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Characterization of synthetic hydrous hematite pigments

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Dedicated to Professor Wolfgang Laqua on the Occasion of his 70th Birthday.

Abstract

The application of synthetic hematite pigments, prepared by the direct precipitation process from an iron(II) sulfate solution, leads to problems in the processing of plastic tubes by injection moulding and extrusion. Undesirable flaws are formed.

A characterization by thermogravimetry (TG) and infrared spectroscopy (IR) proved an incorporation of water (~1.5 mass%) in the crystal lattice. X-ray investigations of tempered hydrous hematite pigments in a temperature range between 100 and 800 °C showed an decrease of the cell volume between 400 and 500 °C. The absence of superstructure reflections by powder X-ray diffraction (XRD) investigations and the small dehydration enthalpy of $\sim 6.1\,\mathrm{kJ\,mol^{-1}}$ determined by differential scanning calorimetry (DSC) indicates a statistical distribution of hydroxyl groups. Pores of hexagonal geometry were observed at the crystal surface by transmission electron microscopy (TEM) after dehydration. The so-called "hydrohematite", described in the literature, with ordered incorporation of hydroxyl groups in the hematite lattice was not found.

Keywords: Synthetic hematite pigments; Thermal analysis; Infrared spectroscopy; X-ray diffraction; Transmission electron microscopy

1. Introduction

Synthetic iron oxide pigments are of great economical importance due to their chemical stability (i.e. against UV radiation or corrosive gases) and their relatively low production costs. The composition of red colored iron pigments corresponds to that of the mineral hematite. Hematite (α-Fe_2O_3) can be prepared by oxidation of magnetite (Fe_3O_4) in air or oxygen atmosphere above ~500 °C. The dehydration of goethite (α-FeOOH) at temperatures above ~400 °C leads to hematite as well [1,2]. Both products could be described by the ideal formula Fe_2O_3. Furthermore it is possible to synthesize hematite by direct precipitation in aqueous solution.

An important industrial aspect is the minimization of the production costs (direct precipitation process) caused by a long reaction time. In this study it could be shown that variation of reaction time and reaction temperature lead to hematite pigments with incorporated water in the crystal structure.

Hydrous hematite pigments cause various problems in engineering processes. For example, thermal stress of the hematite pigments by injection moulding and extrusion of hematite colored plastic tubes leads to undesirable flaws, because water evaporates from the hematite.

It is generally assumed that the formation of a hydrous hematite during precipitation in aqueous solution can be explained by hydroxyl groups which occupy O^{2-} positions within the hematite structure, forming associates with vacancies in the Fe^{3+} sublattice [3]. The formation of disorder can be described by the Kröger–Vink notation

$$\mathrm{Fe_{Fe}}^{x} + 3\mathrm{O_O}^{x} + 3\mathrm{H^+(aq)} = \mathrm{V}'''_{\mathrm{Fe}} + 3\mathrm{OH_O}^{\bullet} + \mathrm{Fe^{3+}(aq)}$$

($\mathrm{V}'''_{\mathrm{Fe}}$ is the vacancy in the Fe^{3+} sublattice; $\mathrm{OH_O}^{\bullet}$ the hydroxyl group which occupies an O^{2-} position).

Hydrous hematite has been described by Wolska et al. [4–7] as "hydrohematite", $Fe_{2-x}O_{3-3x}(OH)_{3x}$ ($x = 0$: α-Fe_2O_3; $x = 1$: $Fe(OH)_3$) as intermediate of the dehydration

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of goethite, but could not be confirmed by other authors [8–10].

2. Experimental

The investigated synthetic hematite samples (with and without incorporated water) are prepared by the direct precipitation process. A solution of iron(II) sulfate ($FeSO_4{\cdot}7H_2O$) was mixed with alkali (NaOH) and oxidized by air. The direct precipitation process is described by the following reaction:

$$2FeSO_4 + \frac{1}{2}O_2 + 4NaOH \rightarrow Fe_2O_3 + 2Na_2SO_4 + 2H_2O$$

The reaction time (10–100 h) depends on the temperature (60–95 °C) and on the desired particle size of the hematite pigment [11,12].

The powder X-ray diffraction was conducted on a Siemens D5000 diffractometer using Cu $K\alpha_1$-radiation (secondary monochromator). TG investigations (thermobalance Linseis L 81) were carried out with samples in corundum crucibles and heating rates of $5\,K\,min^{-1}$. A Perkin-Elmer 7 DSC (sealed gold crucibles, heating rate $20\,K\,min^{-1}$) was used for DSC measurements. The preparation of the hematite samples for the determination of the lattice parameters is described in the text. The IR investigations of the hematite samples (KBr technique) were done in a region of 400–4000 cm^{-1} by using a Bruker FIR spectrometer IFS 25. A Leica Stereoscan 360 FE (SEM) and a Philips TEM 400 (TEM) were used for electron microscopy investigations.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

The prepared synthetic hematite pigments (with and without incorporated water) are of identical flat geometry with hexagonal habitus and identical particle size (Fig. 1).

The diameter of nano crystalline particles amount to ~0.1 μm. A tendency to agglomeration of the particles can be observed.

3.2. Infrared spectroscopy (IR)

In general the interpretation of IR spectra of solid-state samples is difficult, due to the particles size and particles geometry could be cause different bands. Identical size and geometry of the particles allow an arrangement. The hydrous hematite shows a large stretching vibrations band ($\nu_S H_2O$) at $\sim 3424\,cm^{-1}$ coupled at a large bending vibrations band (δH_2O) at $\sim 1634\,cm^{-1}$ (Fig. 2a). A small stretching vibrations band ($\nu_S H_2O$) at $\sim 3441\,cm^{-1}$, which is characteristic for surface adsorbed water [9], in combination with a small bending vibrations band (δH_2O) at $\sim 1634\,cm^{-1}$ is observed (Fig. 2b). The IR spectra of hematite and hydrous hematite with identical particle size and particle geometry show no significant difference in the region $<1500\,cm^{-1}$.

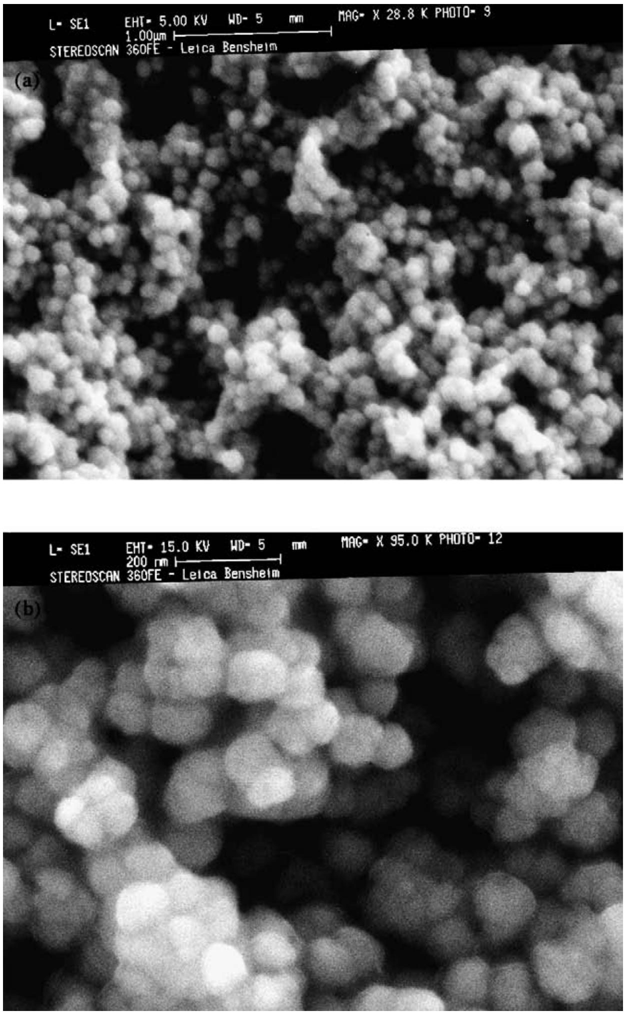

Fig. 1. SEM image of hydrous hematite (magnification: 28 800× (a; top)) and hematite (magnification: 95 000× (b; bottom)) prepared by the direct precipitation process. Diameter of particles: ~0.1 μm.

3.3. Thermogravimetry (TG)

The results of thermogravimetric investigations are given in Fig. 3. Whereas the dehydrated hematite deposits only on the surface adsorbed water (~0.5%), a ~1.5% loss of mass of the hydrous hematite is observed.

3.4. X-ray diffraction

Differences of the diffraction patterns between hematite and hydrous hematite could not obtained. Fig. 4 shows the X-ray diffraction pattern of the hydrous sample. No superstructure diffraction peaks could be observed for the hydrous sample. In contrast with hydrous maghemite (γ-Fe_2O_3) any ordered vacancy distribution in hydrous hematite were not found [13,14]. The absence of superstructure reflections

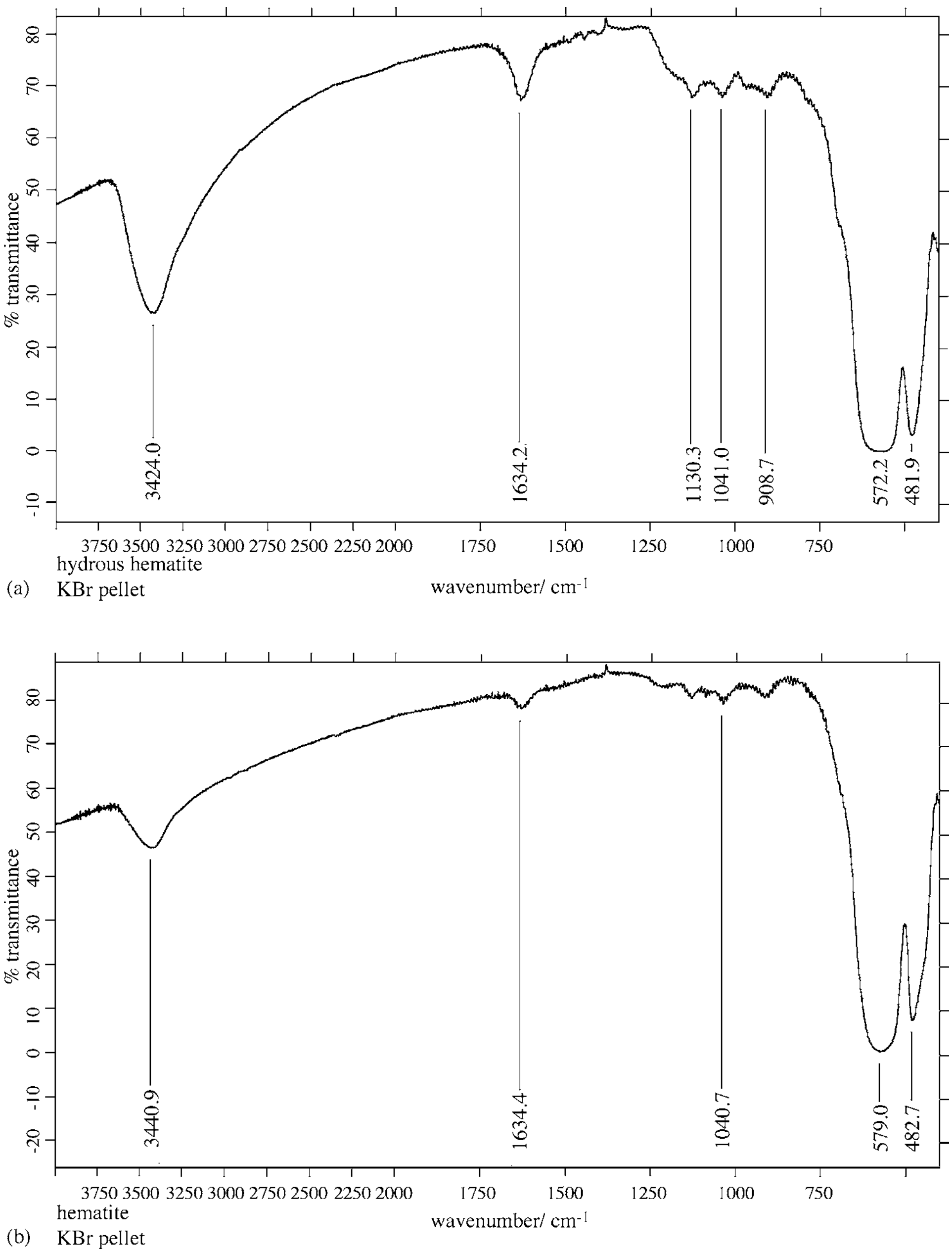

Fig. 2. IR spectra of hydrous hematite (a) and hematite (b).

reveals a statistical distribution of the hydroxyl groups in the hematite lattice.

To verify the variation of the hematite structure by incorporation of water, further X-ray experiments were carried out: samples of hydrous hematite were tempered in a temperature range between 100 and 800 °C (step of temperature increase: 100 K). Thermal non-stressed hydrous hematite and the tempered samples were measured by the reflection method (radiation: Cu Kα_1; 40 kV/40 mA; graphite monochromator) and the lattice parameters were determined, respectively. The samples were mixed with 10% Si as internal standard.

A rapid decrease of the lattice parameters (hexagonal setting) *a* and *c* is observed in a range of temperature between 400 and 500 °C (Table 1). By using a trigonal rhomboedric setting in the same temperature range a decrease of the lattice parameter *a* is observed in good agreement (Table 2).

In the same range the cell volume diminishes about ~1.6% (Fig. 5) [15]. The extension of the hematite structure may be attributed to the incorporation of water.

3.5. Transmission electron microscopy (TEM)

By TEM flat geometry with a hexagonal habitus has been identified. As a consequence of the energy of the electron beam the hydrous hematite dehydrated spontaneously at a

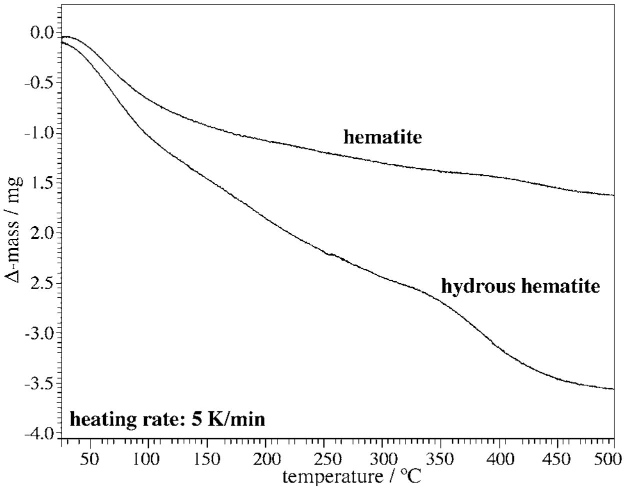

Fig. 3. TG curve of hydrous hematite and hematite.

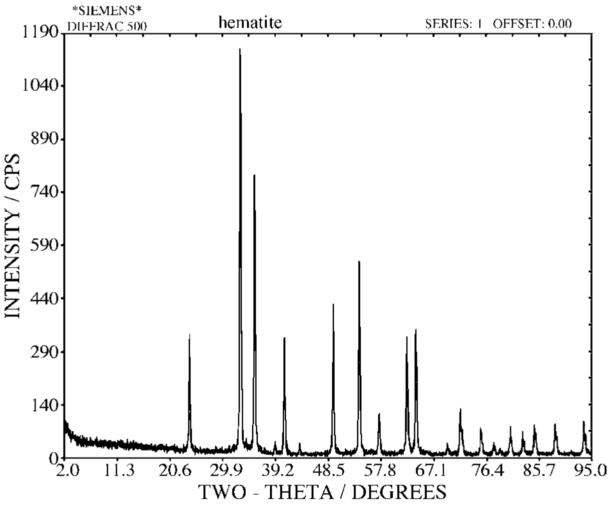

Fig. 4. X-ray diffraction pattern of hydrous hematite.

magnification of >275 000×. At the surface of the hematite particles, hexagonal pores of approximately 0.01 μm diameter were created (Fig. 6). No evidence for micropores, as described for the transformation of goethite to hematite [16–20], as a preliminary step of dehydration, were found.

Table 1
Lattice parameters *a* and *c* (hexagonal setting) of hydrous hematite vs. temperature

T (°C)	*a* (nm)	*c* (nm)
25	0.50525	1.3818
300	0.50536	1.3815
400	0.50501	1.3797
500	0.50310	1.3741
600	0.50294	1.3734
700	0.50306	1.3735
800	0.50281	1.3729

Table 2
Lattice parameter *a* and rhomboedric angle (trigonal rhomboedric setting) of hydrous hematite vs. temperature

T (°C)	*a* (nm)	*α* (°)
25	0.54521	55.207
300	0.54516	55.226
400	0.54454	55.253
500	0.54237	55.265
600	0.54212	55.274
700	0.54218	55.281
800	0.54193	55.279

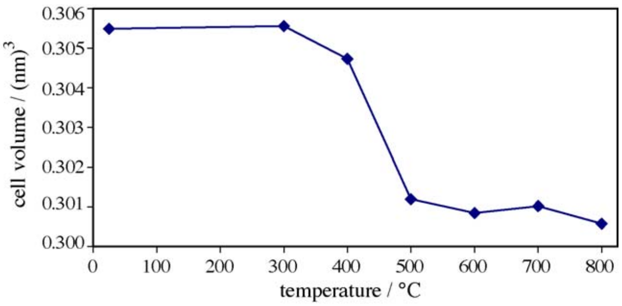

Fig. 5. Variation of cell volume *V* (hexagonal setting) of hydrous hematite vs. temperature.

3.6. *Differential scanning calorimetry (DSC)*

The process of dehydration by TEM indicates a small enthalpy value for the loss of water. This could be confirmed by DSC measurements (gold crucibles). A small endothermic effect is recognizable (Fig. 7). This effect could not detected by using corundum or aluminium crucibles.

The small signal detected by DSC does not agree with a characteristic peak area expected for “hydrohematite” with ordered hydroxyl group positions in the crystal lattice, such it is observed by the thermal dehydration of nano crystalline goethite pigments [9]. The enthalpy determined for the dehydration of hydrous hematite ($\Delta_R H$: ~6.1 kJ mol^{-1}) resulted

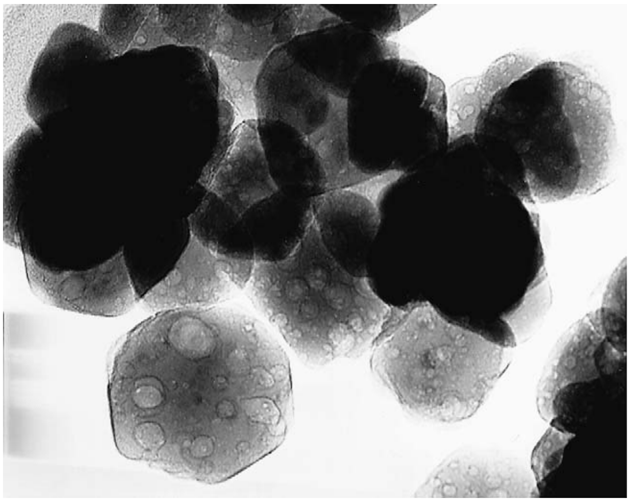

Fig. 6. TEM image of hydrous hematite. Magnification: 275 000×.

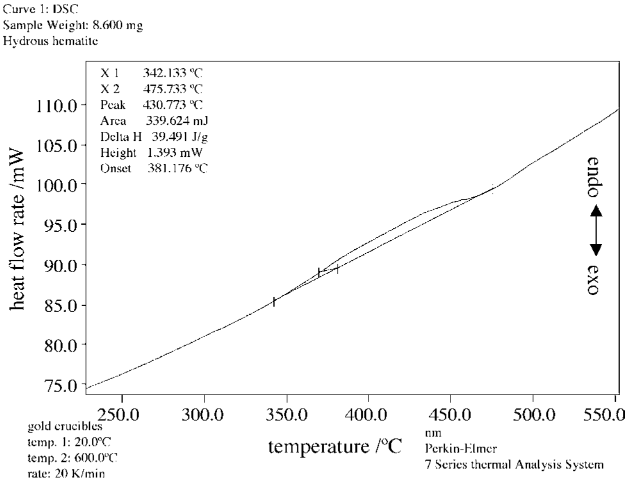

Fig. 7. DSC plot of hydrous hematite.

in a considerably lower value (factor 5.5) than dehydration enthalpy of a goethite sample with comparable particle size [9].

4. Conclusions

By variation of the precipitation conditions (shorter reaction time due to a higher reaction temperature) it is possible to synthesize hematite pigments with incorporated water. There is not enough time for an ideal crystal growth, so the habitus of the nano crystal hematite pigments seems to be perfect, but the crystal lattice is disordered.

Hydroxyl groups occupy positions of the O^{2-} lattice and vacancies in the Fe^{3+} lattice are created. This leads to an extension of the structure. The missing of superstructure reflexes reveals that: it exists no ordered structure of “hydrohematite” ($Fe_{2-x}O_{3-3x}(OH)_{3x}$), corresponding to an incorporation of statistical distributed hydroxyl groups in the hematite structure. The small enthalpy value of $\sim$6.1 kJ mol^{-1} results from the fact, that no reorganization of the crystal structure is necessary. For the same reason no micro-structural changes were observed. The small enthalpy value of the dehydration reaction suggests the following reaction mechanism: protons of the hydroxyl groups migrate from O^{2-} lattice site to O^{2-} lattice site up to the surface and combine there with oxygen ions to water molecules. Accordingly iron ions migrate from the surface into the bulk of the crystal and occupy the vacancies (Fig. 8).

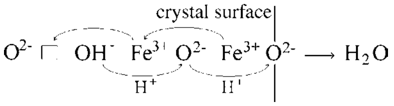

Fig. 8. Sketch of a possible migration mechanism of dehydration of hydrous hematite.

Analogous to the formation of the hematite crystals (hexagonal flats) pores of hexagonal geometry are built at the surface.

“Hydrohematite” as a defined substance with an ordered incorporation of the hydroxyl groups within the crystal lattice could not confirmed by the examined hematite pigments.

Acknowledgement

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