

PREPARATION OF YELLOW AND RED IRON OXIDE PIGMENTS FROM IRON(II) SULFATE BY ALKALI PRECIPITATION

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(Received 11 January 1984)

ABSTRACT

A study was made of the preparation of yellow α -FeOOH pigments from iron(II) sulfate solution by alkali precipitation and gas oxidation methods. The preparation of pure yellow pigments turned out to be difficult. Pigments of composition FeOOH were obtained under acidic ($\text{pH} < 5$) and alkaline ($\text{pH} > 12$) conditions at temperatures below ambient. In slightly alkaline solution some Fe_3O_4 was formed as well, and it stained the products greenish, brownish or black. At 70°C and pH 7–9 a pure black Fe_3O_4 was formed.

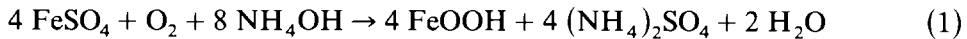
According to TG measurements, the needle-like FeOOH particles decomposed to red α - Fe_2O_3 above 300°C and the pigments then obtained were light red. The preparation of dark red oxides required higher temperatures than the direct firing of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ to oxide.

INTRODUCTION

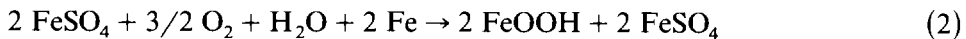
The yellow pigments represent an important group of iron oxide pigments. Like other iron oxide pigments, they are both mined as minerals and manufactured by chemical processes. The principal natural yellow iron oxides are the ochres and siennas found in limonitic ores [1]. Though there is no sharp boundary between ochres and siennas, ochres are usually lighter in colour and have lower iron content than the siennas. The chemical composition of pure yellow iron oxide pigments is FeOOH, presented also as $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or with other water content.

Yellow iron oxide pigments are synthetically prepared from iron compounds by two very similar methods: (i) oxidation of iron(II) hydroxide solution, and (ii) oxidation of iron(II) salt solutions [2]. In the latter method, known as the Penniman–Zoph process [3], metallic iron and FeOOH seed crystals are used to catalyze oxyhydroxide formation. The usual iron source in both methods is iron(II) sulfate solution, but chloride may also be

employed. Hydroxide suspension is obtained by the use of precipitants like NaOH, KOH, NH₃, Ca(OH)₂, Na₂CO₃ and MgO [2,4,5]. Oxidation of the suspension is carried out by blowing air through it, or by the use of O₂, HNO₃, H₂O₂ or NaClO₃ as oxidizing agent [2,6–9]. A simplified reaction for the hydroxide oxidation is



The oxidation of iron(II) salt solutions takes place in a similar way but during the process small FeOOH particles and scrap iron are introduced into the reactor. The iron acts as a pH regulator and keeps the iron concentration constant, and the addition of fine pigment particles promotes the nucleation [2,10,11]. The overall reaction in the Penniman–Zoph process can be written as



Both the temperature of the solution and the pH have a strong effect on the pigment quality. Temperatures from 10 to 90°C [12,13] and a pH from 2 to 13.5 [14,15] have been reported in the literature for the preparation of yellow pigments. The optimum temperature and pH combination depends on the other experimental conditions used; viz. alkali, oxidizing agent, reactor type, catalysts, etc.

The reduction of organic compounds with iron as reducing agent, resulting in iron oxides, is an important manufacturing method for iron oxide pigments. This aniline process, as it is called, is used in the production of yellow pigments [16].

A characteristic of the synthetic yellow iron oxide pigments is an extremely fine and uniform particle size, good hiding power and uniformity of colour. For these reasons, as well as manufacturing costs, synthetic pigments have largely replaced the natural ones. The good chemical resistance, light-fastness and dispersibility of the synthetic pigments makes them useful as colorants in paints and plastics. A limited heat resistance with decomposition to Fe₂O₃ [17] is the only negative property.

The yellow iron oxide pigments decompose to red Fe₂O₃ pigments when calcined in oxidative atmosphere. In the presence of reducing agent the product is black iron oxide or metallic iron. The temperatures needed for calcination to red pigments are lower than those required in the firing of iron(II) sulfate to red oxide, which is a common way of manufacturing red Fe₂O₃ pigments [13–20].

The aim of this study is to investigate the formation of yellow iron oxide pigments in iron(II) sulfate solution using different alkalis as precipitant. A study is also made of the thermal treatment of FeOOH to produce red pigments. In particular, the effect of experimental conditions on the characteristics of both yellow and red pigments is investigated.

EXPERIMENTAL

The yellow iron(III) oxyhydroxides were synthesized in a 3-necked flask (500 cm³) resting in a thermostatted water bath. The hydroxide suspension that formed after the addition of alkali was stirred (10 rps) and a gas flow (200 cm³ min⁻¹), usually air, was led through the suspension. In all experiments the FeSO₄ · 7 H₂O content of the solution was 10 wt.%, or 22 g of FeSO₄ · 7 H₂O dissolved in 200 cm³ of water. The process variables were the alkali (NH₃ or NaOH), its amount, reaction time and temperature. Normally the preparation was carried out as a batch experiment, so that the total alkali was added to the reactor all at once, before the start of oxidation. After the reaction the yellow pigment was filtered, washed with water and dried in an oven for 24 h.

The preparation of red Fe₂O₃ pigments from yellow FeOOH was carried out in isothermal batch experiments under static air atmosphere. The formation of oxide was also studied thermoanalytically with a Perkin-Elmer TGS-2 thermobalance and with DTA-1700 equipment connected to a System 7/4 controller and TADS data station.

For characterization of the pigments the following methods were employed: chemical analysis, X-ray diffraction, transmission electron microscopy, and reflection spectroscopy. Details of the characterization methods as well as the equipment used are described elsewhere [21]. The properties of the pigments were compared with those of commercial pigments from Bayer (Leverkusen, FRG).

RESULTS AND DISCUSSION

Preparation of FeOOH

In the first experiments ammonia was used as precipitant. With small amounts of ammonia, 30% of the stoichiometric amount calculated from eqn. (1), yellow α -FeOOH pigments were obtained with reaction time longer than 16 h at temperatures below 40°C. The solution was neutral after the addition of NH₃, but after the oxidation pH was 2–2.5 depending on the oxidation time. Conversion to FeOOH was low owing to the small amount of NH₃. According to the X-ray diffraction pattern the product was orthorhombic α -FeOOH, which is also known as goethite.

A greenish-brown product was obtained when the ammonia was increased to stoichiometric amount and when an excess of NH₃ was used. In these experiments ($T = 18^\circ\text{C}$, $t = 24$ h) the pH of the solution remained alkaline (9–10) all the time. X-ray diffraction showed that the product contained Fe₃O₄. With a stoichiometric amount of ammonia it was possible to obtain FeOOH but only in dilute solution and at temperatures below 25°C. The pH

TABLE 1

Preparation conditions, colour coordinates and particle sizes of yellow pigments prepared from 10% FeSO₄ solution (values recorded for some commercial pigments are included)

Sample No.	Alkali used	Alkali amount (% of stoichiometric amount)	pH at beginning	Oxidation time (h)	Oxidation temp. (°C)	pH at end	Main phase according to XRD	Colour	Colour coordinates		Particle size (μm)
									X	Y	
1	NH ₃	30	~ 7	24	40	~ 2	α-FeOOH	light yellow	0.45	0.43	0.09
2	NH ₃	100	~ 9	24	18	~ 9	Fe ₃ O ₄	brown	0.45	0.40	0.07
3	NH ₃	100 (dilute)	~ 9.5	24	18	~ 4	α-FeOOH	greenish-yellow	0.45	0.42	0.10
4	NH ₃ (g)		~ 5	144	18	~ 3	α-FeOOH	brownish-yellow	0.48	0.48	0.05
5	NaOH	150	~ 13	24	40	~ 12	α-FeOOH	greenish-yellow	0.41	0.42	0.08
6	NaOH	200	~ 13	72	40	~ 12	α-FeOOH	light yellow	0.43	0.43	0.09
7	NaOH	200	~ 13	24	8	~ 12	α-FeOOH	brownish-yellow	0.46	0.44	0.06
8	NaOH	200	~ 13	24	70	~ 12	Fe ₃ O ₄	black	0.33	0.34	0.29
9	NaOH	150	~ 13	24	18	~ 13	α-FeOOH	brownish-yellow	0.46	0.44	0.06
10	NaOH	150	~ 13	72	18	~ 13	α-FeOOH	brownish-yellow	0.45	0.45	0.05
11	NaOH	150	~ 13	24	18	~ 13	α-FeOOH	brownish-yellow	0.46	0.44	0.06
420H							α-FeOOH	yellow	0.47	0.45	
391O							α-FeOOH	yellow	0.46	0.45	
306F							Fe ₃ O ₄	black	0.34	0.35	0.50

fell during the oxidation from 9.5 to 4, whereas, in more concentrated systems, the end pH was 6 or more. It seems that the pH value after the process has an effect on the composition. The FeOOH formed in the dilute solution was not, however, clear yellow. At higher temperatures (40–70°C) the main component in the precipitation was Fe₃O₄ and the colour brown. With ammonia, therefore, it is possible to prepare yellow pigments only in acidic solution and at low temperatures (Table 1).

Gaseous ammonia can also be used as precipitant and then a continuous process can be carried out. In some experiments gaseous ammonia was added slowly to the solution but the precipitate was not removed during the process. The ammonia was added so slowly, over a period of several days, that the pH remained below 5. The chemical composition of the pigments obtained was FeOOH but their crystallinity and hiding power were poor. The increase of reaction time slightly improved the quality of the precipitation, but the colour was unsatisfactory.

In the stoichiometric mixture of NaOH and FeSO₄ the pH was about 9. After oxidation of this mixture at 40°C for 24 h the pH had decreased to 6 and the colour of the precipitate was brownish-grey. With an NaOH excess of more than 50% and after oxidation for 24 h at 40°C, the product was FeOOH. When an excess of sodium hydroxide was employed, the pH was high (~13) during the process. The colour of the pigments was greenish-yellow. One day was the minimum oxidation time, as before that the product contained Fe₃O₄. The increase of reaction time from 1 to 7 days did not significantly alter the quality of the pigments. The reaction temperature, by contrast, did have an effect on the colour; the lower the temperature the lighter yellow the pigment. The hiding power of the pigments obtained with NaOH was not very good. It may be added that at a reaction temperature of 70°C the product was pure black Fe₃O₄ with good pigment properties. The colour and hiding power were excellent and comparable to commercial black pigments.

The crystals of the yellow iron(III) oxyhydroxide pigment were needle-like in shape. Particle sizes for commercial yellow pigments are usually given by the two dimensions of the needles. Here, however, the particle sizes are given by one number and in the size calculations the particles are approximated to balls. Though this makes comparison of the particle sizes in the present work and those given by the pigment manufacturer somewhat difficult, the sizes are nevertheless in good agreement when determinations are made by the same method. The sizes varied between 50 and 100 nm and the distribution curves show the products to be quite homogeneous (Fig. 1). The hiding power in some pigments was comparable to that of the commercial pigments.

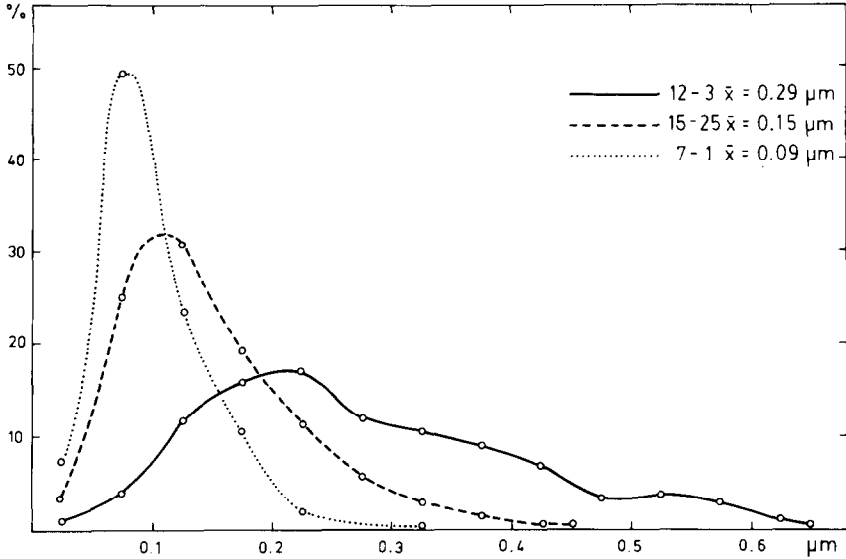


Fig. 1. Particle size distribution curves for some iron oxide pigments. Sample 12-3 corresponds to number 8 and 7-1 to number 1 in Table 1 and 15-25 to sample 3 in Table 2.

Decomposition of FeOOH

Thermoanalytical studies showed iron(III) oxyhydroxide to decompose to Fe_2O_3 in a single step at about 300°C when heated at $10^\circ\text{C min}^{-1}$. This

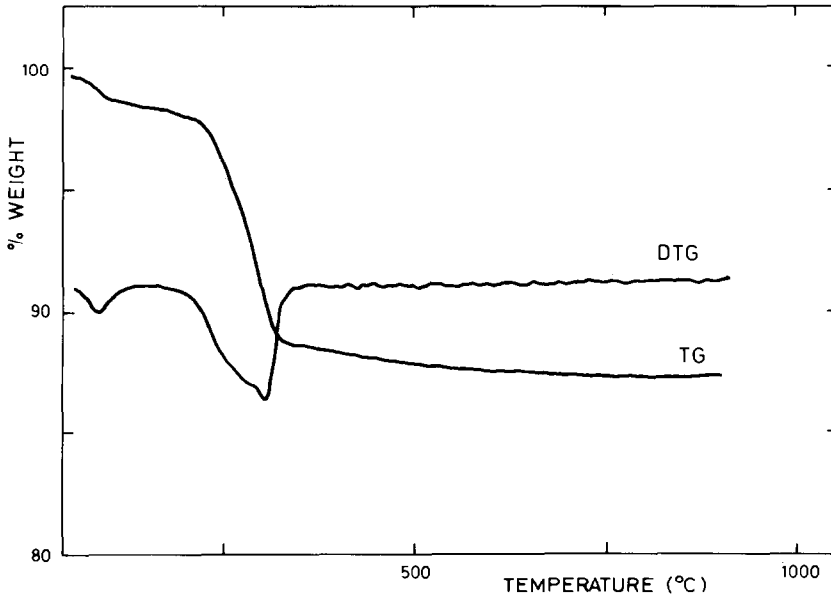


Fig. 2. TG and DTG curves of FeOOH heated in dynamic air atmosphere ($10^\circ\text{C min}^{-1}$). Sample weight 15.2 mg.

TABLE 2

Preparation conditions, colour coordinates and particle sizes of Fe_2O_3 pigments prepared from FeOOH in batch experiments under static air atmosphere (values recorded for some commercial pigments are included)

Sample No.	Heating temp. ($^{\circ}\text{C}$)	Heating time (h)	Colour	Colour coordinates		Particle size (μm)
				X	Y	
1	400	2	red-brown	0.51	0.38	0.06
2	800	2	red-brown	0.53	0.38	0.10
3	800	5	red-brown	0.53	0.37	0.15
4	900	2	dark red	0.49	0.38	0.30
110M			red-brown	0.55	0.38	0.09
130M			red-brown	0.55	0.37	0.17
180M			dark red	0.51	0.35	0.33

endothermic reaction corresponds to the release of water (Fig. 2). The decomposition temperature was also confirmed in bath experiments, which showed that below 300°C the product contained FeOOH and had poor hiding power. The oxides calcined at $300\text{--}400^{\circ}\text{C}$ were microcrystalline and their particle shape was needle-like, resembling that of FeOOH . The colour was yellowish-red. Increasing firing time and temperature caused an increase in crystallinity and darkening in colour. The particles also assumed the more rounded shape typical for red $\alpha\text{-Fe}_2\text{O}_3$ pigments.

The pigment fired from FeOOH at 800°C for 2 h was red-brown, corresponding to the commercial pigment 110M. The oxide obtained from FeSO_4 under the same conditions was darker in colour and the particle size larger [20]. Firing of FeOOH for 5 h at 800°C still gave red-brown oxide, corresponding to the commercial quality 130M (Table 2). The preparation of dark red pigments from FeOOH required high temperatures (900°C) or long times. This indicates that the structure and shape of FeOOH particles are unfavourable for the formation of $\alpha\text{-Fe}_2\text{O}_3$ and thus the formation and growth of round oxide particles from oxyhydroxide needles is a slow process. The hiding power of all the red pigments obtained from FeOOH above 300°C was good and according to chemical analysis and X-ray diffraction patterns they were very pure $\alpha\text{-Fe}_2\text{O}_3$.

CONCLUSIONS

The preparation of high quality yellow FeOOH pigments from FeSO_4 solution by alkali precipitation and gas oxidation methods is not simple. The result depends on so many experimental factors that the process is difficult to control. Preparation was possible under both acidic ($\text{pH} = 3$) and very

alkaline (pH \approx 13) conditions at low temperature. With respect to colour, the pigments obtained with NH_3 under acidic conditions were better than those obtained with NaOH under alkaline conditions, but the yellow colour was still slightly dirty, even in the best samples.

ACKNOWLEDGEMENTS

The authors are indebted to Teknos-Maalit Oy, Arabia Oy and Kemira Oy, Vuorikemia Division, for their cooperation and assistance in the characterization of the pigments. Discussions with Professor Lauri Niinistö during the work were of valuable assistance.

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