

## **Synthesis and Characterization of Eco-friendly Barium Sulphate Extender Pigment**

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### **Abstract**

*The scientific work deals with treatment of Barium sulphate extender pigment with iron oxide, which can be used in different architectural and industrial coatings. By depositing a thin layer of ferric oxide on barium sulphate particles a novel pigment with better optical and functional performance can be obtained when used in various coating systems. This pigment improves physicochemical performance and acts as an active barrier. The treated barium sulphate has many social and practical implications such as eco-friendly and economic than other synthetic pigments. Moreover, it is reinforcing filler in rubber, plastic and ceramic composites.*

**Keywords:**  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/BaSO<sub>4</sub> particle, pigment, surface treatment.

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### **I. Introduction:**

Barytes have high specific gravity and low bulking value as compared to other commonly used extenders which promote rapid and hard settling in paint<sup>1</sup>. Since barytes does not have a high pH it may be used with alkali-sensitive pigments such as iron-blue and chrome green. It is frequently employed in combinations with chrome green to impart greater density and compactness to the paint film<sup>2</sup>. Barytes has outdoor applicability having good light resistance and can be applied to surfaces by the use of absorption technology without advanced skills. The surface of metal is usually covered with chemisorbed water at ordinary temperature. Since hydroxyl groups on the surface play a role in the coagulation of powders, it checks the properties of powder surfaces. Barytes is most easily coagulated because it changes to either a positive charge or a negative charge on a surface depending on its environment. Substantial amount of work on adsorption of inorganic powders has been done by many workers in recent past<sup>3</sup>.

It is an object of the study to synthesize an optically robust pigment and characterize the treated Barium Sulfate extender pigment by adsorption mechanism. The research deals the treatment of Barium Sulfate extender pigment from iron oxide for different architectural and industrial coatings<sup>4</sup>. A novel pigment with better optical and functional performance is obtained by depositing a thin layer of ferric oxide on Barium Sulfate particles. This pigment in various coating system improves physicochemical performance. The treated Barium Sulfate extender pigment acts as an active barrier<sup>5</sup>. The experimental techniques of surface treatment have been discussed along with the instrumental analysis (color, mass and shade) and studied by computer<sup>6</sup>. The powdered treated barium sulfate pigments were characterized and studied its various pigmentary properties. The increasing cost of synthetic pigments has led to this novel research and motivated for commercial application. The process used here for synthesizing the treated Barium Sulfate not only produces pigment grade barium sulphate extender of good quality but also taking care of pollution. Over the last decade, the application of computer technology has provided better efficiency of treated barium sulphate pigment and its applicability. It involves three steps; Miniaturization and greater reliability, low costing and use of easy software. With the use of computer technology, the efficiency, statistical design and experimental analysis has been precised and analyzed in terms of various variables and interactions simultaneously in paint formulations, solvent blend of thinner formulation, optical measurements and manufacturing.

### **II. Material And Methods:**

High purity and AR grade samples used in this experiment were supplied by Fine-Chem Ltd., India and they were purified. The samples were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump. The purity of each compound was checked by gas chromatography and the results indicated that mole fraction purity was higher than 0.99.

### Synthesis of surface treated barium sulfate extender:

The synthesis of surface treated Barium Sulfate extender pigments involves three steps; the preparation of barium sulfate, the conversion of ferrous sulfate into ferrous hydroxide and the material was calcined to ferric oxide. In a 500 ml. beaker, 200g of Barium Sulfate (precipitated) powder was taken and a paste was prepared by adding 50ml of demineralized water in it. The paste was sieved through 300 mesh sieve with the help of demineralized water. The suspension was allowed to settle and the supernatant clear water was thrown. This slurry was transferred to dropping funnel and little amount of water was added if required, to convert it to free flowing slurry. An aqueous ferrous sulfate solution as prepared in three necked flask and the above slurry was added drop wise to this solution at room temperature with vigorous stirring. This was continued for 1 hour and the temperature was raised to 75-80°C. The suspension was transferred to a fine filter paper. The calculated amount of Sodium Hydroxide was prepared in 100 ml of water in dropping funnel and added to the above wet cake slowly with high speed stirring keeping the pH between 5 and 6. After the complete addition of sodium hydroxide solution the slurry was boiled for 3 hrs. It was then filtered and washed until the filtrate is free from soluble salt. This cake was dried in an oven at 110±5°C. The dried and powdered surface treated Barium Sulfate extender pigments were calcined at 600°C for 2h<sup>4</sup>. Thus Barium Sulfate extender pigment gets converted to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> coated Barium Sulfate pigment<sup>1</sup>. This product was characterized for various physical and chemical properties.

### III. Results and Discussion:

#### 3.1 Characterization of surface treated barium sulfate extender pigments

The treated samples, coded as TBS-1, TBS-2, TBS-3, TBS-4, TBS-5, TBS-6, TBS-7, TBS-8, TBS-9, TBS-10, TBS-11, TBS-12, TBS-13, TBS-14, TBS-15, TBS-16, TBS-17, TBS-18, TBS-19, TBS-20, obtained from surface modification process after the calcinations, were characterized along with standard samples of barium sulfate and titanium dioxide (approved by Bureau of Indian Standard) for comparisons of pigmentary properties. The results of all the characteristic properties of treated Barium Sulfate extender pigment are shown in Table 1-

Due to large surface area, all pigments are associated with moisture. The relative humidity is about to 50-80%. In the present investigation, we have taken 0.5% moisture content as per IS:44-1991. Doorgest reviewed that moisture content of 0.5% is even encouraging the dispersibility of pigment in alkyd resin. For better results, moisture content should be low. The barium sulphate extender pigment only contains moisture which is evident in Table 1 in all the samples taken and they are within the limits. This test was performed to assess the content of material of larger that impart an influence on many of the paint properties e.g. gloss, opacity, freedom from settlement, and consistency, hence the particle size should be within the standard limit. All the pigment samples in Table 2 were found to be within the limit. The oil absorption value is usually helpful for the experts to estimate the binder requirement of a pigment. It depends on the surface area of the pigment and also on the nature of the pigment surface which influences the wet ability (Morgan). Figure 1 shows the relationship between surface area and oil absorption<sup>7,8</sup>. With the smaller particles, the surface area and oil absorption value increases. The surface area also increases with the increase in number and size of cavity on the surface.

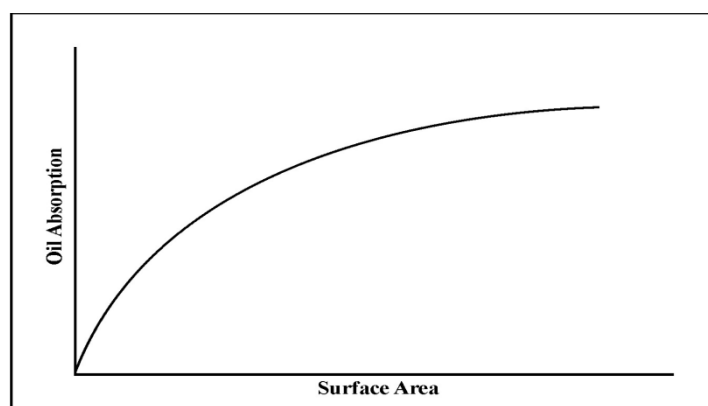
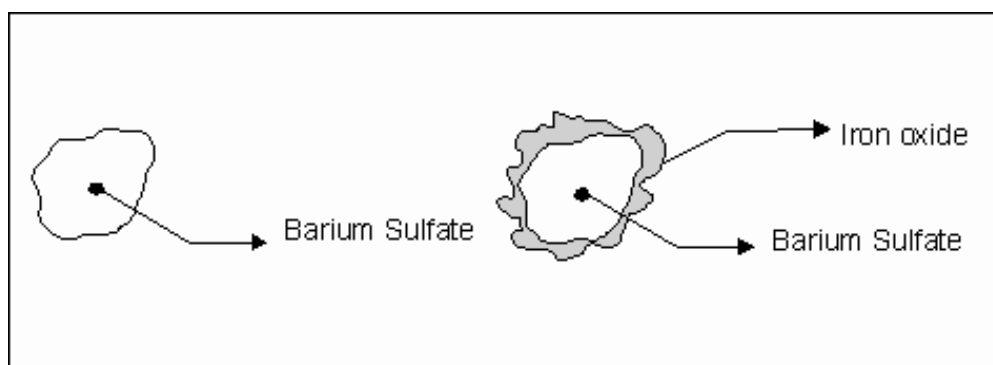


Figure showing the relationship between surface area of the treated Barium sulfate extended pigment particle and oil absorption

Figure 1 Relationship between surface area of the pigment particles and oil absorption

The surface treated Barium Sulfate (Table 1) shows the increase in oil absorption values due to the increase in the surface area which increases the number and size of cavity on the surface<sup>9,10</sup>. The increase in number of cavity and also the size of cavity is due to irregular coverage of surface of Barium Sulfate pigment by iron oxide as shown in figure 2.



**Figure 2.** Surface of the untreated and treated Barium Sulfate extender pigment particle

In barium sulfate extender pigments, water soluble sulphates e.g. sodium sulphate, is produced as a byproduct. It is not possible practically and economically to remove all the soluble salts completely. Though, it is quite difficult to remove the soluble salts from the barium sulphate extender pigment but Morgan found its various uses in primers for metals even the traces of this salt can stimulate corrosion. A maximum limit (0.75%) therefore has been prescribed in IS: 44-1991 (Table 1). All samples were found to have low water soluble matter compared to standard limit. As the treated barium sulphate extender pigments were prepared by adsorption in acidic medium, the free acid part could remain associated with the pigment surface. Theoretically a properly prepared pigment should be entirely free from any trace of acid/alkali but in practice all industrial pigment contain traces of acid or alkali depending upon the pH of the medium<sup>11-13</sup>. The acidity or alkalinity should not amount to more than 0.1 percent with the pigment. A content of acidity/alkalinity above this limit indicates faulty preparation. Generally ineffective washing is responsible for reactive pigments. Table 1 represents that none of the pigment was found crossing the limit.

### 3.2 Paint Preparation and Evaluation

Air drying synthetic enamel paint (decorative) formulation of the type currently popular in India was used for evaluating the pigment properties. The attempt was made to ensure that the supplier of all raw materials used throughout the study remain the same. The paint was prepared in lab of 500 ml capacity in bead mill.

Part A was charged into the send grinder and run for one hour. The grinder was checked by Hegman gauge. The materials of part B were added in the grinder and run for 10 minutes. Finally the mill base discharged and missed with part C. the finished paint was called as full shade. The reduced shade was prepared by mixing 100 parts volume of white, prepared in the above manner, with 2 parts by volume of full shade. The reduced shade, thus obtained by reduction of full shade with white paint was used to compare strength.

### 3.3 Evaluation of Paint

The full shade paint samples were evaluated for following characteristics as per BIS specification No. IS: 101-1964: Fineness of grind, Consistency and Covering capacity. The fineness of grind, also known as degree of dispersion was seen with the help of Hegman gauge as described in IS : 101 – 1964. The sample was spread in a calibrated tapered groove with the help of scraper. A direct reading (Hegman Scale) was then made at the point where visible pigment particles appeared (Tables 2). The consistency of the paint was seen with the help of ford cup No. 4 at 30°C according to I.S : 101 -1964. The bubble free paint sample of full shade at 30°C was taken in ford cup No. 4 and orifice of ford cup was closed with finger. The excess of sample was flowed into the gallery with the help of flat tin sheet. The receiver was placed under the cup. The finger was removed from the orifice and the stop watch was started simultaneously. At the first evidence of the break of the stream into droplets, the stop watch was stopped. The time taken was recorded in seconds as the time of flow from ford cup (Table 2). The covering capacity of the prepared paint samples (full shade) was seen with the help of checker board having alternate black and white squares and also on Morest chart. The black and white square was seen to be satisfactory obliterated by minimum quantity of paint and no contrast was found. The covering capacity was calculated by difference in paint weighed before and after the use, along with brush and the area covered. The number of square meter of checker board per 10 litre of paint was reported as covering capacity<sup>14-16</sup>. In case of Morest chart, which was designed in one square foot area and supplied by Morest corporation – 101 Board

AVE., Fairview, N.J. 07022, the paint was applied with a bar coater and wet opacity /covering capacity or hiding power of paint was calculated (Table 2).

$$\text{Hiding Power} = \frac{\text{No. of square metre}}{\text{Volume of paint sample in it}} \times 10$$

### 3.4 Evaluation of Film Characteristics of Paint

The prepared panels were used to evaluate the following paint film characteristics: Gloss ( $20^{\circ}/45^{\circ}/60^{\circ}$ ), full shade or Mass color and reducing power. The painted panels, after 24 hrs of drying, were tested for gloss with the glossometer (AIMIL), generally used for the objective measurement of specular gloss and measure specular reflection of various angle of incidence, after adjusting with a standard panel, provided along with glossometer. The  $20^{\circ}$ ,  $45^{\circ}$  and  $60^{\circ}$  angle of reflection was measured by the instrument (Table 3).

## IV. Conclusion

The purpose of the present investigation is to develop economical pigment from extender pigment and to replace the premier pigment titanium dioxide. The barium sulfate extender was selected for surface modifications having similar properties as titanium dioxide has. There are certain properties, such as mechanical strength, low oil absorption very low cost etc. where Barium Sulfate is superior to titanium dioxide. Considering these properties, the barium sulfate extender was selected for modification to increase its optical and physiochemical performance. At the first stage the ferrous hydroxide was precipitated on the surface of Barium Sulfate, keeping pH acidic. The slurry was then boiled, filtered, and dried and annealed. By annealing, a strong chemical bond between the surface of Barium Sulfate extender pigment and layer of hematite  $\alpha\text{-Fe}_2\text{O}_3/\text{BaSO}_4$  is formed. The Barium Sulfate extender after surface treatment with  $\alpha\text{-Fe}_2\text{O}_3$  was annealed at a temperature of  $600^{\circ}\text{C}$ . The surface-treated Barium Sulfate extender pigment was then subjected to optical and physicochemical analysis. Moreover, tests were performed aiming at defining morphology and surface structure. It can further be concluded that though the opacity of the samples from TBS-4 to TBS-20 is increasing but the hue values are also shifting from pale yellow to red. As the cost of these modified extender pigments are comparatively quite low, the modified colored extender pigments can be used the corresponding colored products with satisfactory opacity.

Further, the treated barium sulfate extender pigment can be used in architectural and industrial coatings. It can be applied as reinforcing filler in rubber, plastic and ceramic composites. The increasing cost of synthetic pigments has led to this novel research which is believed to have commercial application and will help in reducing the cost of final products significantly. The preliminary investigation of the practical application of these surface treated Barium Sulfate pigments revealed that they are suitable for using in paints, inks, plastics, board maulers and textile printing.

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**Table: 1**  
**Characteristics of untreated and treated Barium Sulfate extender pigments**

Sl. No.	Sample Code	Volatile matter (% by wt)	Residue on sieve (% by wt) 325 mesh	Oil absorption (wt/wt)	Matter soluble in water (% by wt)	Acidity as H <sub>2</sub> SO <sub>4</sub> (% by wt)
		BIS Value	0.5 max	0.5 max	±5% of approved sample (14)	0.75
1	UBS*	0.31	0.05	13	0.28	0.06
2	TBS-1	0.17	0.05	13	0.35	0.07
3	TBS-2	0.28	0.05	13	0.35	0.06
4	TBS-3	0.27	0.05	13	0.34	0.08
5	TBS-4	0.26	0.05	12	0.31	0.05
6	TBS-5	0.25	0.04	12	0.34	0.07
7	TBS-6	0.24	0.04	14	0.36	0.06
8	TBS-7	0.23	0.04	14	0.36	0.05
9	TBS-8	0.22	0.04	15	0.37	0.03
10	TBS-9	0.21	0.03	15	0.36	0.06
11	TBS-10	0.20	0.03	15	0.34	0.07
12	TBS-11	0.19	0.03	16	0.32	0.08
13	TBS-12	0.18	0.03	17	0.34	0.06
14	TBS-13	0.17	0.03	17	0.33	0.07
15	TBS-14	0.16	0.03	17	0.37	0.07
16	TBS-15	0.15	0.03	18	0.38	0.06
17	TBS-16	0.14	0.02	18	0.36	0.08
18	TBS-17	0.13	0.02	20	0.36	0.05
19	TBS-18	0.14	0.02	20	0.34	0.03
20	TBS-19	0.13	0.01	20	0.35	0.06
21	TBS-20	0.12	0.01	20	0.35	0.07

\*Assuming untreated Barium Sulfate as standard sample.

**Table:2**  
**Characteristics of paint prepared from untreated and treated berium sulfate extender pigments**

Sl. No.	Sample Code	Characteristics		
		Finesse of grind (Hegman gauge reading)	Consistency at 30 <sup>0</sup> C in sec By ford cup no.4	Covering Capacity (m/l)
1	UBS*	7 <sup>+</sup>	67	-
2	TBS-1	7 <sup>+</sup>	70	-
3	TBS-2	7 <sup>+</sup>	70	-
4	TBS-3	7 <sup>+</sup>	70	30
5	TBS-4	7 <sup>+</sup>	71	30
6	TBS-5	7 <sup>+</sup>	71	35
7	TBS-6	7 <sup>+</sup>	72	40
8	TBS-7	7 <sup>+</sup>	72	40
9	TBS-8	7 <sup>+</sup>	72	48
10	TBS-9	7 <sup>+</sup>	73	51
11	TBS-10	7 <sup>+</sup>	74	55
12	TBS-11	7 <sup>+</sup>	74	59
13	TBS-12	7 <sup>+</sup>	75	60
14	TBS-13	7 <sup>+</sup>	75	60
15	TBS-14	7 <sup>+</sup>	76	65
16	TBS-15	7 <sup>+</sup>	76	66
17	TBS-16	7 <sup>+</sup>	79	66
18	TBS-17	7 <sup>+</sup>	80	66
19	TBS-18	7 <sup>+</sup>	82	80
20	TBS-19	7 <sup>+</sup>	82	85
21	TBS-20	7 <sup>+</sup>	83	101

\*Assuming untreated Barium Sulfate as standard sample.

Table: 3  
Gloss of paint film

Sl. No.	Sample Code	Glossometer Reading		
		20 <sup>0</sup>	45 <sup>0</sup>	60 <sup>0</sup>
1	UBS*	66	95	85
2	TBS-1	66	94	85
3	TBS-2	66	94	85
4	TBS-3	65	94	84
5	TBS-4	65	93	84
6	TBS-5	64	93	84
7	TBS-6	64	93	83
8	TBS-7	63	92	83
9	TBS-8	63	92	83
10	TBS-9	62	92	82
11	TBS-10	62	91	82
12	TBS-11	61	91	82
13	TBS-12	61	91	81
14	TBS-13	60	90	81
15	TBS-14	60	90	80
16	TBS-15	60	89	80
17	TBS-16	59	89	80
18	TBS-17	59	88	80
19	TBS-18	59	88	79
20	TBS-19	58	88	79
21	TBS-20	58	88	79

\*Assuming untreated Barium Sulfate as standard sample.

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