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Studies on Black Iron Oxide Pigment. Part I: Effect of Preparation Parameter on Physical and Optical Properties of Ferrosoferric Oxide

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Abstract

Black iron oxide pigment has been successfully prepared by traditional method. Ferrous sulphate was used as the starting iron source. The effect of amount of acid, type and amount of alkali and oxidizing agent on colour and yield were also studied. It was found that, the conversion of insitu produced ferrous chloride to ferrosoferric oxide yielded brilliant colour hue than that produced directly from ferrous sulphate. The produced ferrosoferric oxide were analyzed for purity and characterized for physical properties to be used as a pigment. The prepared samples were found to be comparable with BAYER bayferrox 318. Statistical evaluation also confirmed the experimental result.

Key words : Black oxide pigment, Optical properties, Ferrous sulphate, Oxidizing agent

Itroduction

Iron based black pigment is termed as black iron oxide and is chemically known as ferrosoferric oxide represented by the formula Fe_3O_4 or $FeO.Fe_2O_3$. Black oxide is found in nature associated with ilmenite, clay and sand particle.

Two forms of black iron oxide pigment are known- the cubical form and the acicular form. The cubical form black iron oxide finds use as a pigment. It may be prepared by precipitating the intermediate from either ferrous sulphate or ferrous chloride solution with an alkali and then oxidized to black product. The second or acicular form of black iron oxide pigment is manufactured by chemically reducing red oxide or ferrite to give a black acicular shaped substance. As this paper discussed about the pigment grade, therefore only cubical form of black iron oxide pigment is included in this study.

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Synthetic black iron oxide pigments possess excellent bleed resistance, chemical resistance (against both acid and alkali), and lightfastness (both interior and exterior). It has also very low or negligible toxicity. Dispersibility is ranging from good to excellent. Heat resistance is rated only as good since the black iron oxide tends to oxidize to red iron oxide at about 350^{O}F (177^{O}C). Some other important physical properties are density (4.95-5.18 g/cm^{3}), oil absorption value (18-28 lb/100 lb), refractive index (2.42), hiding power (900-1200 lb/ft^{2}) and particle size, (0.1-0.8 mm) (Bayer 1991, Chapman And Hall 1966, David 1967, Fuller 1965, Kirk-Othmer 1968, Kerr And Howard 1965, Turner 1965, Ullmann 1995).

They can be applied as "metal protective" paint, in fiberglass reinforced polyesters, tire sealant and bullet proof fuel tanks, as a black colorant for use in Portland cement, concrete and other building compositions. They are also used in both primers and finish coats for structural steel, railway maintenance finishes, steel equipment and as a pigment in stains emulsion and water paint (Bayer 1991, Chapman and Hall 1966, David 1967, Fuller 1965, Kirk-Othmer 1968, Kerr and Howard 1965, Turner 1965, Ullmann 1995).

There are several methods for the preparation of black iron oxide pigment (Ayers and Joseph 1939, Budapesti *et. al.* 1963, Dobos *et. al.* 1963, Frey and Friedrich 1962, Farbenind 1936, Maruschek and Hans 1959, Manfred and August 1970, Reymer 1955, Srivastava *et.al.* 1958, Szigeti and Gyorgy 1961, Toma *et. al.* 1964, Williams *et. al.* 1941, Yoshiro 1958). The quality of the pigment and yield depend on a number of parameters. Among them, nature of iron source used, precipitating agent and oxidizing agent, concentration, temperature and pressure in the reaction tank, pH of the solution, rate of stirring etc. are important.

The objective of this study is to prepare pigment grade black iron oxide pigment by precipitation method and to characterize them. Correlation among the physical properties through correlation-matrix format and comparison with BAYER sample (Bayferrox 318 standard 88) through statistical evaluation by SPSS program also aimed at in this paper.

Materials and Methods

Commercial grade raw materials and chemicals were used for the production of black iron oxide pigment. Ferrous sulphate heptahydrate (97.87%), hydrochloric acid (32%), calcium hydroxide, sodium carbonate, sodium hydroxide, ammonium hydroxide (17%), sodium nitrate, hydrazine hydrochloride, phosphorous pentoxide and sodium hexametaphosphate were used in this research work.

Preparation of the product

The process for the preparation of the sample consists in the partial conversion of ferrous sulphate to ferrous chloride by reaction of

ferrous sulphate solution with hydrochloric acid. This ferrous chloride-ferrous sulphate solution was then treated with a precipitating agent in presence of an oxidizing agent at an elevated temperature. Stirring of the solution at a definite speed, passing of air at a definite rate and heating the content at a fixed temperature are the important criteria to precipitate the product. It was then washed with water to free it from alkali and dissolved unreacted salt, filtered and dried under vacuum.

The reaction that takes place during the operation may be represented by the equations as follows:

$$6FeSO_4+12HCI \longrightarrow 6FeCl_2 + 6H_2SO_4$$

$$6FeCl_2+12NH_4OH \longrightarrow 6Fe(OH)_2+12\ NH_4CI$$

$$6Fe(OH)_2+O_2 \xrightarrow[\text{(as oxidising agent)}]{NaNO_3} 2Fe_3O_4 + 6H_2O$$

Overall reaction:

$$6FeSO_4+12HCI+12NH_4OH +O_2 \xrightarrow[\text{(as oxidising agent)}]{NaNO_3} 2Fe_3O_4+6H_2SO_4+12NH_4CI+6H_2O$$

Five series of experiments were performed by varying reaction parameters like amount of hydrochloric acid, type and amount of precipitating agent and oxidizing agent. During these reactions, 100g ferrous sulphate heptahydrate was made 2.5 percent aqueous solution, temperature of the solution was kept fixed at $95^{O}C$ and rate of air passage was kept fixed at 20 lbs./min for each experiment. (These three fixed variables are achieved by doing several experiments earlier in this laboratory). All these products were purified, isolated, dried, pulverized and analyzed according to the standard procedure.

Measurement of properties

Determination of physical properties

Physical properties like spreadability, water wettability, pH-value of aqueous extracts (Bayer 1991 and Chapman and Hall 1966), sieve residue, oil absorption value, external surface area and average particle size (Bayer 1991, Chapman and Hall 1966 and Ullmann 1995), density (David 1967), atmospheric curing stability (ASTM 1992 and 1986, Bayer 1991, Chapman and Hall 1966 and Ullmann 1995), and light fastness (ASTM 1992 and 1961, Bayer 1991, Chapman and Hall 1966 and Ullmann 1995) of all pigments (both prepared and standard) were determined according to the standard procedure.

Determination of optical properties

Optical properties such as brightness (Bayer 1991, Chapman and Hall 1966 and Ullmann 1995) are determined by using Dr. Lange reflectometer of model Refo-3. Colour and tinting power (Bayer 1991, Chapman and Hall 1966 and Ullmann 1995) were evaluat-

ed by measurement of spectral reflectance in the visible region using UV spectrophotometer of model UV 2201, Shimadju, Japan.

Statistical evaluation

Statistical evaluation especially correlation among the analytical results, physical and optical properties which have numerical values, descriptive statistics of the methods and comparison of prepared samples with BAYER sample were carried out with the help of SPSS program (Howitt and Cramer 1999 and Mostafa 1984). The sample size for the variable pH-value, sieve residue, oil absorption value, contrast ratio, brightness, percentage of loss on ignition and density is 18 and that for external surface area and particle size is 10.

Results and Discussion

The effects of different precipitating agent on the yield and colour shade of the produts were shown in the Table I. Here, ammonium hydroxide, sodium hydroxide, sodium carbonate and calcium hydroxide were used as precipitating agent. The type of alkali, which was used as precipitating agent in the preparation of black iron oxide pigment, seems to have some important role in determining the colour and shade of the pigment. Table I depicts that ammonia produced the best pigment in respect of colour and shade in this series. Though the highest yield in this series was obtained with calcium hydroxide (107%), but the colour as well as FeO, Fe_2O_3, Fe_3O_4 content was not suitable (total Fe_3O_4 content is only around 89%). The analysis indicates that some calcium hydroxide remained with the pigment (around 10%), which affected the physical characteristics.

Actually ammonia is a protonic solvent (Manku 1980 and Sisler 1965) i.e. it has a strong tendency to pick up proton leaving ammoniated electron. These electrons are

Table I. Effect of different alkali on the yield and colour shade of black iron oxide pigment

Sample No.	Name of precipitating agent	Yield (g)	Percent of yield	Percent of Fe_3O_4	Percent of FeO	Percent of Fe_2O_3	Loss on ignition	Colour shade
1	Ammonium hydoxide	25.310	91.040	97.190	30.130	67.020	0.64	Black
2	Sodium carbonate	25.200	90.640	96.570	29.940	66.690	0.70	Dull black
3	Sodium hydroxide	25.330	91.110	98.630	30.570	68.010	0.56	Dull black
4	Calcium hydroxide	29.980	107.840	88.910	27.560	61.310	0.98	Dull black

Conditions:

a) Molar ratio of iron to hydrochloric acid used : 1:0.5
b) Molar ratio of iron to sodium nitrate : 1:0.16
c) Molar ratio of iron to precipitating agent : 1:3

believed to occupy the cavities in the solvent by ammonia molecules whose protons get oriented towards the free electrons. It also acts as reducing agent. Here ammonia acts as a solvent rather than a precipitating agent. In the preparation of black iron oxide pigment, both reduction and oxidation takes place. In aqueous system containing ferrous ion, ammonia was added into it in excess so that the reaction media became strongly ammoniated. The suspended ferrous ion was then converted to ammoniated ferrous ion. As the concentration of ammoniated ferrous ion and ammoniated electrons get increased, the ammoniated ferrous cations tend to bond together by ammoniated electron into aggregates to Fe_3. Then oxidation takes place to obtain ferrosoferric oxide.

The partial conversion of ferrous sulphate to ferrous chloride is necessary to control the ratio of Fe^{+2} and Fe^{+3} in the reaction medium. The rate of dissociation of ferrous sulphate is much higher than that of ferrous chloride. If we use ferrous sulphate solely, the quantity of Fe^{+2} available is higher than those required to take part in the reaction to form Fe_3O_4. As a result more number of Fe^{+2} are converted to Fe^{+3} resulting in reddish tint in the product, which affects the brightness.

In the Table II, the effect of amount of hydrochloric acid is shown. Here, six different molar ratio of iron to hydrochloric acid has been carried out. It is found that the molar ratio of iron to hydrochloric acid of 1:1.24 and 1:1.74 produce products (Sample No 7 and 8) with good colour tone. Between these two conditions, molar ratio of iron to hydrochloric acid 1:1.74 produces the best result in respect of colour and Fe_3O_4 content. Lower molar ratio than 1:0.5 or higher molar

Table II. Effect of amount of hydrochloric acid on the yield and colour shade of black iron oxide pigment

Sample No.	Molar ratio of iron to Hydrochloric acid	Yield (g)	Percent of yield	Percent of Fe_3O_4	Percent of FeO	Percent of Fe_2O_3	Loss on ignition	Colour shade
5	1:0.25	25.100	90.230	96.030	29.800	68.230	0.97	Blackish brown
1	1:0.50	25.310	91.040	97.190	30.130	67.020	0.64	Black
6	1:0.75	25.600	92.090	98.590	30.560	67.990	0.98	Black
7	1:1.24	25.300	91.010	98.790	30.620	68.120	0.91	Deep black
8	1:1.74	25.400	91.370	98.230	30.450	67.740	0.98	Deep black
9	1:2.23	25.300	91.010	98.310	29.270	69.040	0.99	Brownish black

Conditions:

a) Molar ratio of iron to sodium nitrate : 1:0.16

b) Molar ration of iron to ammonium hydroxide : 1:3

ratio than 1:1.74 affected the colour and other properties negatively. It may be due to the fact that, with much lower molar ratio, the required conversion to ferrous chloride was not completed. This resulted in the conversion of more Fe^{+2} ions to Fe^{+3} ions causing reddish tone in the pigment. With higher molar ratio, the free acid was used up by the alkali. At this, there was a shortage of precipitating agent for producing black iron oxide pigment causing the same negative effect.

The effect of the molar ratio of iron to precipitating agent in the preparation of black iron oxide pigment is shown in Table III. Seven experiments have been done in this series using different molar ratio of iron to ammonium hydroxide as precipitating agent. Molar ratio of iron to precipitation agent below 1:2.71 could not produce black iron oxide pigment in the desired form that could be separated by filtration. (Stoicheo metrically, for complete conversion of iron to ferrous hydroxide, the required molar ratio of iron to precipitating agent is 1:2). From this observation, it is clear that air should be passed through the reaction vessel in high alkaline medium. Otherwise, the ratio of Fe^{+2}: Fe^{+3} will not within the limit thereby producing gel type precipitation. Again, molar ratio more than 1:4.07 iron to precipitating agent could not improve yield or colour shade. The excess of precipitating agent added over the molar ratio 1:4.07 probably did not take part in the reaction and was washed away.

Precise control of oxidation seems to be the dominating parameter in the preparation of black iron oxide pigment. This control of

Table III. Effect of amount of ammonia on the yield and colour shade of black iron oxide pigment

Sample No.	Molar ratio of iron to Ammonium hydoxide	Yield (g)	Percent of yield	Percent of Fe_3O_4	Percent of FeO	Percent of Fe_2O_3	Loss on ignition	Colour shade
10	1:2.03	A bluish gel type ppt. formed.						
11	1:2.71	25.150	90.470	98.710	30.600	68.070	0.23	Black
8	1:1.74	25.400	91.370	98.230	30.450	67.740	0.98	Deep black
12	1:3.39	25.480	91.650	98.850	30.640	68.170	0.28	Deep black
13	1:4.07	25.600	92.210	98.990	30.690	68.260	0.21	Bright black
14	1:4.75	25.630	92.190	98.810	30.630	68.140	0.22	Bright black
15	1:5.00	25.410	91.400	98.750	30.610	68.100	0.25	Bright black

Conditions:

a) Molar ratio of iron to hydrochloric acid : 1:1.74

b) Molar ratio of iron to sodium nitrate : 1:0.16

oxidation was done in different manner like controlled passage of air, hydrogen or oxidizing or reducing agent used alone or in combination. In the present work oxidation was controlled by the addition of an oxidizing agent in combination with the passage of air at definite rate. Phosphorous pentoxide, sodium hexametaphosphate, hydrazine hydrochloride and sodium nitrate were used for the purpose. Among them first two oxi

Table IV. Effect of different oxidizing agent on the yield and colour shade of black iron oxide pigment

Sample. No.	Name of oxidizing agent	Yield in 'g'	Percent of yield	Percent of Fe_3O_4	Percent of FeO	Percent of Fe_2O_3	Loss on ignition	Colour shade
16	Phosphorous pentoxide	A bluish gel type ppt. formed.						
17	Sodium hexametaphosphate	A bluish gel type ppt. formed.						
18	Hydrazine hydrochloride	25.70	92.24	98.71	30.60	68.07	1.10	Black
13	Sodium nitrate	25.60	92.21	98.99	30.69	68.26	0.21	bright black
19	Without oxidizing agent	A bluish gel type ppt. formed.						
Standard sample	-	-	-	97.88	30.34	67.50	3.50	Deep black

Conditions:

a) Molar ratio of iron to hydrochloric acid : 1:1.74

b) Molar ratio of iron to ammonium hydroxide : 1:4.07

c) Molar ratio of iron to oxidizing agent : 1:0.33

TableV. Effect of amount of sodium nitrate on the colour shade and yield of black iron oxide pigment

Sample No.	Molar ratio of iron to sodium nitrate	Yield (g)	Percent of yield	Percent of Fe_3O_4	Percent of FeO	Percent of Fe_2O_3	Loss on ignition	Colour shade
20	1:0.10	A bluish gel type ppt. formed.						
13	1:0.16	25.600	92.210	98.990	30.690	68.260	0.21	Bright black
21	1:0.33	25.710	92.480	98.750	30.610	68.100	0.98	Bright black
22	1:0.49	25.780	92.730	98.880	30.650	68.190	0.81	Bright black
23	1:0.66	25.690	92.410	98.690	30.590	68.060	0.90	Bright black

Conditions:

a) Concentrated hydrochloric acid taken : 1:1.74

b) Amount of ammonia (17%) taken : 1:4.07

dizing agent were not responding to the conversion reaction and cannot produce black iron oxide pigment. It may be due to the fact that these two chemicals are very weak oxidizing agent and sodium nitrate is the strongest oxidizing agent among these four chemicals. Hence the pigment, which was prepared using sodium nitrate as oxidizing agent, gave very good and clear colour-tone with comparison to standard sample collected from BAYER Germany (Bayferrox 318 Standard 88). The results are shown in Table IV.

Table VI. Technical data on physical properties of black iron oxide pigment

No of sample	pH-value	Sieve residue %	Oil absorption value	External surface area m^2/g	Brightness	Average particle size (μm)	Density g/cm^3	Spreading power	Wettability	Weather resistance	Light fastness
1	5.960	0.020	18.660	0.258	0.80	8.308	5.393	Exc.	Exc.	Exc.	Good
2	6.030	6.502	18.660	0.203	0.30	7.642	6.138	Exc.	Exc.	Exc.	Good
3	6.100	3.005	28.000	0.148	0.50	9.460	6.138	Exc.	Exc.	Exc.	Good
4	5.980	15.108	18.660	0.131	0.86	6.630	5.633	Exc.	Exc.	Exc.	Good
5	5.900	16.102	18.660	N.D.	0.30	N.D.	4.032	Exc.	Exc.	Exc.	Good
6	5.930	11.091	18.660	0.134	0.40	6.430	4.989	Exc.	Exc.	Exc.	Good
7	6.070	9.301	28.000	N.D.	0.30	N.D.	4.990	Exc.	Exc.	Exc.	Good
8	5.910	6.027	28.000	0.172	0.36	7.270	4.954	Exc.	Exc.	Exc.	Good
9	6.000	3.021	18.660	N.D.	0.43	N.D.	4.313	Exc.	Exc.	Exc.	Good
10	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
11	6.150	25.433	28.000	0.101	0.20	4.675	5.635	Exc.	Exc.	Exc.	Good
12	6.080	20.335	28.000	0.147	0.20	5.067	5.694	Exc.	Exc.	Exc.	Good
13	5.990	5.091	18.660	0.155	0.33	9.240	5.081	Exc.	Exc.	Exc.	Good
14	6.010	4.086	28.000	N.D.	0.30	N.D.	4.982	Exc.	Exc.	Exc.	Good
15	5.910	3.981	28.000	N.D.	0.30	N.D.	4.993	Exc.	Exc.	Exc.	Good
16	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
17	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
18	5.930	0.010	18.660	N.D.	0.30	N.D.	3.424	Exc.	Exc.	Exc.	Good
19	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
20	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
21	6.050	5.210	18.660	0.136	0.37	7.717	4.969	Exc.	Exc.	Exc.	Good
22	5.950	5.190	18.660	N.D.	0.63	N.D.	4.981	Exc.	Exc.	Exc.	Good
23	5.890	5.074	28.000	N.D.	0.37	N.D.	4.985	Exc.	Exc.	Exc.	Good
Bayer	5.970	4.201	9.330	0.159	0.40	7.592	4.967	Exc.	Exc.	Exc.	Good

N.D.= Not done, Exc.=Excellent

In Table V, the effect of molar ratio of iron to sodium nitrate as oxidizing agent on the preparation of black iron oxide pigment is tabulated. Here, five different molar ratio of iron to oxidizing agent are shown. It is found that, at lower molar ratio less than 1:0.16, could not produce black iron oxide pigment in the desired colour shade. Again, molar ratio more than 1:0.16 iron to oxidizing agent could not improve yield or colour shade significantly.

A coloured inorganic material can be termed as a pigment only if it confirms to some physical properties. Some important technical data on physical properties of black iron oxide pigments are given in Table VI. It was seen that all the samples are nearly neutral and in acid range. All these samples have higher oil absorption value (ranged from18-28) with respect to standard sample (9.33). Reported oil absorption value for black iron oxide pigment is (18-28) (Fuller 1965). Hiding power of black iron oxide pigment is not possible to measure, as the measuring procedure stated in this paper was contrast ratio method. But according to report (Bayer-1991), black iron oxide pigments have extensively good hiding power. Though these samples have no such brightness but they can be compared to standard sample. All these samples have low percent of loss on ignition in comparison with standard sample. These pigments have density 4.950 g/cm^3 to 5.694 g/cm^3 except Sample No 18. The reported value for density of black iron oxide is 4.95 g/cm^3 to 5.18 g/cm^3. Product obtained with hydrazine hydrochloride has the surface area and lowest density. These samples have high sieve residue on 400 ASTM sieve. Spreadability, wettability, weather resistance and lightfastness were evaluated visiually and found to be comparable to standard sample.

Black colour cannot reflect light. So percent reflectance curve for black iron oxide pigment is not a curve at all. In Fig I, curve 1 represents the percentage of spectral reflectance for the sample No 13, curve 2 for the standard sample and curve 3 for sample No 13 blended with titanium dioxide in the ratio 1:5 (w/w). It is found from figure 1 that curve 1 and 2 are very similar in nature which indicate that sample no 13 is very close to standard sample with respect to brightness. When this sample is five times diluted with titanium dioxide, it is found

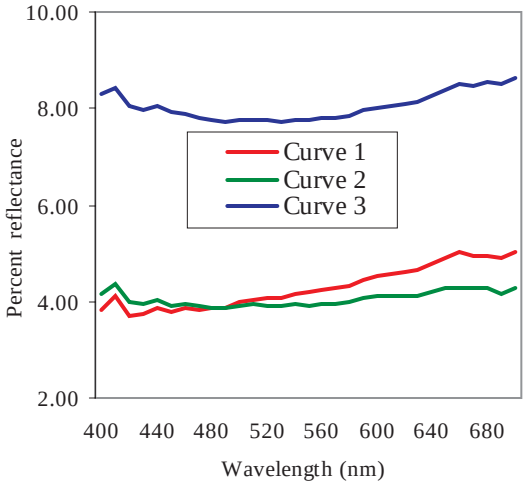

Fig-1: Spectral reflectance curves of some Black Iron Oxide pigment, Curve-1: Sanple No-13; Curve-2: Standard Sample and Curve-3: Sample No-13: TiO2 (5:1).

from the figure 1 that its brightness is increased tremendously without changing the trend of the curve. It is also an indication of high tinting power of black iron oxide pigment.

After obtaining experimental results, some comments from a given number of observations can be made through statistical analysis. In this paper, discussion was done on two statistical aspects: i) correlation between the physical properties and ii) local and global mean comparison with standard sample.

18 samples of black iron oxide pigment were studied here for statistical evaluation. The properties of a pigment studied here are - pH-value, sieve residue, oil absorption value, contrast ratio, brightness, percent loss on ignition, density, external surface area and average particle size. Table VII shows the correlation among the numerical values of the physical properties of prepared black iron oxide pigment. It was prepared as correlation matrix format with the help of SPSS program.

Table VII. Correlation between the physical properties of black iron oxide pigment

Variables	pH - value	Sieve residue	Oil absorption value	Brightness	Percentage of loss on ignition	Density	External surface area	Average particle size
pH value	1	0.411** (0.091)	0.289 (0.245)	-0.213 (0.395)	-0.421** (0.082)	0.562* (0.015)	-0.428 (0.217)	-0.450 (0.192)
Sieve residue	0.411** (0.091)	1	0.214 (0.395)	-0.269 (0.281)	-0.222 (0.376)	0.270 (0.278)	-0.674* (0.032)	-0.980* (0.000)
Oil absorption value	0.289 (0.245)	0.214 (0.395)	1	-0.430** (0.075)	-0.461** (0.054)	0.302 (0.223)	-0.320 (0.368)	-0.497 (0.144)
Brightness	-0.213 (0.395)	-0.269 (0.281)	-0.430** (0.075)	1	0.307 (0.215)	0.191 (0.447)	0.396 (0.258)	0.465 (0.176)
Percentage of loss on ignition	-0.421** (0.082)	-0.222 (0.376)	-0.461** (0.054)	0.307 (0.215)	1	-0.464** (0.052)	0.090 (0.804)	0.375 (0.286)
Density	0.562* (0.015)	0.270 (0.278)	0.302 (0.223)	0.191 (0.447)	-0.464** (0.052)	1	0.090 (0.805)	-0.091 (0.802)
External surface area	-0.428 (0.217)	-0.674* (0.032)	-0.320 (0.368)	0.396 (0.258)	0.090 (0.804)	0.090 (0.805)	1	0.646* (0.043)
Average particle size	-0.450 (0.192)	-0.980* (0.000)	-0.497 (0.144)	0.465 (0.176)	0.375 (0.286)	-0.091 (0.802)	0.646* (0.043)	1

It is found from table VII that there are positive correlations between pH-value and density, pH-value and sieve residue and a negative correlation between pH-value and percentage of loss on ignition at 5%, 10% and 10% level of significant respectively. Sieve residue is negatively correlated with external surface area and average particle size at 5% level of significant. Oil absorption value is negatively correlated with brightness and percentage of loss on ignition. These correlations are significant at 10% level. Percentage of loss on ignition is negatively correlated with density at 10% significant level. External surface area is positively correlated with average particle size and is significant at 5% level.

Descriptive statistics on the physical properties of prepared black iron oxide pigment are shown in the Table VIII. In this table, mean and standard deviation on physical properties, which have numerical values for total and a group of samples are shown. It is found from this table that standard deviations of six variables out of eight variables are high for total samples. Again, standard deviations of four variables out of eight variables are high when the samples were prepared with different amount of hydrochloric acid and ammonium hydroxide. But, only standard deviations of three variables out of eight variables have high values, when the samples were prepared with different amount of sodium nitrate. From this statistical observation, it is clear that physical properties of a pigment depend so much on the preparation parameter. For slightest change in the preparation parameter, physical properties changed remarkably. But variation of amount of oxidizing agent has no such effect on the physical properties of black iron oxide pigment. That means, here oxidizing agent was used during the preparation of the pigment to get bright black product only.

For the comparison of prepared sample, a standard sample is considered under study. It can be done by one sample t-test method. Mean of the variables are compared with the values of standard sample. Here the Null Hypothesis was tested. It was considered that the average values of pH, percentage of sieve residue, percentage of oil absorption value, contrast ratio, brightness, percentage of loss on ignition, external surface area, density and particle size are statistically equal to that of the values of standard sample. From the comparison of Global mean with standard sample by one sample t-test (Table-IX), it can be stated that the null hypothesis which was taken to test is significantly accepted for five values of variables (as significance value is > 0.05). That means, five values for variables are significantly close to the standard sample. Almost same picture is appeared for the samples prepared by varying molar ratio of iron to ammonium hydroxide. But for the samples prepared by varying molar ratio of iron to hydrochloric acid, six values for variables are significantly close to the standard sample, which indi

Table VIII. Descriptive statistics of black iron oxide pigment

Variables	Total sample of black iron oxide pigment			Difference in molar ratio of iron to hydrochloric acid			Difference in molar ratio of iron to ammonia			Difference in molar ratio of iron to oxi-dizing agent		
	No of Sample	Mean	Standard deviation	No of Sample	Mean	Standard deviation	No of Sample	Mean	Standard deviation	No of Sample	Mean	Standard deviation
pH- value	18	5.991	0.076	5	5.962	0.072	5	6.028	0.091	4	5.970	0.067
Sieve residue	18	8.032	6.992	5	9.108	4.986	5	11.785	10.300	4	5.140	0.070
Oil absorption vale	18	22.811	4.776	5	22.396	5.116	5	26.132	4.177	4	20.995	4.670
Brightness	18	0.403	0.185	5	0.358	0.058	5	0.266	0.061	4	0.425	0.138
Percentage of loss on ignition	18	0.705	0.327	5	0.966	0.032	5	0.238	0.028	4	0.725	0.350
Density	18	5.074	0.679	5	4.656	0.452	5	5.277	0.356	4	5.004	0.052
External surface area	10	0.158	0.044	2	0.152	0.028	3	0.134	0.029	2	0.145	0.013
Particle size	10	7.245	1.591	2	6.854	0.595	3	5.814	1.645	2	7.708	0.012

Table 1X. Local mean comparison and global mean comparison of black iron oxide pigment with standard sample

Variables	Values of Standard sample	Total sample of black iron oxide pigment			Difference in molar ratio of iron to hydrochloric acid			Difference in molar ratio of iron to ammonium hydroxide			Difference in molar ratio of iron to oxi-dizing agent		
		Mean	Mean diff.	Sig.	Mean	Mean diff.	Sig.	Mean	Mean diff.	Sig.	Mean	Mean diff.	Sig.
pH- value	5.970	5.991	0.021	0.256	5.962	0.008	0.816	6.028	0.058	0.228	5.970	0.000	1.000
Sieve residue	4.201	8.032	3.831	0.033	9.108	4.907	0.093	11.785	7.584	0.175	5.140	0.939	0.000
Oil absorption value	9.330	22.811	13.481	0.000	22.396	13.066	0.005	26.132	16.802	0.001	20.995	11.665	0.015
Brightness	0.400	0.403	0.003	0.950	0.358	-0.042	0.184	0.266	-0.134	0.008	0.425	0.025	0.741
% of loss on ignition	3.500	0.705	-2.795	0.000	0.966	-2.534	0.000	0.238	-3.262	0.000	0.725	-2.775	0.001
Density	4.967	5.074	0.107	0.514	4.656	-0.311	0.199	5.277	0.310	0.124	5.004	0.037	0.248
External surface area	0.159	0.158	-0.001	0.967	0.152	-0.006	0.795	0.134	-0.025	0.280	0.145	-0.013	0.390
Average particle size	7.592	7.245	-0.347	0.508	6.854	-0.738	0.330	5.814	-1.778	0.202	7.708	0.116	0.046

cates that the partial conversion of ferrous sulphate to ferrous chloride is an important step for preparation of black iron oxide pigment. On the other hand, only four values for variables are significantly close to the standard sample when samples are prepared by varying molar ratio of iron to oxidizing agent which indicates that higher molar ratio has no such effect on the preparation of black iron oxide pigment.

Conclusion

From this work, it can be concluded that preparation parameters affect the physical properties of the black iron oxide pigment very much. Black iron oxide pigment could not be prepared without oxidizing agent. Ammonia as solvent, sodium nitrate as oxidizing agent and air passing throughout the system produces the best black iron oxide pigment. This black iron oxide can be compared with standard sample. Partial conversion of ferrous sulfate to ferrous chloride is a vital step for this preparation though the higher molar ratio of iron to oxidizing agent has no significant effect on the preparation of black iron oxide pigment. Application of statistical analysis confirms the above findings.

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