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PREPARATION OF RED IRON OXIDE PIGMENTS BY THERMAL TREATMENT OF IRON(II) SULFATE

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ABSTRACT

Preparation of red α-Fe_2O_3 pigments by thermal treatment of $FeSO_4 \cdot 7H_2O$ has been investigated by batch experiments; for comparison some thermoanalytical curves were recorded. The pigments obtained were characterized by measuring their colour coordinates, particle size distribution curves, and by estimating their hiding power. Under isothermal conditions in air, orange pigments were obtained at 600°C while the preparation of dark red pigments required calcination at 800°C. Also the increase of heating time darkened the colour by increasing the particle size of the pigments. In dynamic air and oxygen atmospheres the decomposition temperatures were appreciably higher than under static conditions. If less pure raw material was used, higher temperatures were needed in calcination. The colour of the oxides prepared from technical $FeSO_4 \cdot 7H_2O$ were also somewhat darker than that of the oxides prepared from analytical grade material.

INTRODUCTION

Various oxides of iron are the most important materials in the group of red and brown inorganic pigments. Iron oxide pigments are available in the nature as minerals but they can also be manufactured by chemical processes. The reasons for the large-scale synthetic production are twofold. Firstly, the natural iron oxides are impure as well as inhomogeneous. Secondly, large amounts of waste iron salts originating from iron and steel pickling and titanium dioxide production from ilmenite with sulfuric acid, are available as cheap raw material for synthetic iron oxide pigments (ref. 1).

The most common starting material for the manufacture of the synthetic iron oxides is the iron(II) sulfate heptahydrate $FeSO_4 \cdot 7H_2O$, coming mainly from the titanium dioxide process, but chlorides may be used as well (ref. 2). The colour range of the synthetic materials comprises yellow, red, brown, and black. Among these the red pigments are most important and they have extensive applications.

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Two principal processes have been developed for red iron oxide pigments using sulfate as starting material: (i) calcination of $FeSO_4 \cdot 7H_2O$ in oxidative atmosphere and (ii) precipitation of iron in solution by alkali addition to obtain a hydrated oxide which is then calcinated. The calcination process may utilize pure $FeSO_4 \cdot 7H_2O$ as starting material (refs. 3,4) or $FeSO_4 \cdot 7H_2O$ containing some additives, e.g. cellulosic materials, zinc sulfate, kieselguhr, sodium carbonate (refs. 5-8). In the precipitation method, iron is precipitated by alkali addition and simultaneously oxidized by air or oxygen flow into yellow FeOOH pigments. The yellow material is then fired to a red Fe_2O_3 pigment; a lower temperature is needed than in the direct firing of $FeSO_4 \cdot 7H_2O$ (refs. 9,10). Furthermore, the recovery problem due to escaping sulfur oxides is avoided in the precipitation method.

Some further methods of preparation for red Fe_2O_3 pigments have been reported. They include the slow precipitation of oxide from solution in presence of oxygen and metallic iron powder and the calcination of black iron oxide pigments, having the composition Fe_3O_4, in oxidative atmospheres (refs. 11-13). These methods are of minor importance, however, as compared to the two main types of processes.

The aim of the present work was to study the preparation of red iron oxide pigments from iron(II) sulfate heptahydrate. Especially, the effect of experimental conditions on the characteristics of the pigments was investigated.

EXPERIMENTAL

One gram samples of $FeSO_4 \cdot 7H_2O$ were isothermally fired in a muffle furnace inside a 20 cm^3 porcelain crucible under static air atmosphere. In experiments with dynamic gas atmosphere (100 $cm^3\ min^{-1}$) a tube furnace with a quartz boat inside a 50 cm^3 quartz reactor was employed. Temperature was measured inside the furnace near the sample with an accuracy of 5°C. Both pro analysis grade iron(II) sulfate heptahydrate and a waste material of technical grade from a TiO_2 factory were used in the experiments.

After firing the composition of the product was studied by means of X-ray powder diffraction. The oxide product was washed with 500 cm^3 of hot distilled water and the content of water soluble salts was determined gravimetrically.

The pigments obtained were mixed with a colourless urethane lacquer (Helo produced by Teknos-Maalit Oy) into paint (1:13, w:w) in an Automatic Muller 2000 mixer (made by Braive Instruments). A paint layer with thickness of 200 μm was spread on a glass sheet for colour measurements. The colour coordinates were determined with a standard method by recording the percentage of reflection of the layers when irradiated with standard blue, green and red light. The colour coordinates were calculated from the reflection values; the apparatus used was a Colormaster V from Meeco Instruments. The determination of hiding power of the pigments is generally difficult; an estimate can be obtained when the reflection properties are recorded against black and white backgrounds as was done in this work.

The particle size measurements were carried out with a transmission electron microscopy (JEOL JEM 100). The samples were disperged in a solution of dibutylftalate in nitrocellulose and amyl alcohol. The TEM photos (magnification 10 000x), were analyzed with a computerized system which calculated the size and distribution of the particles. In each distribution determination the size of 500-600 particles was calculated.

The samples were also studied by thermoanalytical methods using a Perkin-Elmer TGS-2 thermobalance and DTA-1700 equipment connected to System 7/4 controller and TADS data station.

RESULTS AND DISCUSSION

The TG curve of $FeSO_4 \cdot 7H_2O$ in dynamic air atmosphere is presented in Fig. 1. Under these conditions, the dehydration of $FeSO_4 \cdot 7H_2O$ takes places in three steps. At first three water molecules are released below 100°C followed by the loss of three molecules of water at 140°C. According to the TG curve the last water molecule starts to escape above 400°C, but it is difficult to determine the exact temperature because the oxidation process of iron occurs simultaneously. The trivalent sulfate $Fe_2(SO_4)_3$ decomposes to an oxide with a DTG maximum at 695°C. The X-ray diffraction pattern of the product corresponds to hexagonal α-Fe_2O_3. The TG results as well as the DTA pattern (Fig. 2) are in good agreement with literature data, see for instance ref. 14.

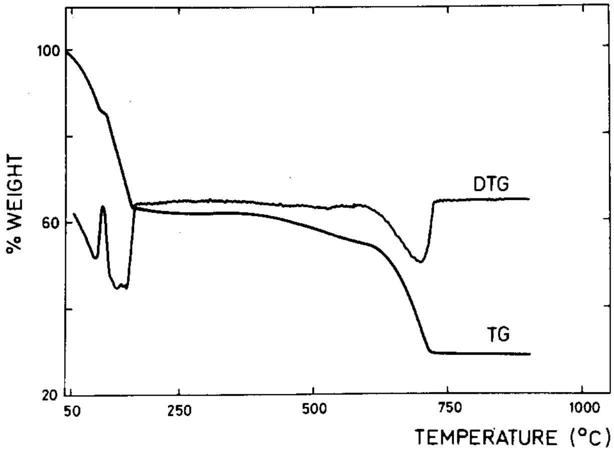

Fig. 1. TG curve of $FeSO_4 \cdot 7H_2O$ heated in dynamic air atmosphere ($10^{o}C\ min^{-1}$). Sample weight 29.6 mg.

The iron(III) oxide pigments studied were mainly prepared in isothermal batch experiments. The properties of the pigments obtained were compared to three commercial red pigments 110M, 130M and 180M, manufactured by Bayer, Leverkusen, FRG (Table 2). The particle sizes and colours determined for these commercial pigments are in good agreement with the values given by the producer.

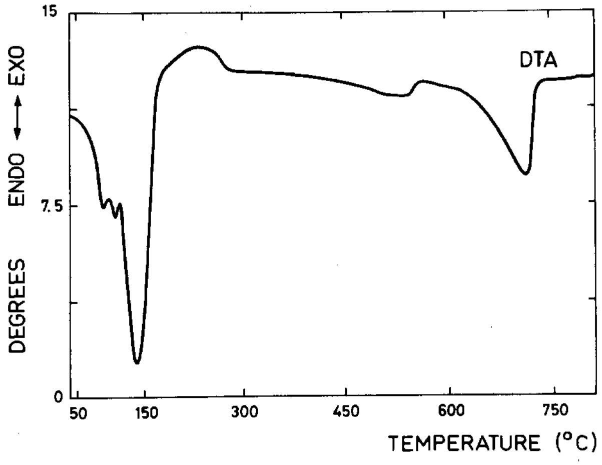

Fig. 2. DTA curve of $FeSO_4 \cdot 7H_2O$. Reference material Al_2O_3, heating rate $10^{o}C\ min^{-1}$, sample size 10 mg, dynamic air atmosphere.

TABLE 1

Preparative conditions, colour coordinates and particle sizes of some Fe_2O_3 pigments prepared from pro analysis pure $FeSO_4 \cdot 7H_2O$.

Heating temp. (°C)	Heating time (h)	Heating conditions	Water soluble compounds (%)	Colour	Colour coordinates X	Colour coordinates Y	Particle size (µm)
600	2	static air	1.1	orange	.52	.39	.11
750	2	"	.1	red brown	.54	.38	.16
750	5	"	<.1	"	.53	.37	.18
800	3	"	<.1	dark red	.51	.35	.31
800	5	"	<.1	"	.51	.35	.30
850	2	"	<.1	"	.47	.35*	.35
900	1	"	<.1	"	.45	.33*	.49
750	3	dynamic air	.2	orange	.53	.38	.09
800	1	"	.2	"	.53	.38	.09**
850	3	"	<.1	red brown	.53	.37	.19
850	2	"	<.1	"	.53	.37	.17**
900	3	"	<.1	dark red	.52	.36	.28
850	2	dynamic O_2	<.1	dark red	.50	.36	.28
900	1	"	<.1	"	.47	.35	.35

* poor opacity

**slower gas flow

In static air atmosphere using isothermal conditions below 600°C the product is mainly iron(III) sulfate. Above this temperature the chemical composition of the products corresponds exactly to Fe_2O_3. The colour of the oxide is orange at 600°C and the particle size is small, about 0.1 µm corresponding to the commercial pigment 110M. An increase in heating time and temperature darkens the colour and increases the particle size of the oxide. The pigments calcined at 800°C for three hours are dark red with particle size of 0.3 µm and thus near to the commercial 180M. The intermediate modification corresponding to 130M with red brown colour is obtained in static atmosphere when fired at 700-750°C for 2-3 hours.

In dynamic air atmosphere the decomposition temperatures are clearly higher than in static conditions. The preparation of orange α-Fe_2O_3 pigments requires a temperature of 750°C whereas the same quality was obtained in static conditions at 600°C. With dark red pigments the difference in calcination temperatures between static and dynamic conditions decreases but is, however, 50-100°C. The reason for the need of higher temperatures may be due to the cooling effect of the cold flowing gas and, partially, to the different furnace and crucible geometries. A decrease of the normal rate of gas flow from 100 to 50 $cm^3\ min^{-1}$ had not a significant effect on the product (Table 1).

The use of oxygen as flowing gas did not have significant effect on the formation of oxide as compared to air. The particle sizes are slighly larger when oxygen is used but the colour of the products was nearly identical in both cases.

If less pure $FeSO_4 \cdot 7H_2O$ of technical grade is used as raw material, higher temperatures are needed for the oxide formation when compared to analytical grade raw material. With respect to particle size the temperature increase is more than 100°C but with respect to colour only about 50°C (Table 2). This means that the colour in the oxides prepared from technical raw material is darker than in oxides from pure material. This may be due to the impurities in the technical $FeSO_4 \cdot 7H_2O$. The amount of the water soluble compounds is also higher in the pigments fired from technical raw material.

TABLE 2

Preparative conditions, colour coordinates and particle sizes of some Fe_2O_3 pigments prepared from technical $FeSO_4 \cdot 7H_2O$. The values recorded for the three commercial pigments are also presented.

Heating temp. (°C)	Heating time (h)	Heating conditions	Water soluble compounds (%)	Colour	Colour coordinates X	Colour coordinates Y	Particle size (μm)
700	1	static air	8.8	orange	.51	.38	.09
800	3	"	4.7	"	.52	.38	.11
850	1	"	.4	red brown	.52	.37	.16
850	2	"	.3	dark red	.51	.37	.21
900	1	"	.1	"	.48	.35	.31
Commercial pigments		110M	.4	red brown	.55	.38	.09
		130M	.3	"	.55	.37	.17
		180M	.2	dark red	.51	.35	.33

The hiding power of the red α-Fe_2O_3 pigments, determined as difference of colour coordinates measured against black and white backgrounds, is usually good. Some exceptions were noticed, however. Oxides fired in static air atmosphere at high temperature (about 900°C) have poor opacity; the reason for this has remained unclear. On the other hand, if the products, prepared at lower temperatures, contain even a small amount of $Fe_2(SO_4)_3$ the hiding power decreases significantly.

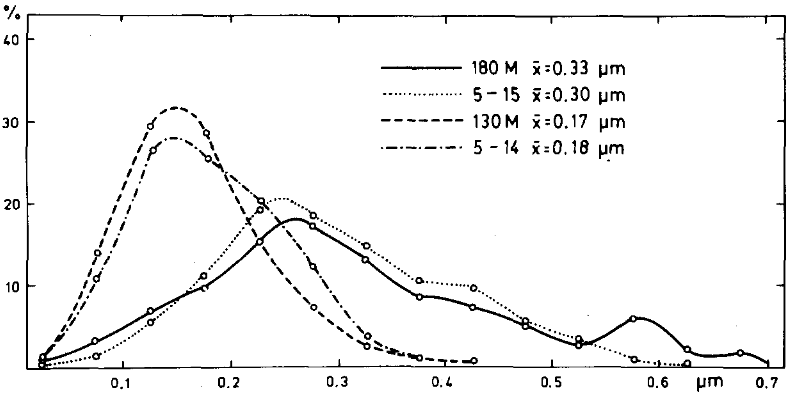

Fig. 3. Particle size distribution curves for some red Fe_2O_3 pigments. The preparative conditions for samples 5-14 and 5-15: heating 5 hrs in a static air atmosphere at 750 and 800°C, respectively.

The particle size distribution curves for some pigments prepared in the present work as well as for some of the commercial ones are presented in Fig. 3. It can be seen that the darker pigments have more inhomogenious particle size distributions. The growing rate of the particles thus differs in the sample. The mean particle size of the dark pigments is about 0.3 µm but they may contain a remarkable number of particles with sizes above 0.5 µm. The shapes of the particles as well as the particle size distribution curves of the pigments prepared in the present work are closely similar to those measured for the commercial ones.

CONCLUSION

Red iron(III) oxide pigments of satisfactory colour and particle size characteristics can be prepared by thermal treatment of iron(II) sulfate heptahydrate which is available as an inexpensive raw material in excess of demand.

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