Surface Modification Research of Ultrafine Iron Oxide Red Pigment Powders

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China as a large export of iron oxide pigments, iron oxide pigments production is out of low level. So in this paper, the effects of different modifiers and dosage on the dispersion of ultrafine iron oxide red pigment in aqueous solution and dry dispersion were studied by dry surface modification method. At the same time, we analyse the mechanism of modifier and iron oxide red. Finally, it is concluded that the best modifier formula for improving the dispersion performance of superfine iron oxide red pigment in aqueous solution and dry state is modifier D3008. Experiments show that the modified ultrafine iron oxide red pigment with the formula is strong, and can have better dispersion stability in aqueous solution.

1. Introduction

Iron oxide pigments mainly iron red, iron yellow, iron and iron brown, etc., is a variety of chemical raw materials. In the world, iron and steel pigments production and sales, second only to titanium dioxide, is the second large amount of wide range of inorganic pigments (Ghoroi, 2013). Among them, iron oxide red iron oxide pigments in the production and the largest amount of products. In the United States, for example, in the annual consumption of iron oxide pigments, iron red accounted for 42.9%. The chemical composition of iron oxide red is α-Fe2O3, belonging to the rhombohedral crystal system. The density is 5.28g/cm3 and α-Fe2O3 is the most stable iron oxide pigment. Iron oxide red is widely used as rubber, paint, artificial marble, ground terrazzo colour agent; plastic, asbestos, artificial leather, leather wiping pulp and other colorants and fillers; precision instruments, optical glass polishing agent; and it is the manufacture of magnetic materials ferrite components of the important raw materials; and for ceramics, paper, ink and art paint and other industries.

China has become the world's production of iron oxide pigments, the output of the world's total of about 1/3, exports more than 50% of the total, so that China is second only to Germany's second largest producer of iron oxide pigments (Mirzababaei, 2013). However, the current production of most of our untreated general-purpose iron oxide pigments, the industry more than 80% of the products are monochrome primary products. This iron oxide pigment low price, low value-added products, is a low-end products. One of the reasons is that post-processing or deep processing technology behind.

At present, the inorganic modification of inorganic pigments used in polymer-based composites or the surface modification of inorganic pigments has been studied in this paper (Li, 2013). For inorganic materials such as ceramic blanks, building materials and water paint, etc. improving the dispersion and storage stability of the surface modification technology has been studied very little. The former as long as the organic pigment surface can be resolved at the same time the dispersion and compatibility with organic base material; the latter is not only requires surface modification of inorganic pigments were well dispersed state, but also requires compatibility with inorganic base material Good (that is, surface hydrophilic, spontaneous dispersion in the water phase) (Snow, 2014).

2. Pigment powder dispersion, stability principle

2.1 The process of pigment powder dispersion

In the medium, the pigment is required to be highly dispersed in the form of fine particles (Wong, 2014). So that its particle size, dispersion stability largely affect the pigment application performance, while the pigment

primary particles have a large specific surface area and a higher specific surface energy, in the preparation and post-treatment prone to agglomeration, flocculation, the formation of secondary particles. So that the particle size becomes larger, and ultimately lost the performance of which. Therefore, the use of paint, it should first solve its dispersion in the media. The dispersion of the pigment particles in the medium generally involves the following three steps:

Wetting: The so-called wetting of the pigment powder means that the pigment is completely wetted with a dispersion medium to remove air and other impurities in the particle surface and the aggregates. Factors affecting the wetting properties of pigment particles are: particle shape, surface chemical polarity, surface adsorption of air and the dispersion of the polarity of the medium (Forest, 2014). Good wetting properties allow the pigment particles to interact with the media quickly and facilitate the separation of the particle aggregates.

Refinement: The refinement of the material means that the aggregates of the pigment particles are opened into separate primary particles or smaller aggregates under mechanical forces. The dispersion of the aggregates can be considered from both energy and volume. The overall probability of occurrence in the aggregate depolymerization process is two parts: the probability that the aggregate enters into the effective region where the dispersion can occur. The energy that exists when the aggregate is in the active region can overcome the role of the native particles (Jadhav, 2014). The probability of the aggregation of the probability of aggregation in a certain energy density:

$$P_T = P_t + P_r = \frac{N_d}{N_0} = (1 - e^{-K_t \frac{V_H}{V_T}})(1 - e^{-\frac{QE}{\delta V_T}})$$ (1)

P_T:The overall probability of dispersion; P_t:The probability of aggregates in the effective area; P_r:The probability of depolymerization in the effective region of the aggregate; N_d:The number of aggregates that have been depolymerized at a time; N_0: The total number of aggregates at a time.

2.2 Particles interact in the medium

There are a variety of interactions between the particles in the dispersion system, and it is these interactions that allow the particles to be stably present in the dispersion medium (Zhao, 2014). Each of these interactions corresponds to the corresponding role of energy, the main role can be: vanderwaals energy, electric double layer electrostatic energy, solvate the role of the film, the role of steric hindrance, hydrophobic energy. Vanderwaals action energy: two radii of r_1 and r_2 dissimilar spherical particles, respectively, the expression of energy:

$$U_A = -\frac{A_{132} r_1 r_2}{6H(r_1 + r_2)}$$ (2)

Where A is the Hamaker constant; H is the spacing between the particles r_1 and r_2 the liquid medium. The Hamaker constant A_{132} of the particles and particles in the liquid phase can be expressed as follows:

$$A_{132} \approx (\sqrt{A_{11}} - \sqrt{A_{33}}) \times (\sqrt{A_{22}} - \sqrt{A_{33}})$$ (3)

If the same medium between the Hamaker constant:

$$A_{131} = A_{11} + A_{33} - 2A_{13} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})^2$$ (4)

Where A_{11} and A_{22} are the Hamaker constant of the particles 1 and 2 in vacuum, A_{33} is the Hamaker constant of the liquid 3 in vacuum, A_{131} is the aHmaker constant between the homogeneous particles 1 in the liquid 3, A_{13} is the Hamaker constant for the interaction of heterogeneous particles 1 and 2 in liquid 3.

Electrostatic energy: For two spheres with radius r_1 and r_2, the double layer action can be approximated by the following equation:

$$U_r = \frac{\varepsilon r_1 r_2}{4(r_1 r_2)} (\varphi_1^2 + \varphi_2^2)[\frac{2\varphi_1 \varphi_2}{\varphi_1^2 + \varphi_2^2} \ln(\frac{1 + e^{-zH}}{1 - e^{-zH}}) + \ln(1 - e^{-2zH})]$$ (5)

Hydrophobic energy: the hydrophobic particles due to the attractiveness of the hydrophobic surface and reunion, which will destroy the stability of the suspension system (Sivkov, 2015). The hydrophobic force is a long-range force and is attenuated exponentially with the particle spacing. The formula can be expressed as follows:

$$U_{HI} = -2.51 \times 10^{-3} r \bullet k_1 \bullet h_0 \exp(-\frac{H}{h_0})$$ (6)

Where k_1 is the attenuation length coefficient h_0.

2.3 Theory of dispersion stability

DLVO theory: DLVO theory is to study the stability of charged particles in the system theory. It was born in 1941 by Soviet scholars Darjaguin and Landan, as well as by the Dutch scholars Verwey and Ovehteek, respectively, in 1948. This theory holds that there are two interactions between the charged particles: the electrostatic repulsion at the time of the overlap of the electric double layer and the long van der Waals attraction between the particles (Palimi, 2015). Their interaction determines the stability of the dispersion. When the attraction is dominant, the particles are agglomerated with each other to produce precipitation; and when the repulsive force is dominant and large enough to prevent the particles from colliding and agglomeration due to Brownian motion, the dispersion is in a steady state.

Spatial stability mechanism: In practice, only the natural dispersion of particles in the liquid medium often doesn't achieve the desired effect, and generally add some kind of dispersant (especially the polymer dispersant and super-dispersant to achieve the desired effect. In the dispersion system with dispersant, only DVLO theory can't explain the actual existence of the phenomenon, because DLVO theory is one of the starting point of the double layer of particles overlap and produce exclusion, but non-aqueous medium in the double. The role of the layers is rather vague, and even in aqueous systems, the addition of nonionic surfactants or macromolecules tends to increase the stability of colloids, and their potentials are often reduced by the addition of these substances. Theory of spatial stability (Pietroiusti and Magrini, 2015). The basic idea of the theory of spatial stability is that when the adsorbent layer is formed after the adsorbent molecules which are adsorbed on the surface of the solid particles, the interaction between the adsorbent layers is repulsive when the particles are close to each other. There are two explanations for this exclusion: 1. The theory of entropy stability, based on rigorous statistics, assumes that the other surface of the adsorbent layer can't penetrate and that the compression of the adsorbent layer reduces the configuration of the dispersant molecules in the region produce a compassion. 2. With the dispersant molecular statistical thermodynamics based on osmotic repulsion or mixed thermal repulsion stability theory. The two collisional particle adsorption layers may overlap, and the overlap region is brought into contact with the dispersing medium due to the dispersant molecular contact to reduce and produce a mixture of changes.

Vacancy mechanism: the stability of the polymer on the dispersion can be divided into two types: one is due to the adsorption of polymer molecules on the surface of the polymer layer to form a layer of polymer adsorption. Stabilization mainly depends on the adsorption layer to reduce the attraction force and the adsorption layer overlap when the space repulsion potential energy. This is the aforementioned space stability. On the other hand, it is because the particles are negatively adsorbed on the polymer, so the concentration of the polymer on the surface of the particle is lower than that in the dispersion. As a result of this negative adsorption phenomenon caused by the particle surface to form a layer of "blank layer", when the gap layer overlap occurs when the generation of repulsive potential or attractive potential energy (Anusha, 2015; Khakzad and Reniers, 2016,). In a low concentration dispersion, the overlap of the voids leads to the predominant concentration of the attracting force and the accumulation of particles (dispersed phase), whereas in highly concentrated dispersions, the repulsive force is predominant, System stability (Wehmeier and Mitropetros, 2016).

3. Research content and program

The objective of this study is to study the surface modification of ultrafine iron oxide red pigment, to determine the best formulation and optimum process conditions for surface modifier to improve the dispersion power of such pigment and to study its modification by testing and analysis mechanism.

3.1 The process of experiment

In this paper, the experiment was dry modified. 1, weighed 1009 iron oxide pigments, into the 200lm triangular bottle; 2, according to the specific conditions of the configuration of modifier; 3, control other experimental conditions, the first agent in the water bath outside the pot And the pigment is pre-mixed (side by side with stirring), and then the flask is placed in a heating and stirring reactor, and the modifier is allowed to react on

the surface of the pigment at a certain temperature and stirring speed. 4, after the sample is dried, High-speed break up; 5, the last addition of modified additives, according to the device in step 3 will be modified with the sample mixing agent (about stirring minutes); 6, the final product.
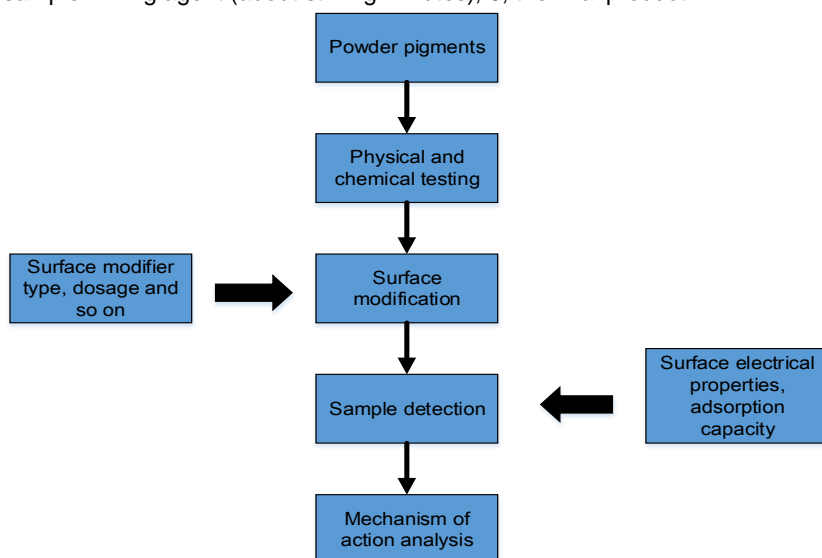

Figure 1: The process of research

3.2 Test raw materials and reagents

The experimental indicators of iron oxide powder from Hunan Sanhuan Pigment Co., Ltd. H130-type iron oxide red products, the experimental sample of the technical indicators are as follows: shade similar to the standard sample, Fe_2O_3 content$\geq$95%, 1.0% moisture, powder Fineness+0.044mm$\leq$0.3%, water content$\leq$0.3%, oil absorption 0.38mL/g, pH 6~9, color strength (with the standard ratio) 100%±2%. The surface modifiers used in the experiments are listed in the table. The use of the auxiliary silica is provided by Beijing Saide Powder Co., Ltd., calcined kaolin provided by Shanxi Jinyang Kaolin Co., Ltd., diatomaceous earth for laboratory purification, pickling, ultra-fine diatomaceous earth.

Table 1: H130 type iron oxide red technical indicators

Color	F_2O_3 (lowest)	Water	Fineness (the bigest is 320)	Water solubility (the highest)	Oil absorption	Tinting power
1~0	94	0.9	0.4	0.4	0.38	97~102

A variety of surface modifiers for powder modification are generally selected according to the performance of the powder, the application field, and the like. In the coating, often with polyelectrolytes, such as polyacrylates, polyamides and other dispersants are used as inorganic pigments. Such molecules contain some or all of the ionizable groups, a macromolecule compound. Its molecular structure is characterized by a considerable ion skeleton and a small equivalent, with the opposite charge, it can separate ionization of the balance of ions, so it is easy to dissolve in water, and have a strong polarity, and the system both to provide two-layer stability, but also to provide steric hindrance effect. It is commonly used in water-based system for inorganic pigments dispersed with voll. Among the commercially available polymer dispersants for aqueous coatings, the proportion of polyelectrolyte dispersants is the largest and the most widely used, followed by nonionic polymer dispersants such as polyoxyethylene derivatives, polyvinylpyrrolidine Ketone, etc.) 7IIJ. Therefore, this paper mainly uses several different polyacrylates to modify the iron oxide red.

3.3 Test methods

(1) Bulk density: Weigh a certain quality of the sample into the cylinder, the hand cylinder on the rubber pad several times, each measured a sample, the number of times and the height of the lifting cylinder should be the same. The ratio of the mass of the sample to the reading of the rear cylinder is the bulk density of the sample. (2) Settling time: take 50mL tap water in a dry beaker, add 0.25g sample, stirring with a stirrer for 10min, remove the 25mL suspension placed in 25mL test tube, put it aside and start timing, through the test tube can clearly see 5mL scale line so far, this period of time is the measured sample settling time. (3) Particle size: The sample size was determined by a BT-1500 centrifugal sedimentation particle size analyzer. (4) zeta

potential (electric potential): the use of electrophoretic light powder method, the pH value of the adjustment using 0.1mol/L of HCl and 0.1mol/L of NH3•H2O, test solution KCl concentration of 0.001mol/L, the mass ratio of solution to solid was 2000: 1.

3.4 Results and discussion

Comparison of surface modifiers: Table 2 shows the surface modification test and sample test results of various surface modifiers under the same amount of ultrafine iron oxide red samples when no additives are added. 101 # samples have a longer settling time, and the settling time of 102 # and 106 # is the second, indicating that the dispersion stability of 101 # in water is the best, indicating that iron oxide treated with D3008 has a good dispersion in water medium Stable performance. 101 # surface modifier is polyacrylic acid sodium salt, 106 # modifier for polyacrylic acid salt, 103 # modifier for polyacrylic acid ammonium salt. Therefore, the treatment order of the surface treatment agent is: polyacrylic acid sodium salt, polyacrylic acid salt, polyacrylic acid ammonium salt.

Table 2: The comparison of different additives

sample	111	112	113	114	115	116
Improved varieties	D3008	D3007	D3021	D3002	A1000	A2000
Precipitation time/h	4.17	1.70	0.97	0.73	1.10	2.03
Potential	-47.88	-45.42	-39.34	-37.38	-42.3	42.35
d	1.02	1.07	1.03	1.07	1.02	1.03
Tinting power	100	100	110	100	110	100

Table 3 shows the surface treatment test and sample test results of the ultra-fine iron oxide red samples of the same amount of surface treatment agent in the case of adding the auxiliary silica. The settling time of the remaining samples was significantly prolonged except for the addition of the auxiliary silica in addition to the 116 # sample, such as 101 # extending from 4.17h to 4.92h and extending from 1.7h to 2.87h. The particle size of each sample is still small, but the coloring of the sample is increased or decreased. Only from the color point of view, the white carbon will reduce the D3008, D3002, A1000 treatment effect, and improve the D3021 treatment effect. After adding white carbon, the color difference of the sample increases, increasing the brightness of the sample.

Table 3: The comparison of different surface

sample	111	112	113	114	115	116
Improved varieties	D3008	D3007	D3021	D3002	A1000	A2000
Precipitation time/h	4.93	2.86	1.45	1.69	2.07	1.97
d	0.94	0.99	0.95	1.02	0.93	1.03
Tinting power	100	100	110	100	110	100

Additive dosage: The main purpose of adding additives is to improve the dry dispersion of iron oxide red pigment. Fig. 2 shows the effect of the amount of auxiliary silica on the density of iron oxide red sample under the condition that the surface treatment agent is 1.2g and the treatment temperature is 97~98 °C. The bulk density of the sample decreases with the increase of the amount of silica, which indicates that the dispersion of iron oxide powder is getting better and better with the increase of the amount of silica, but the excess silica will make the iron oxide powder fade, the colouring strength drop. Therefore, the comprehensive consideration, the amount of silica to 3.5 ~ 4.5g is appropriate.
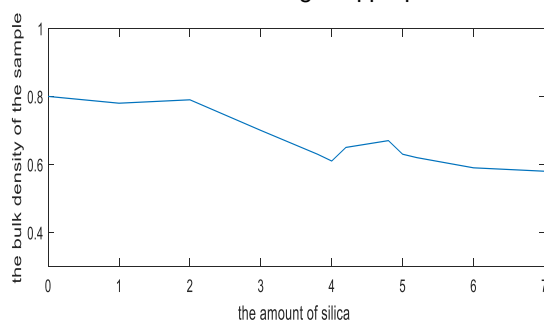

Figure 2: The relationship between the amount of silica and the bulk density of the sample

4. Conclusion

In this paper, the optimum technological formula of superfine iron red pigment surface treatment was obtained by modification experiment of ultrafine iron oxide red pigment powder. And we prepare ultrafine iron with good dispersion performance in aqueous solution and natural dry condition. Red pigment according to the characteristics of the application in different applications, the dispersion performance of the powder should be divided into two cases: the dispersion performance in the liquid phase and the dispersion performance in the natural dry state, and regard the sedimentation time and bulk density as the evaluation method. Based on the analysis of the samples, the adsorption model of the surface of the iron red particles was established, and the mechanism of the water - soluble surface modifier and the iron oxide red particles was put forward.

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