH}$, $-\text{NHR}$ or $-\text{NH}_2$ to increase the auxochromic power of the aromatic entity. During the synthesis of the azo dyes the auxochromes activate the hydrogens in the *ortho* or *para* positions to the electron releasing groups of the secondary compound, to react with the diazonium group of the primary compound [5, 6]. In the present study the azo dye was synthesized in the presence of montmorillonite. For this purpose naphthyl-1-ammonium was used as the anilinium derivative and naphthyl-1-amine as the secondary aromatic entity, the latter obtained from the deprotonation of the naphthylammonium cation. Quantum chemical considerations showed that azo coupling reactions of naphthalene-1-diazonium with naphthyl-1-amine results in the formation of 4-(1-naphthylazo)-1-naphthylamine (Fig. 1) [7].

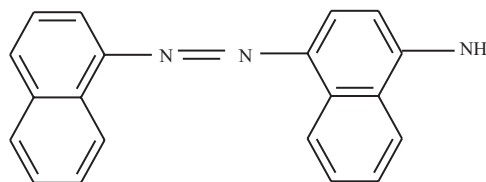
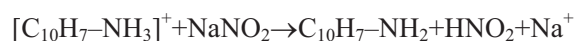


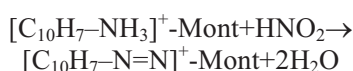
Fig. 1 4-(1-naphthylazo)-1-naphthylamine

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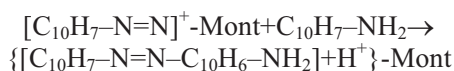
Excess naphthylammonium chloride is added into an aqueous montmorillonite suspension. In the first stage much of the naphthylammonium is adsorbed into the interlayer by cation exchange. When the suspension is treated with sodium nitrite in the second stage, about half of the naphthylammonium is deprotonated by proton donation to nitrite anion to form naphthylamine and nitrous acid as follows:



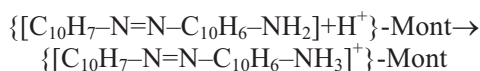
In the third stage, probably occurring inside the interlayer space, the reaction between the second half of the naphthylammonium cation and the nitrous acid, known as diazotization, results in the formation of naphthalenediazonium-montmorillonite:



In the fourth stage a reaction known as coupling occurs, the nitrogen of the diazonium group being retained in the 4-(1-naphthylazo)-1-naphthylamine azo dye as follows:



The protons, which are released in the coupling process, may react with the basic amine group to form the naphthylazonaphthylammonium cationic variety inside the interlayer space as follows:



The purpose of the present study was to examine whether the synthesized azo dye naphthylazonaphthylamine was located inside the interlayer of montmorillonite. For this purpose samples treated with different amounts of naphthylammonium and sodium nitrite were investigated by thermo-XRD-analysis [8]. This technique supplies information about the effect of temperature on crystallographic features of the clay. From these features one may conclude whether the organic component of the organo-clay pigment was located inside the interlayer space. In the present study the azo-clay complexes were diffracted before and after being heated at 360°C. At the latter temperature if the azo dye was formed inside the interlayer it might be oxidized to charcoal, preventing the collapse of the clay. If it was not located in the interlayer, the clay would collapse and the spacing drops to 0.97–1.04 nm.

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 supplied by Baker A R Chemical Co. and naphthyl-1-ammonium chloride (98%) by Merck. They were used as received.

Preparation of pigments for the thermo-XRD-analysis

- Group A: Four different samples were prepared. In each sample to 25.0 mL of an aqueous suspension of Na-montmorillonite (1.0 mass%) 2.5 mL of $1.0 \cdot 10^{-1}$ M naphthyl-1-ammonium chloride aqueous solution was slowly added (100 mmol naphthylammonium chloride per 100 g clay). After 2 h 0, 1.25, 2.5 and 3.75 mL NaNO_2 aqueous solution ($1.0 \cdot 10^{-1}$ M) were slowly added to obtain $[\text{NaNO}_2]/[\text{C}_{10}\text{H}_7\text{NH}_3]$ molar ratios 0 (blank, with no NaNO_2), 0.5, 1.0 and 1.5, respectively.
- Group B: Four different samples were prepared. In each sample to 25.0 mL 1% Na-montmorillonite aqueous suspension 2.5 (blank), 1.5, 2.5 and 4.0 mL naphthyl-1-ammonium chloride ($1.0 \cdot 10^{-1}$ M) was slowly added (100, 60, 100 and 160 mmol naphthylammonium chloride per 100 g clay, respectively). No NaNO_2 was added to the blank. After 2 h 1.5, 2.5 and 4 mL NaNO_2 aqueous solution ($1.0 \cdot 10^{-1}$ M) were added to the other three suspensions, respectively, to get $[\text{NaNO}_2]/[\text{C}_{10}\text{H}_7\text{NH}_3]$ molar ratio 1.

Each suspension of groups A and B was treated for ten minutes in an ultrasonic bath (Medenet super-sonic cleaner mini DG-1) before and after adding the NaNO_2 solution. After adding NaNO_2 the clays became blue whereas the blank was white. Suspensions were aged for 1, 7 and 56 days and solid fractions were slowly settled with a preferred orientation on glass-slides and dried for the thermo-XRD-analysis.

Methods

Thermo-XRD-analysis

Diffractograms of air-dried samples, before and after heating at 360°C for two hours, were recorded at room temperature and at ambient atmosphere, using a Philips Automatic Diffractometer (PW1710) with a Cu tube anode.

Curve fitting

X-ray diffractograms, obtained before and after the thermal treatment, were fitted by 'PHILIPS' (Automatic Powder Diffraction) software previously described [9, 10]. Gaussian shapes were used for the bands.

Results and discussion

An aqueous solution of naphthylazonaphthylamine synthesized in the absence of clay was first red. After few hours reddish-brown particles settled. The commercial name of the product is 'Solvent Brown 3'. It is soluble in ethanol, acetone and benzene [11]. The particles became blue after acidifying the system with HCl. The azo dye synthesized in the presence of montmorillonite was immediately blue, suggesting that the blue staining resulted from the surface acidity of montmorillonite interlayer [12]. By adding acetone to the system the color changed into red. After centrifugation the color of the liquid (acetone-water) was red, similar to the initial color obtained in the synthesis of the dye in the absence of clay, but the clay remained blue. Red azo dye can be extracted from the clay by repeated washings with acetone.

Representative curve-fitted X-ray diffractograms of samples before any thermal treatment and after heating at 360°C are shown in Figs 2 and 3. The locations of the maxima of the different peak components and their areas (in percentage) relative to the total areas of the peaks (in short 'relative areas') are shown in Tables 1 and 2.

Blank

The blank sample for groups A and B was prepared by treating the Na-clay with 100 mmol naphthyl-

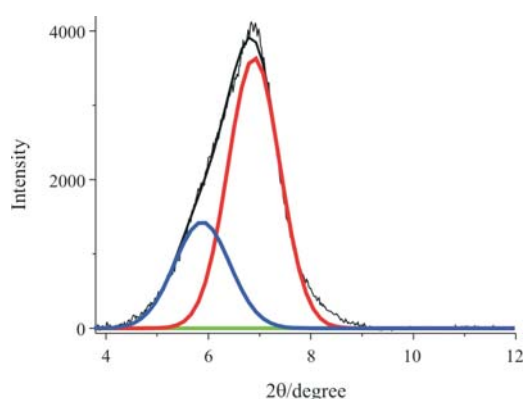


Fig. 2 Curve-fitted X-ray diffractogram of montmorillonite treated with 100 mmol naphthylammonium and 50 mmol sodium nitrite in aqueous suspension, aged one day before the sedimentation of the clay, recorded before the thermal treatment of the pigment

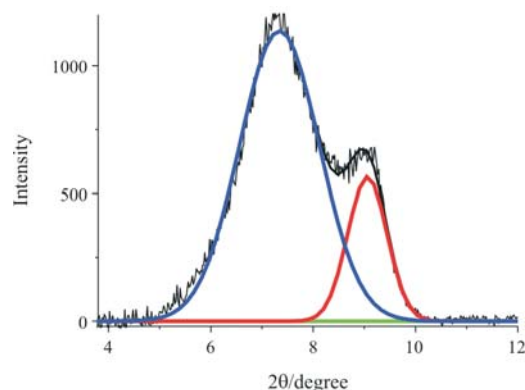


Fig. 3 Curve-fitted X-ray diffractogram of montmorillonite treated with 100 mmol naphthylammonium and 50 mmol sodium nitrite in aqueous suspension, aged one day before the sedimentation of the clay, recorded after heating the pigment at 360°C

ammonium chloride per 100 g clay. The clay fraction was separated from the suspension and washed thoroughly with distilled water until no Cl^- was detected in the supernatant. As a result of the extensive washing only naphthylammonium cations occupying exchangeable sites were present. After being air-dried C and N were determined by microanalysis. The washed sample contained 67.5 mmol naphthylammonium per 100 g clay. This observation proved our assumption mentioned in the Introduction that in the first stage of the synthesis montmorillonite adsorbed part of the added naphthylammonium by cation exchange mechanism.

The curve fitted diffractogram recorded before the thermal treatment showed two components with maxima at 1.35 and 1.58 nm and relative areas of ≈ 20 and $\approx 80\%$, respectively, from the total peak area, indicating the presence of two types of tactoids (Tables 1 and 2). The first component characterized tactoids with monolayers of hydrated naphthylammonium, lying parallel to the TOT clay layers [13–15]. The second component characterized tactoids with hydrated naphthylammonium-naphthylamine associations tilted relative to the TOT clay-layers [12, 15, 16].

After seven aging-days there were changes in the basal spacings. The curve fitted diffractogram before the thermal treatment showed two components with maxima at 1.42 and 1.67 nm and relative areas of ≈ 65 and $\approx 35\%$, respectively, from the total peak areas, probably associated with further adsorption of water and the decomposition of some tilted hydrated naphthylammonium-naphthylamine associations to form naphthylammonium tactoids. A basal spacing of 1.42 nm can be obtained from water bilayers parallel to the TOT clay-layers [17, 18], with the organic cations in vacancies between water molecules of the two layers.

The curve fitted diffractograms of one and seven aging-days, both recorded after heating at 360°C,

Table 1 Characteristic features of curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium chloride per 100 g clay and with 0 (blank), 50, 100 and 150 mmol NaNO₂ per 100 g clay ([NaNO₂]/[C₁₀H₇NH₃] molar ratio 0, 0.5, 1.0 and 1.5 respectively) before and after heating at 360°C. The organo-clays were separated from the suspensions 1 and 7 days after their preparation

Aging/ days	Temperature/ °C	Sodium-nitrite: naphthylammonium molar ratio							
		0.0		0.5		1.0		1.5	
		components		components		components		components	
		maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%
1	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
	360	0.97	50	0.97	37	0.98	20	–	–
		1.01	50	–	–	–	–	1.04	15
		–	–	1.16	63	1.21	80	1.22	55
		–	–	–	–	–	–	1.38	30
7	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
	360	0.97	50	0.97	32	0.97	36	0.97	34
		1.01	50	1.04	41	1.00	46	1.03	48
		–	–	1.28	27	1.22	18	1.29	18
		–	–	–	–	–	–	–	–

Table 2 Characteristic features of curve-fitted X-ray diffractograms of montmorillonite treated with 100 mmol naphthylammonium chloride per 100 g clay and of montmorillonite treated with 60, 100 and 160 mmol naphthylammonium chloride and sodium nitrite ([NaNO₂]/[C₁₀H₇NH₃] molar ratio 1.0), before and after heating at 360°C. The organo-clays were separated from the suspensions 1 and 7 days after their preparation

Aging/ days	Temperature/ °C	Loading (mmol/100 g clay)							
		Naphthyl- ammonium		Sodium nitrite/naphthylammonium molar ratio 1					
		100 (blank)		60		100		160	
		components		components		components		components	
		maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%	maxima/ nm	relative areas/%
1	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
	360	0.97	50	0.99	12	0.98	20	0.98	13
		1.01	50	–	–	–	–	–	–
		–	–	1.16	88	1.21	80	1.21	78
		–	–	–	–	–	–	1.60	9
7	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
	360	0.97	50	0.97	56	0.97	36	0.97	28
		1.01	50	1.03	44	1.00	46	1.04	38
		–	–	–	–	1.22	18	–	–
		–	–	–	–	–	–	1.52	36

showed two components with maxima at 0.97 and 1.01 nm, proving a thermal collapse of the clay. No charcoal was formed inside the interlayer space, suggesting that the naphthylammonium cation was

deprotonated and evolved at temperatures lower than those required for its transformation into charcoal. Melting and boiling points of naphthylamine are 50 and 301°C, respectively.

The effect of the amount of NaNO₂ (Group A)

Samples separated from the suspensions after one aging-day

By adding NaNO₂ the adsorbed naphthylammonium reacted to form an azo dye, shown by the blue staining of the samples. Diffractograms of NaNO₂-treated samples differed from that of naphthylammonium-montmorillonite. Curve fitted diffractograms of samples with [NaNO₂]/[C₁₀H₇NH₃] ratios of 0.5, 1.0 and 1.5 before heating showed 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 [12–14]. Relative areas of peak component attributed to tactoids with monolayers increased from ≈20% in the diffractogram of naphthylammonium-montmorillonite to ≈70% after NaNO₂ treatment. Consequently this component is attributed mainly to tactoids with azo dye in the interlayers. The decrease in basal spacing as a result of the transformation of the naphthylammonium into the azo dye indicated stronger surface π interactions between the clay O-plane and the dye molecules compared with surface π interactions with naphthylammonium [4, 12]. Tactoids with bilayer or tilted organic compounds in the interlayers contain excess of organic matter, which did not react with NaNO₂ to form an azo dye. Additional organic matter not transformed to dye is located in the interparticle space of the flocs.

The thermal behavior of the NaNO₂-treated naphthylammonium-clay differed significantly from that of the untreated blank. At 360°C only small fractions of the former collapsed but the latter collapsed completely. The non-collapsed fractions showed peak component maxima at >1.15 nm, indicating the presence of tactoids with charcoal in the interlayers [19]. With the ratios [NaNO₂]/[C₁₀H₇NH₃] of 0.5 or 1.0, tactoids with monolayer charcoal with carbon atoms penetrating into the hexagonal holes of the oxygen plane (1.16–1.22 nm) were obtained [9]. However, when this ratio was 1.5, a monolayer charcoal with no carbons penetrating into the hexagonal holes was also obtained (1.38 nm). Since naphthylammonium-montmorillonite at 360°C did not form charcoal, the present results demonstrated that charcoal was obtained from the azo dye located inside the clay interlayer. The boiling point of 4-(1-naphthylazo)-1-naphthylamine at 760 Torr is 537±25°C [20].

The relative areas of the peak components showed that the percentage of collapsed tactoids decreased and those with interlayer charcoal increased with the amounts of NaNO₂. It is therefore concluded that the amount of azo dye molecules, formed during one aging-day increased with the amount of NaNO₂.

Samples separated from the suspensions after seven aging-days (1 week)

Curve fitted diffractograms of samples with [NaNO₂]/[C₁₀H₇NH₃] ratios of 0.5–1.5 before the thermal treatment showed two peak components, with maxima at 1.28 and ≈1.45 nm, representing two types of tactoids, with monolayers and bilayers or tilted organic matter in the interlayers, respectively [12–14]. Similar two types were detected after one aging-day, but the relative areas of the peak components were different. After seven aging-days percentage of the 1.28 nm component significantly decreased. As was previously mentioned, the 1.28 nm tactoids contained the azo dye in the interlayers. Their percentage decreased from ≈70% (one day) to ≈25% (7 days), suggesting that some dye decomposed during this one-week aging.

After heating the seven aging-days samples at 360°C, the relative areas of peak components at 1.22–1.29 nm, characteristic for charcoal-tactoids, were smaller than those obtained in diffractograms of one aging-day samples (≈20 vs. ≈75% from total peak areas, respectively). Since charcoal was formed from interlayer azo dye, this observation supports the suggestion that some dye decomposed during this week.

The effect of the amount of naphthylammonium (Group B)

Samples separated from the suspensions after one aging-day

In this series the [NaNO₂]/[C₁₀H₇NH₃] ratio was 1. The clays were treated with 60, 100 and 160 mmol naphthylammonium chloride and equivalent amounts of NaNO₂ per 100 g clay. Curve-fitted X-ray diffractograms of these samples (Table 2) recorded before heating showed the presence of two types of tactoids, with basal spacings of 1.28 nm (with monolayer azo dye in the interlayers) and of 1.50 nm (with non-azo organic matter in the interlayers). Here again the relative areas of the peak component attributed to tactoids with monolayers increased from ≈20% in the diffractogram of naphthylammonium-montmorillonite to ≈75% after NaNO₂ treatment.

After heating the samples at 360°C the diffractograms showed peak components at ≈1.00 nm (collapsed) and at >1.15 nm with charcoal in the interlayers. From relative areas of the peak components it appears that the ratio between them almost did not change with the loading, probably due to the fact that the [NaNO₂]/[C₁₀H₇NH₃] ratio was always 1.

Samples separated from the suspensions after seven aging days (1 week)

Curve-fitted X-ray diffractograms of these samples recorded before heating (Table 2) showed the presence of two types of tactoids, with basal spacings of 1.28–1.32 nm ($\approx 35\%$, with monolayer azo dye in the interlayer) and 1.37–1.54 nm (with non-azo organic matter in the interlayers). The percentage of the monolayer component decreased during the seven aging-days suggesting that some of the dye decomposed.

Charcoal was not formed during heating the sample with 60 mmol naphthylammonium per 100 g clay at 360°C. Most of the azo dye, which was detected after one aging-day, decomposed during seven aging-days, and the rest decomposed during the thermal treatment. Only samples with 100 and 160 mmol naphthylammonium per 100 g clay, showed after the thermal-treatment the presence of charcoal, proving the presence of the azo dye before the thermal-treatment. However, the relative areas of these diagnostic peak components (1.22 or 1.52 nm) in the diffractograms of the thermal treated seven aging-days samples, were smaller than those obtained in the thermal treated diffractograms of the one aging-day samples, indicating that much of the azo dyes decomposed during the seven aging-days.

Samples separated from the suspensions after 56 aging days (8 weeks)

Samples were aged up to 56 days. Unfortunately after aging the results of the X-ray diffraction and the curve fitting became less reproducible. Nevertheless they showed the trend of decomposition of the interlayer azo dye with aging. For example, montmorillonite treated with 160 mmol naphthylammonium and 160 mmol sodium nitrite, before the thermal treatment showed two peak components at 1.28 and 1.50 nm. After one aging day the percent of the relative area of this component was $\approx 65\%$. It decreased to ≈ 35 and $\approx 20\%$ after seven and 56 aging days, respectively.

Conclusions

- A high quality blue naphthylazonaphthylammonium-montmorillonite pigment was obtained when the azo dye was synthesized from its source materi-

als in the presence of the clay. The synthesized dye was located inside the interlayer space of the clay.

- Pigments obtained after one aging-day of the synthesis-suspension showed better qualities compared with pigments obtained after seven and 56 aging-days. Aging resulted in partial decomposition of the interlayer azo dye.

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