

Preparation and Surface Modification of Transparent Yellow Iron Oxide Pigment

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Nowadays the transparent yellow iron oxide pigment is widely applied in many industries. In recent years, China has been a large producer of iron oxide pigments with over 50% of its total annual output being exported. So it is of necessity to have a comprehensive understanding of the domestic iron oxide pigments production and its development status. According to the characteristics and application of transparent yellow iron oxide pigment. This paper studies several preparation and surface modification methods of the pigment. By adding various additives during and after the reaction, a transparent iron yellow colour can be obtained with excellent transparency, good dispersibility, pure hue and excellent heat resistance.

1. Introduction

Transparent iron oxide is a very important inorganic material, and to use it appropriately as raw materials, we should select appropriate process to process it into ultrafine transparent yellow iron oxide pigment of high industrial value.

However, as the reaction involving three phases, the gas, liquid and solid phases, the production process is more complex. Transparent iron oxide is especially an important material for production of iron oxide pigment series with particle size less than 100 nm. With a chemical formula of α -FeOOH, this pigment is also known as permeable yellow which has good dispersion in transparent medium. Its particles may exhibit different shapes according to the preparation methods, including the needle-like, spindle-like and spherical shapes. Among them, the needle-shaped one displays mercerizing effect, so the spindle and spherical shape is better. Transparent iron oxide pigments have a very strong colour effect, good weather ability, light resistance and good absorption ability (Liang et al., 2017). When the temperature exceeds 177 °C, it will become dehydrated and reddish, strongly absorbing the ultraviolet and visible blue spectra, so the pigment is capable of shielding radiation, thus prolonging the service life of coating. Besides, it is also widely used in production of flash coatings, leather, transparent plastics, high-grade automotive topcoats, food (or pharmaceutical) colorants (Chen et al., 2014).

Since late 1970s, it has seen improvements in production processes and applications of permeable yellow. Titanium were mainly made of ferrous sulphate and steel pickling waste. In most iron oxide plants in China where iron was used to produce ordinary iron and yellow pigment, the production of yellow iron requires less iron, thus reducing production costs and improving product-added value. Therefore, it is undoubtedly of great practical significance to understand and master the preparation as well as surface modification of transparent iron oxide yellow.

The properties of the iron oxide yellow pigment are as shown in Table 1.

The iron yellow is the second best-selling pigment next only to the bulk products of iron oxide red. At the same time, the oxide iron yellow is the raw material for preparation of iron red, iron black, and especially high-quality iron powder γ -Fe₂O₃. The iron oxide yellow pigment is widely used in construction, ink, rubber and paper making industries. Therefore, it is of great application significance to study the technological conditions of the transparent iron oxide yellow.

Table 1: Properties of yellow iron pigment

Property	Indicator
Appearance	Yellow power
Density (g/cm ³)	4.07
Oil absorption (%)	25-30
Refractive index	2.3-2.4
Covering power (g/m ²)	10-15
Purity (Fe ₂ O ₃ %)	86-88
Particle size (μm)	0.1-0.8
Crystal habit	Needle

2. Preparation of Transparent Iron Yellow

There can be found many methods for preparation of transparent yellow iron oxide pigment in the literature. They are summarized as the dry method and the wet method (Li et al., 2015), and in some files they are summarized as the acid method and the alkali method (Kumazawa, 1977). According to the intermediate phases during the preparation process, we can summarize the preparation methods as the ferrous conversion method, ferric iron conversion method and direct conversion method.

2.1 Ferrous conversion method

The ferrous conversion method refers to forming a mesophase, Fe(OH)₂, in preparation of transparent iron yellow by controlling a certain reaction conditions so that Fe(OH)₂ is directly oxidated into α-FeOOH particle. Fe(OH)₂ conversion method can also be divided into the acid method and the alkali method according to different preparation processes.

The acid method, also known as the seed crystal method or the two-step method, can be divided into two stages: seed crystal preparation and crystal growth. The relative rate between the two stages determines the size, morphology and distribution of pigment particle. Therefore, one can change the process conditions to control the relative speed between the two stages so as to meet the requirements (Liu et al., 2015). This method is advantageous in avoiding the precipitation of metal impurities and consuming low alkali while disadvantageous in containing anions even still after repeated washing, which will degrade its dispersion. And to get a higher degree of dispersion, a certain degree of transparency need be sacrificed. The acid method is as shown in Figure 1.

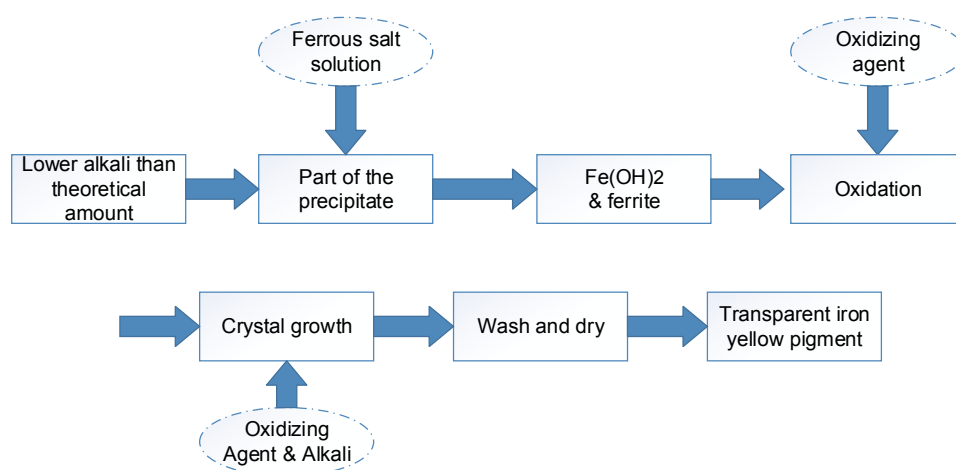


Figure 1: The acid method process

Compared to the acid method, the alkali method is advantageous in narrow size distribution of the pigment particles, and intact micro crystals obtained which are easy to be refined. Besides, the transparent yellow iron particles have better dispersion and higher yield. But it's disadvantageous in that the impurity metal ions can easily precipitate through the same precipitation process, resulting in the preparation of variegated transparent iron yellow particles (Bu et al., 2013) and in that the Manganese ions will precipitate into the yellow powder which will cause the pigment to be blue-green. Therefore the ferrous salt metal impurities can not be too high.

Another drawback is that it will produce a lot of alkali waste which must be treated, otherwise, it will cause serious environmental pollution. Figure 2 illustrates the process of alkali method.

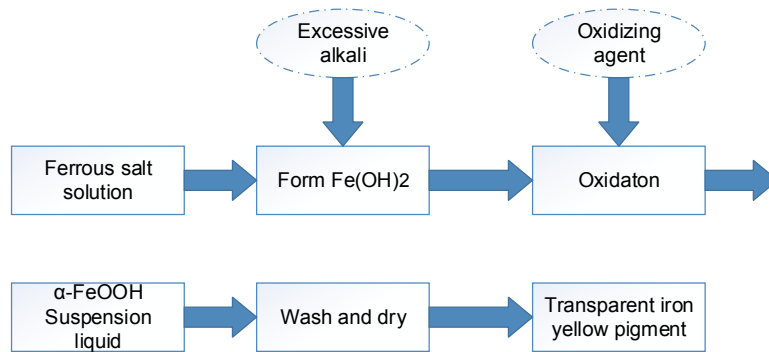
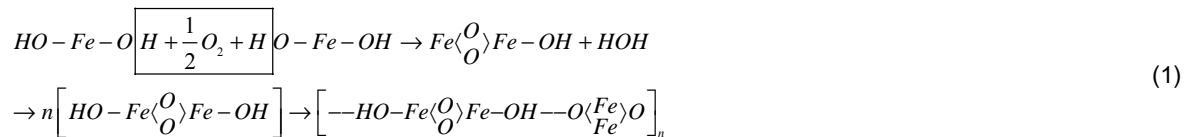


Figure 2: The process of alkali method

The product grows on the surface of the solid particles. In the α -FeOOH crystal structure, one unit cell contains two Fe atoms, so during the reaction process the structure changes as below:



In terms of homogeneous nucleation process, the nucleation rate is:

$$J = A \exp\left[\frac{-16\pi v r^3}{3R^2}\right] / T^3 \ln^2 S \quad (2)$$

Where A is the pre-exponential factor, T is the temperature of the system, and S is the supersaturation. $S = C^*/C$, C^* and C means the equilibrium concentration of the solution and the actual concentration of the solution respectively. r is the surface tension of the nucleus, and v is the molar volume of the new phase. According to the theory of crystal growth and diffusion, the crystallization rate is:

$$dm/dt = \left[AD\right] / \left[\delta C^*\right] (S-1) \quad (3)$$

Where D is the diffusion coefficient of the crystalline component and also the thickness of particle's diffusion layer and A is the particle surface area. From equation (1) and equation (2), we can see that the nucleation rate of the crystal has a strong non-linear relationship with the supersaturation while its growth rate is linear with the supersaturation. Therefore, the factors that affect the process of super saturation will impact the nucleation and growth rate of the particles, and ultimately the morphology of the particles.

As the particle size requirement is less than 70nm for transparent iron oxide pigments, it is necessary to study the reaction conditions, especially the impact from engineering factors. First, the pH value of the reaction system has a significant effect on the pigment quality. The pH value is generally controlled at 8-10 for the alkaline method. It will be easy to form stromatite if the pH value is too high and the ion will fast diffuse if the value is too low, which will cause crystal grow uncontrollably fast and large. And the pH value for the acid method is controlled within 3-5. If the pH is too high, it's easy to produce Fe₃O₄ impurities, resulting in darker pigments. Besides, controlling the rate of adding oxidant is the most direct way to control the oxidation rate. In the process of using air as an oxidant, flow rate control of the air and ventilation are made to adjust the nucleation and crystallization of the pigment so as to control pigment particles growth. Last but not the least, the temperature is another important factor in control condition. Figure 3 shows the relationship between temperature and reaction speed. 35-40 °C is the best temperature for the alkaline method. When the temperature is lower, the crystal growth will be too slow, when the reaction time will be too long though fine particles can be obtained and it will be easy to form γ -FeOOH crystal. By contrast, if the temperature is higher, the ferrous ion will diffuse too fast, resulting in fast growth of crystal and generation of rough pigment particles. During formation of crystal nuclei for the acid method, the temperature is generally controlled at 25-45 °C. If the temperature is lower than 25 °C, it's easy to produce particles of fine γ -FeOOH complex crystal. If the temperature is higher than 50 °C, the crystal will be coarse and short and Fe₃O₄ impurities will be generated.

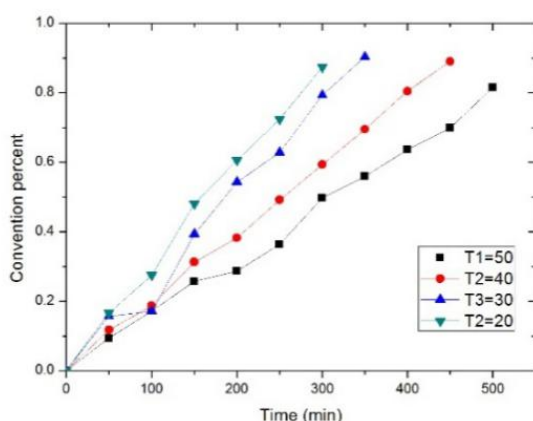


Figure 3: The relationship between temperature and reaction speed

2.2 Ferric iron conversion method

The ferric iron conversion method refers to transformation of the $\text{Fe}(\text{OH})_3$ generated into transparent iron yellow particles during preparation (Müller et al., 2015). The principle is that the $\text{Fe}(\text{OH})_3$ colloid generated during the preparation process is amorphous and thermodynamically unstable. It tends to spontaneously convert into crystals. So we can make it convert into $\alpha\text{-FeOOH}$ crystal by controlling certain conditions. There are two ferric iron conversion methods for preparation of transparent iron yellow pigment.

The first one is the sol-gel method, the process of which is shown in Figure 4. Spherical transparent yellow pigment particles can be obtained by this method (Liang et al., 2017). Quite small amount of salt solution added into the ferric iron solution, the positively charged $\text{Fe}(\text{OH})_3$ particles can be generated in the hydrosol system, and at the same time can be added anionic surfactant such as the sodium dodecyl benzene sulfonate (SDBS). Ionized in the solution, the surfactant can generate negative ions, which will be neutralized with the positively charged colloidal particles, which, coated with organic thin layer, are hydrophobic and lipophilic.

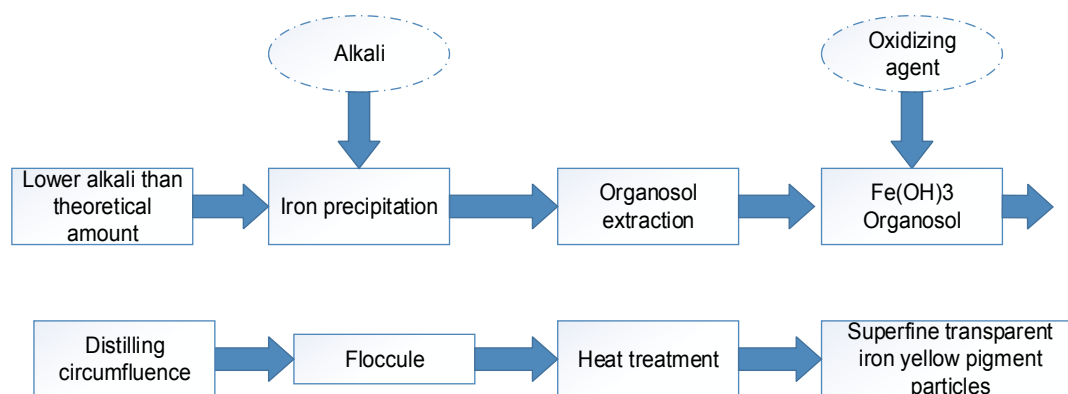
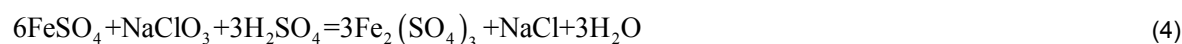
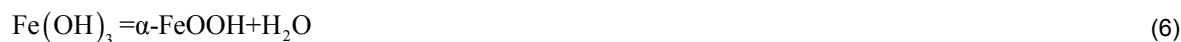


Figure 4: The sol-gel method and its process

Another method is the sodium chlorate oxidation method which uses FeSO_4 as raw material. Different from the previous acid method, for this method sodium chlorate divalent ions are added into ferric irons in an acidic environment. With the addition of NaOH , the ferric irons will precipitate as $\text{Fe}(\text{OH})_3$ gel, which, under some certain conditions, will convert into $\alpha\text{-FeOOH}$. And with the use of modifier such as sodium dodecyl benzene sulfonate or diphenyl guanidine, the $\alpha\text{-FeOOH}$ slurry will undergo surface modification of hydrophobicity as well as filter and dry process. Finally, the yellow pigment will be obtained after the dry process. The main reactions are as follows:





The process requires little time, but as it is difficult to control, the pigment quality is unstable.

2.3 Direct Conversion Method

This method uses carbonyl iron oxide $[\text{Fe}(\text{CO})_5]$ as raw material, and N_2 is as carrier. $\text{Fe}(\text{CO})_5$ combusts at 600°C after its evaporation. Mixed with the high-speed injected air, $\text{Fe}(\text{CO})_5$ undergoes a violent oxidation reaction, generating ultra-fine particle after the quenching and the cyclone separation process. The BASF company has produced a new industrial product of titanium yellow pigment which, with molecular formula as $\text{Fe}_2\text{O}_3 \cdot 0.960\text{--}2.999\text{C}_0.01\text{--}0.05$, owns a specific surface area of $150\text{ m}^2/\text{g}$ and an average particle size of $5\text{--}10\text{ nm}$. This method features of short process flow, good operating environment, high product quality, fine particle size and good dispersibility. But it is relatively complicated requiring large equipment investment, so the production cost is high.

3. Surface Modification of the Transparent Iron Yellow

Except the colloid chemical method, transparent yellow pigment particles produced with other preparation methods have a large surface area, which makes them strong polar molecules with strong hydrophilicity. So they will be easy to agglomerate during the drying and storage process, resulting in a decrease in the transparency. Besides, there will be need for long-term grinding during addition of paint or other media, which will not only increase the production cost of the coating but also make it inconvenient for use. So surface modification treatment is of great importance. In addition, surface modification treatment is able to enhance the thermal stability and chemical purity of the pigment. Therefore, surface treatment after the oxidation during industrial production is of considerable significance.

The surface modification of the transparent iron yellow pigment can be conducted by adding dispersant and surfactant. By this method, surface treatment can be carried out at the same time as the formation of the pigment particles. Usually dispersant is added before the formation of iron yellow particles, and the surface active agent is added at the same time as $\alpha\text{-FeOOH}$ is formed. Thus the surface properties of the pigment particles has been improved together with the light and weather resistance as well as other properties of the pigment.

Another surface modification method is to filter and wash the transparent iron yellow until it's neutral and unsalted. Set the ferric oxide content in the filter cake as $40\% \text{--}60\%$, then add alcohol slightly soluble in water with iron oxide content of $5\% \text{--}15\%$ and stir the the solution for $15\text{--}30\text{ min}$. Here a homogeneous and bright slurry pigment is obtained. After drying it by freezing, the transparent iron yellow with high tinting strength, high dispersibility and no impurity can be applied directly to the media without grinding.

The measurement of transparency is as below. Select the visible light with specific wavelengths of 489.4nm , 515.1nm , 529.8nm , 541.4nm , 557.1nm , 561.8nm , 572.5nm , 584.8nm , 600.7nm and 627.1nm ; Detect the TT and TD of this visible light with spectrophotometer; Calculate the transparency by division of the total TT and the sum of the measured TDs collected. Brightness greater than 75% can be considered as transparency. Figure 5 shows the definition of transparency (Baran et al., 2015).

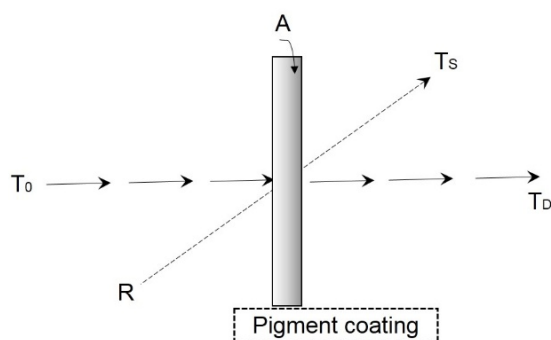


Figure 5: The definition of transparency

Where T_0 is the total incident light, R is the catoptric light, A is the absorbed light, T_s is the scattered light and T_D is the transmission light. D stands for the transparency. The relationship between these factors is as shown in the following equations:

$$T_0 = R + A + T_s + T_D \quad (7)$$

$$T_T = T_s + T_D \quad (8)$$

After the surface modification treatment, the transparency and heat resistance of the transparent iron yellow is improved. By dispersing the pigment into alkali solution with concentration of more than 10N and heating it at 100-250 °C for about 5 hours, its heat resistance can be increased by about 50%, and the pigment will be non-toxic. Similarly, through dispersing the transparent yellow pigment into the aqueous solution containing ferric iron ions and adding alkali as well as aluminum salts into the solution, then heating it at 100-250 °C for about 4 hours, the pigment surface will be coated with a layer of S film, its heat resistance will be increased by about 50% and it will be non-toxic.

4. Conclusion

Transparent iron oxide is a very important inorganic material, and it should be appropriately used as raw materials and the appropriate process should be selected to produce ultrafine transparent yellow iron oxide pigment of high industrial value. However, due to the reaction involving three phases, the gas, liquid and solid phases, the production process is more complex. However, the reaction and crystallization mechanism is not very clear and the process is also very difficult to achieve precisely control. Therefore, producing high quality and low cost transparent yellow iron oxide pigment should be an important direction of the current study. In addition, a lot of research for the dispersion and particle surface properties as well as the heat resistance still need to perform in the future.

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