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A NEW SERIES OF MATERIALS CONTAINING BASIC SULPHATES OF IRON(III)

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Abstract

Series of basic sulphates which were precipitated by the hydrolysis of $Fe(OH)SO_4$ in the presence and absence of metallic iron were studied from compositional, crystallographic and thermal decomposition points of view. The results are presented and discussed. It was found that high pure iron oxides as well as high grade red iron oxide pigments can be obtained by agitating the basic sulphates in hot ammonical medium followed by roasting. Commercial exploitation of the results is suggested.

Keywords: application as high pure iron oxides and pigments, basic sulphates of iron(III), chemical composition, $Fe(OH)SO_4$, hydrolysis, kinetics of decomposition, X-ray crystallography, washing of basic sulphates

Introduction

Basic sulphates of iron(III) are the products resulting from the hydrolysis of iron(III) and iron(II) salts [1]. When normal salts of iron(II) and iron(III) such as the chloride, sulphate and nitrate [the last one only in case of iron(III)] are hydrolysed, the hydrolysis goes to some extent and then stops. The degree of hydrolysis naturally depends on (1) the temperature of the hydrolytic reaction and (2) the concentration of the salt used. However, in all such cases, the degree of hydrolysis is not favourable for commercial exploitation of the products of hydrolysis. It has been felt, therefore, that the hydrolysis of basic salts such as $Fe(OH)SO_4$ may be attempted to get a favourable degree of hydrolysis so that the products obtained may be studied for commercial exploitation.

It is now well established that the basic sulphate, $Fe(OH)SO_4$, is produced during the solid-state thermal decomposition of hydrates of iron(II) sulphate [2, 3]. However, no attempt has been made till now, to study the hydrolysis of

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[*] Left the laboratory to settle in domestic life.

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this salt from application point of view. A detailed investigation of this aspect has been made in this laboratory by the author and his colleagues. A small portion of this work has appeared in the literature which will be quoted in this communication at appropriate places.

The hydrolysis of $Fe(OH)SO_4$ was carried out in two ways: the first is a simple hydrolysis involving the system: $Fe(OH)SO_4+H_2O$ (System-1) and the other involving the system: $Fe(OH)SO_4+Fe+H_2O$ (System-2), that is hydrolysis in the presence of metallic iron.

Experimental

Materials

The starting material required for this investigation is iron(II) sulphate heptahydrate of Analytical Reagent grade. The basic sulphate, $Fe(OH)SO_4$, was obtained by solid-state hydrolysis of the heptahydrate as described earlier [2]. The products of hydrolysis were prepared as per the earlier communication [4].

Apparatus

The apparatus used for the thermal decomposition studies was a Derivatograph, Model OD-102, supplied by M/s. Metrimpex, Budapest, Hungary. The apparatus records simultaneously and photographically, the TG, DTG and DTA curves on a temperature-weight calibrated photographic paper. The sample cups are cylindrical and are made of Platinum-Rhodium alloy, made to order in India.

To study the phases formed during the hydrolysis of $Fe(OH)SO_4$, a Philips automatic Powder diffractometer of 1700 series, was used.

Methods

For the thermal decomposition studies, 300 to 400 mg of the sample was loaded into the sample cup by gently tapping three times after each addition. α-alumina also was loaded into the reference cup in the same manner. The thermal decomposition experiments were carried out from ambient to 1000°C under self-generated and static atmosphere.

To get the X-ray diffraction patterns, about 500 mg of the sample passing through a 100 mesh sieve (Indian standards) was used. The diffractograms were obtained using copper K_α radiation with a scanning rate of 2° min^{-1}

To get chemical composition of the products of hydrolysis, the iron content was determined by the standard dichromate method [5] and the sulphate content by the standard barium sulphate method [6].

The kinetics of thermal decomposition were evaluated using the nine reaction models used earlier [7]. To fit the thermal decomposition data (α, T) into various models, a LOTUS SPREAD-SHEET MACRO programme was used for obtaining R^2 values as well as linear kinetic equations. An account of this programme was presented elsewhere [8].

Results and discussion

Products of hydrolysis

Compositions

The hydrolysis products were obtained at six different temperatures (15, 20, 27.5, 40, 60 and 80°C) and three concentrations (5, 10 and 15 g l^{-1} suspensions). The chemical compositions of basic sulphates obtained in the System-1 [$Fe(OH)SO_4+H_2O$] were presented elsewhere [4]. The compositional aspects of basic sulphates obtained in the System-2 [$Fe(OH)SO_4+Fe+H_2O$] are given in Table 1. Typical X-ray crystallographic data are presented in Tables 2 and 3.

Table 1 Compositions of basic sulphates obtained by the hydrolysis of $Fe(OH)SO_4$ in the presence of metallic iron

No.	$T_{hydrolysis}$/ °C	$C_{suspension}$/ g l^{-1}	Composition of the products	Cryst. phases
1	15	5	X0.125Y1.66Z	α-FeOOH ε-Fe_2O_3
2	15	10	X0.144Y1.7617	–do–
3	15	15	X0.226Y1.975Z	–do–
4	20	5	X0.163Y1.806Z	–do–
5	20	10	X0.222Y1.743Z	–do–
6	20	15	X0.123Y1.776Z	–do–
7	27.5	5	X0.177Y2.301Z	–do–
8	27.5	10	X0.162Y1.882Z	–do–
9	27.5	15	X0.03Y 1.635Z	–do–
10	40	5	X0.040Y1.251Z	–do–
11	40	10	X0.048Y1.614Z	–do–
12	40	15	X0.090Y1.471Z	–do–
13	60	5	X0.069Y1.456Z	–do–
14	60	10	X0.053Y1.629Z	–do–
15	60	15	X0.051Y1.163Z	–do–
16	80	5	X0.069Y1.546Z	–do–
17	80	10	X0.064Y1.376Z	–do–
18	80	15	X0.065Y2.631Z	–do–

$X=Fe_2O_3$; $Y=SO_3$; $Z=H_2O$

The hydrolysis products obtained in the System-1 are highly complex basic sulphates precipitated along with simple compounds such as β-FeOOH, α-Fe_2O_3 etc. The basic sulphates identified in this system were: $Fe_2O_3{\cdot}2SO_3{\cdot}nH_2O$ and $1/2(3Fe_2O_3{\cdot}4SO_3{\cdot}9H_2O)$ (Table 2). The sulphate is also associated with the normal slats mentioned above presumably as occluded one [4].

The hydrolysis products obtained in the System-2 are normal compounds and are invariably the α-FeOOH and ε-Fe_2O_3 (Table 3). These compounds also have some sulphate as evidenced by their chemical compositions (Table 1). The

Table 2 Typical X-Ray crystallographic data for basic sulphates from System-1 ($Fe(OH)SO_4+H_2O$)

No.	d/Å(I/I_o)	d/Å(I/I_o) standards		
	(exptl.)	$Fe_2O_3{\cdot}2SO_3{\cdot}nH_2O$*	β-FeOOH**	$1/2(3Fe_2O_3{\cdot}4SO_3{\cdot}9H_2O)$***
1. Basic sulphate: $Fe_2O_3{\cdot}1.1SO_3{\cdot}2.3H_2O$				
1.	5.1(62)	5.05(20)	–	5.11(95)
2.	4.78(57)	4.75(4)	–	–
3.	4.53(43)	–	–	–
4.	3.59(48)	3.56(60)	–	–
5.	3.27(100)	3.25(100)	3.31(100)	–
6.	3.22(79)	3.20(80)	–	–
7.	3.13(60)	–	–	3.13(95)
9.	2.29(33)	2.28(20)	2.29(40)	2.27(40)
10.	2.08(33)	2.05(20)	2.06(20)	–
11.	1.99(38)	1.99(20)	1.94(60)	1.99(40)
15.	1.56(29)	1.55(40)	1.52(40)	–
2. Basic sulphate: $Fe_2O_3{\cdot}0.2SO_3{\cdot}2.4H_2O$				
		ε-Fe_2O_3^{1}	δ-FeOOH^2	
1.	4.26(80)	–	–	
2.	2.72(86)	2.74(20)	–	
3.	2.52(95)	–	2.55(100)	
4.	2.48(100)	2.46(100)	–	
5.	2.27(59)	–	2.26(100)$_B$	
6.	1.74(71)	1.74(60)	1.69(100)$_{VB}$	
7.	1.52(71)	1.52(100)	–	

X-Ray Card Index Numbers:
*21-928(1980), **13-157(1972), ***18-653(1974)
1.16-895(1974), 2.13-87(1972). B: broad, VB: very broad.

X-ray diffraction results however, did not show the presence of any basic sulphate. Hence it may safely be assumed that the sulphate in these series of products is present as adsorbed or occluded one. The absence of any basic sulphate in System-2 is attributed to the presence of metallic iron which

Table 3 Typical X-Ray crystallographic data for basic sulphates from System-2 ($Fe(OH)SO_4+Fe+H_2O$)

No.	$d/Å(I/I_o)$ (exptl.)	$d/Å(I/I_o)$ standards ε-Fe_2O_3*	$d/Å(I/I_o)$ standards α-FeOOH**
1. Basic sulphate: $Fe_2O_3{\cdot}0.125SO_3{\cdot}1.663H_2O$			
1.	4.93(27)	–	4.98(10)
2.	4.19(63)	–	4.18(100)
3.	3.39(19)	–	3.38(10)
4.	2.68(50)	–	2.69(30)
5.	2.56(47)	2.55(20)	2.58(8)
6.	2.45(100)	2.46(100)	2.45(25)
7.	2.24(28)	2.24(60)	2.25(10)
8.	2.19(28)	2.18(10)	2.19(20)
17.	1.45(27)	1.47(100)	1.45(10)
18.	1.42(12)	1.43(10)	1.42(2)
19.	1.36(17)	1.39(20)	1.36(8)
2. Basic sulphate: $Fe_2O_3{\cdot}0.065SO_3{\cdot}2.631H_2O$			
1.	4.93(23)	–	4.98(10)
2.	4.15(72)	–	4.18(100)
3.	3.39(16)	–	3.38(10)
4.	2.68(56)	–	2.69(30)
5.	2.58(51)	2.55(20)	2.58(8)
6.	2.44(100)	2.46(100)	2.45(25)
7.	2.24(25)	2.24(60)	2.25(10)
8.	2.18(33)	2.18(10)	2.19(20)
16.	1.57(54)	1.54(30)	1.56(16)
17.	1.51(54)	1.52(100)	1.51(10)
20.	1.42(17)	1.43(10)	1.42(2)
21.	1.36(20)	1.39(20)	1.36(5)

X-Ray Card Index * 16–895 (1974), ** 17–536 (1974)

Table 4 Thermal decomposition data for the products of hydrolysis of $Fe(OH)SO_4$

No.	$-H_2O$/	Cryst. trans./	$-SO_3$/	Nature of cryst. trans.
		°C		
1.	50–450(205)	525–565(550)	550–810 (565,745)	β to α Fe_2O_3
2.	50–490 (225,220,385)	490–545(525)	525–800 (565,755)	–do–
3.	40–335(275)	475–565(545)	565–705(675)	δ to α Fe_2O_3
4.	40–415(220)	545–615(595)	615–795(715)	β to α Fe_2O_3
5.	40–280(230)	495–555(525)	525–590(555)	–do–
6.	40–405(205)	565–650(635)	650–770(735)	ε to β Fe_2O_3
7.	40–415(210)	535–645(590)	625–780(745)	ε to α Fe_2O_3
8.	40–470(230)	530–650(610)	650–830(790)	ε to α Fe_2O_3
9.	40–415(215)	480–565(535)	595–760(715)	β to α Fe_2O_3
10.	40–260(185) 260–410(310)	510–575(535)	595–770(725)	δ to α Fe_2O_3
11.	40–400(235)	460–570(535)	600–750(720)	δ to α Fe_2O_3
12.	40–270(200) 270–395(290)	490–550(530)	600–750(710)	δ to α Fe_2O_3
13.	40–250(160) 250–395(295)	515–600(540)	600–750(715)	ε, δ to α Fe_2O_3
14.	40–270(185) 270–425(315)	520–595(555)	625–775(735)	ε to α Fe_2O_3
15.	40–220(140) 220–375(285)	530–585(550)	585–710(685)	–do–
16.	40–220(125) 220–360(280)	530–560(540)	590–690(665)	–do–
17.	40–235(165) 235–390(305)	525–80(565)	580–765(720)	–do–

1. The figures in the parantheses indicate DTA peaks
2. The DTA peaks are endothermic for water and SO_3 losses and exothermic for crystal transformations

immediately neutralises the acid liberated by the hydrolytic reaction. The accumulating acid in the absence of metallic iron is assumed to be the reason for the formation of complex basic sulphates.

From Table 1 we observe that the compositions of the products in System-2 vary over a wide range. The sulphate content varies from 0.03 to 0.226 mol of SO_3 per mol of Fe_2O_3 where as the water content varies from 1.163 to

2.631 moles of water per mol of Fe_2O_3. Similar variations were observed in the case of products obtained in System-1 where [4] the SO_3 content varies from 0.24 to 2.35 and water from 0.5 to 6.89 moles per mol of Fe_2O_3. These wide variations together with absence of any trends of these entities with temperature or concentration (e.g., no systematic variation of sulphate content either with temperature or amount of $Fe(OH)SO_4$ used for hydrolysis), shows that the products are not equilibrium compounds.

Thermal decomposition of the products

The products obtained in the System-1 show three prominent regions of weight loss. They are: (1) loss of water which generally occurs in the temperature region of 40–500°C, (2) crystalline transformations which occur in the region of 460–650°C and (3) loss of SO_3 (desulphurisation) which generally occurs in the region 550–810°C. Again, water loss as well as desulphurisation may occur, in some cases, in two or more sub-steps. Some crystal transforma-

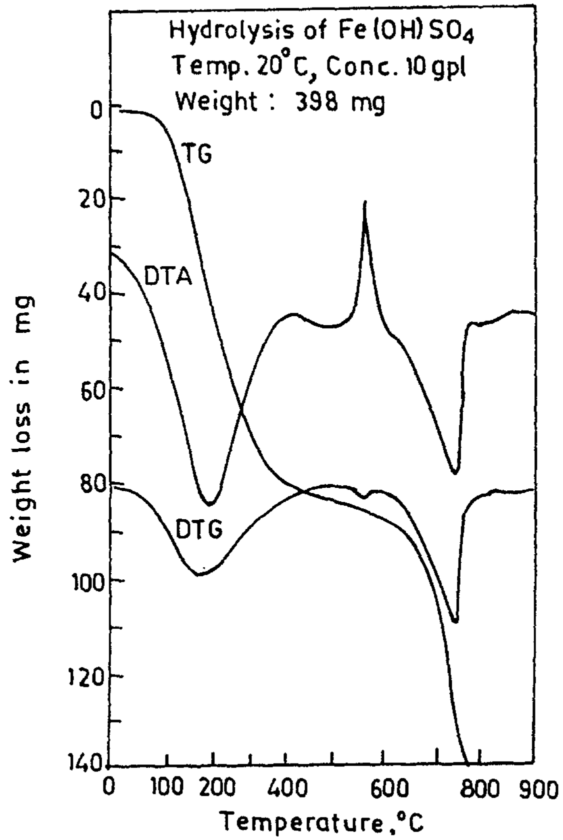

Fig. 1 Typical thermal decomposition of a basic sulphate obtained by the hydrolysis of $Fe(OH)SO_4$

tions are not evident on the DTA curves, as they occur along with water loss and hence are masked. Their presence was ascertained by heating the product to different temperatures and examining the product thus obtained by X-ray powder diffraction analysis. Such studies did reveal the transformations such as: α-FeOOH to ε-FeOOH, δ-Fe_2O_3 to α-Fe_2O_3, ε-Fe_2O_3 to α-Fe_2O_3. The detailed thermal data are presented in Table 4. Typical thermal decomposition patterns is presented in Fig. 1. From the above data the following observations may be made.

Where the loss of water occurs in single broad step and comparitively at lower temperatures the water is mostly present as adsorbed or occluded one, the rest being structural.

The activation energies reflect this by being low (8–10 kJ mol^{-1}). Where a broad peak occurs with higher *E*, the peak extends to higher temperatures and

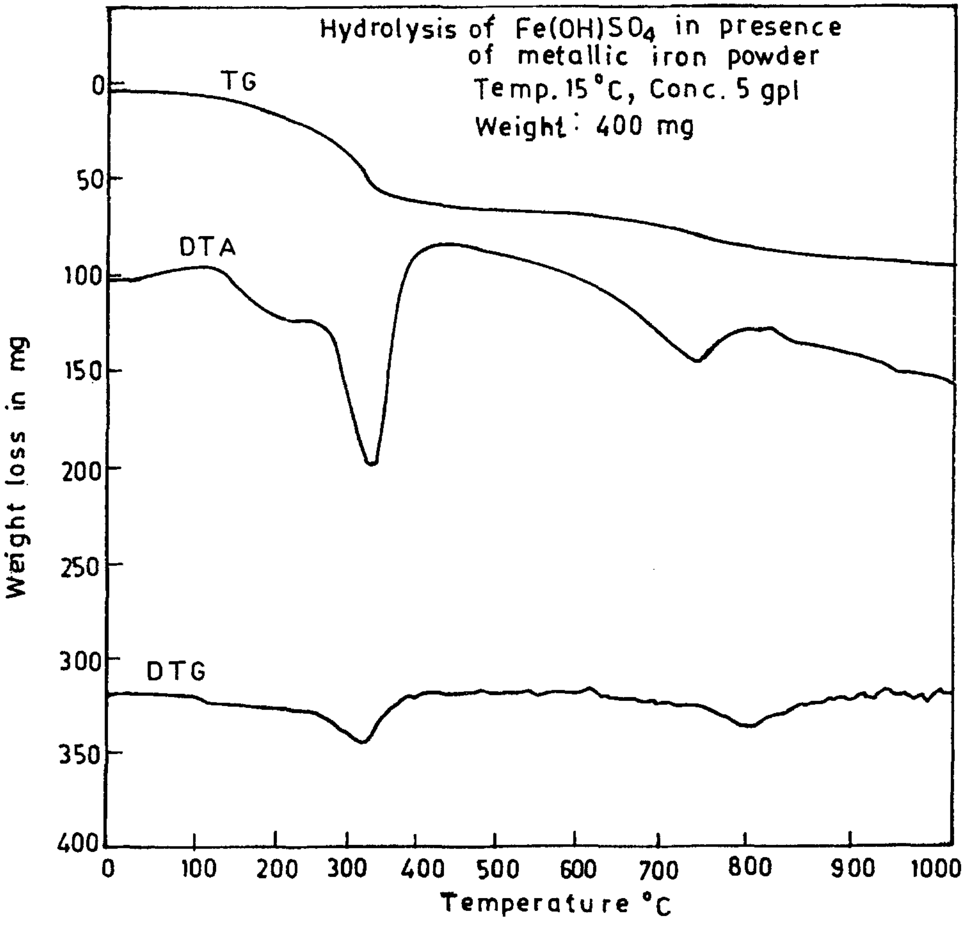

Fig. 2 Typical thermal decomposition of a basic sulphate obtained by the hydrolysis of $Fe(OH)SO_4$ in the presence of metallic iron

is a combined effect of adsorbed as well as structural water (The proportions of adsorbed and combined water are indicated, presumably by the magnitude of the *E* value). Where water is lost in two steps, the first one occurs at a lower temperature with a broad peak and lower *E* value and the second one occurs as a much sharper one and at higher temperature regions and has invariably higher *E* value. It is easy to understand such cases as the first one naturally is the adsorbed and the second one is combined water. Where the loss of SO_3 occurs with a single sharp DTA peak with medium (ca. 50) to high *E* value (more than say 100 kJ mol^{-1}), then it is a part of single basic sulphate. Where its loss is represented by two sharp DTA peaks with *E* values one medium and other high then the sulphate is distributed between two types of basic sulphate. The tem-

Table 5 Thermal decomposition data for the products of hydrolysis of $Fe(OH)SO_4$ in the presence of metallic iron

No.	$-H_2O$/	Cryst. trans./ °C	$-SO_3$/	Nature of cryst. trans.
1	RT–420(330)	*	560–800(740)	ε to α Fe_2O_3
2	100–405(300)	*	580–800(710)	–do–
3	100–410(200,290)	*	580–780(710)	–do–
4	40–330(200,300)	*	590–760(730)	–do–
5	40–300(235)	*	470–670(510)	–do–
6	40–230(140) 290–360(300)	*	610–730(680)	–do–
7	55–415(205,295)	*	550–745(705)	–do–
8	RT–395(305)	*	565–785(685)	–do–
9	265–405(315)	*	+	
10	240–395(315)	*	+	
11	260–400(320)	*	+	
12	265–405(330)	*	+	
13	240–350(290)	*	+	
14	180–370(280)	*	+	
15	240–370(300)	*	+	
16	60–240(130) 240–400(320)	*	+	
17	240–380(310)	*	+	
18	200–400(310)	*	+	

1. * Could not be accurately determined as transformation and water loss overlap. The transformation was ascertained by separate experiments as described in the text.
2. + Continuous loss without any peak
3. Figures in the parantheses, DTA peak temperatures
4. The peaks are endothermic for water and SO_3 loss and exothermic for crystal transformation

perature of the DTA peak depends presumably on the type of basic sulphate that decomposes.

The products obtained in the System-2 also have three regions of thermal change. They are the water loss, the crystal transformation and desulphurisation. Water loss may start right from the room temperature and may consist of a shoulder followed by a sharp peak (Fig. 2) or a broad split peak or may occur as one broad peak followed by a sharper one. In case where a shoulder occurs, it represents a null reaction between endothermic loss of adsorbed water and an exothermic crystal transformation. In all other cases, the first part with lower E represents adsorbed water and the second sharper peak with higher E represents the combined water. The thermal data are presented in Table 5.

The crystal transformations are invariably ε-Fe_2O_3 to α-Fe_2O_3 and are masked in majority of cases by the huge water loss peaks. Their presence was ascertained as mentioned earlier.

The sulphate loss occurs in the region 470–590°C. Firstly, the loss occurs in a lower temperature range than the previous case. Secondly, the loss occurs in a single step and hence it is bound only one way and as the activation energy is very much lower for the decomposition it is concluded that it is not present as crystallographic entity. When the sulphate is present in the lower range (0.03 to 0.09 mol SO_3 per mol Fe_2O_3), no DTA peak was observed and the loss of SO_3 occurs continuously in the whole temperature region pertaining to desulphurisation.

Kinetics of thermal decomposition

The kinetic parameters were determined in each case of dehydration and desulphurisation. Wherever the sub-stages are well defined, the kinetic data were obtained separately for each sub-step.

The thermal decomposition data (α, T) were fitted into the general equation:

$$\ln g(\alpha) = -E/RT + \ln A \tag{1}$$

In majority of cases for the basic sulphates of System-1 the mechanism of dehydration as well as desulphurisation involves random nucleation A_3 of Avrami. In a few other cases the mechanisms R3 and D1 are also followed. Wherever the diffusion is the mechanism, the activation energy remained very low. The loss of water following a diffusion path in some cases may be attributed to the simplicity of the matrix. Other cases of activation energy were already discussed under section, 'Thermal decomposition of products'.

In majority of cases, the kinetics of dehydration of water for the basic sulphate of System-2 also follow random nucleation model A_3 of Avrami. Considerable dehydration also follows the model: $g(\alpha)=\alpha^2$. The activation energies for both water loss and SO_3 loss are very low when compared to the other system. This is expected as the compounds in this series are simple ones and the combined water is associated with α-FeOOH. In the System-1, the various forms of FeOOH and the basic sulphates are present together in a complex matrix and hence the water was not easily removed.

Washing of the basic sulphates

Washing of the basic sulphates is necessary to remove the sulphate present in them to make them suitable for application as high pure materials or high grade pigments. Washing consisted of vigorous agitation of suspensions in cold and hot water and in cold and hot ammonical medium (ammonia water). The last operation was carried out as a reflux operation to prevent huge losses of ammonia during agitation. The basic sulphates obtained in the System-1 responded only to the last treatment where 100% removal was achieved. In case of System-2, removal of sulphate was observed in all cases of agitation but to different degrees: 5% with cold water, 10% with hot water, 50% with cold ammonical water and 100% with hot ammonical reflux. The time of agitation in all cases was 1 to 2 hours.

After all the sulphate was removed from these compounds, the oxides chiefly were; α-FeOOH, α-Fe_2O_3 and ε-Fe_2O_3. On roasting, they were converted to high-pure α-iron(III) oxide which also has very good red colour comparable to the imported synthetic iron red pigments.

Conclusion

Series of basic sulphates of iron(III), which were precipitated earlier by the hydrolysis of $Fe(OH)SO_4$ in the absence and presence of metallic iron, were studied from compositional, crystallographic and thermal decomposition points of view. It was found that high pure iron(III) oxides as well as high grade red oxide pigments can be obtained from these basic sulphates by hot ammonical treatment of these products followed by roasting. Commercial exploitation of the results suggested.

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