Surface modification effect on particle size and stability of Yellow Pigment

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Abstract. NaOH solutions with different concentration were used to pre-treat YPs (yellow pigments) in order to investigate surface modification effects on stability and particle size of pre-treated yellow pigments (PYPs). The coupling agent KH550 was used to treat PYP10 (yellow pigment pre-treated with 10% NaOH) to be compared for PYPs. The YPs (yellow pigments) were pre-treated by NaOH solutions and rinsed with C2H5OH, then the filtrates and residues were analysed by spectrophotometer and laser granularity analyser; The filtrates are stratified after the PYPs rinsed with C2H5OH. Microscope and Natural settling experiment were used to analyse the particle size and stability in residues. The results show that the particle size of wet PYPs decreased with the concentration of NaOH, and the particle size of PYP30 was smaller than that of PYP10-KH550 (PYP10 treated with 5% KH550). The laser granularity analyser results show that the particle size of dry PYPs increased with the concentration of NaOH. The settle time of PYPs in water indicated that the stability of PYPs increased with the concentration of NaOH and PYP10-KH550 has the poorest stability. These results indicated that PYP30 has smallest particles and best stability, and it has the potential to be used in industry.

Key words: yellow pigment; NaOH; stability; particle size; settling time.

1. Introduction

Inorganic pigments have the advantages of high hiding power, tinting strength, heat resistance etc., and are widely used in the field of inks, coatings and other pigments, which play an important role in the performance of the product [1]. With the development of science and technology, the ultra-attenuation is the development tendency for the pigment, and the particle size can be less than 1 micron. Because of high surface energy, the particles would reunion easily and agglomeration can be found between particles, affecting the dispensability, coloration, and thus the performance of the pigment [2]. So it is necessary to modify the surface in order to improve the qualities of pigment.

Some researchers have found that some surface modifiers can modify pigment’s surface properties to improve their dispersion capacity [3-7]. NaOH solution was used pre-treat the surface of the particles
to increase the chemisorption activity of the surface of the particles before modification [8], but the effect of NaOH on particle size and stability has not been investigated. In this research, the yellow pigments were pre-treated by different concentrations of NaOH solution, and coupling agent KH550 was also used to be compared. The effects of different concentrations of NaOH solution and KH550 on the particle size of the YPs were studied by spectrophotometer and laser particle size analyser, and the stability of YPs after pre-treated was also investigated.

2. Experimental

2.1. Sample preparation

NaOH treatment of yellow pigments

The NaOH was carefully weighed and dissolved in deionized water, the concentrations of NaOH solutions were adjusted to 0%, 10%, 20%, 30%, 40% and 50%. The yellow pigments were pretreated with 0%, 10%, 20%, 30%, 40% and 50% of NaOH and named as YP0, PYP10, PYP20, PYP30, PYP40 and PYP50, respectively and the samples were listed in Table 1. The yellow pigments were weighted and added into NaOH solutions respectively and stirred at 50 ℃ for 30 min, then they were rinsed by using alcohol (99%) after filtered, finally the samples were prepared after the residues were dried at 80℃ in oven for 8 h.

The preparation of the sample PYP10-KH550

The powder of PYP10-KH550 was synthesized via following process, 0.25 g KH550 (coupling agent) was weighted and added to 10 mL alcohol (99%), and pH was adjusted to 4-5 by using 2% HCl (1.0 mol/L) solution, then the solution was stirred at room temperature for 30 min. After that, the PYP10 was added with weight ratio of PYP10:KH550 = 95:5, the solution was refluxed under magnetic stirring at 50℃ for 90 min, and dried at 80℃ in oven for 12 h.

Table 1. The samples treated with different solutions

| Sr. No. | Treatment solution | Sample name |
|---------|--------------------|-------------|
| 1       | 0                  | YP0         |
| 2       | 10% NaOH           | PYP10       |
| 3       | 20% NaOH           | PYP20       |
| 4       | 30% NaOH           | PYP30       |
| 5       | 40% NaOH           | PYP40       |
| 6       | 50% NaOH           | PYP50       |
| 7       | 10% NaOH +5% KH550 (Coupling agent) | PYP10-KH550 |

2.2. Characterization of PYPs (YP0, YP10, YP20, YP30, YP10-KH550)

Several analytic methods were used to investigate particle size and stability of PYPs. The average particle sizes of the wet and dry of PYPs were measured by microscope and Laser granularity analyzer respectively. The stability of PYPs was by using Complete Settlement Test Analysis.

2.2.1. Observation of particle size and distribution by optical microscope. 1.0 g of PYPs was kept in a conical flask, and then dispersed in 50 ml deionized water with the aid of ultra sonication at 40 ℃ for 30 min. 1 ml the dispersion was extracted using a plastic pipette into a clean beaker and diluted to 10 ml, then the particle size and distribution of diluted sample was observed with an optical microscope.

2.2.2. Laser granularity analyzer. The particle size and distribution of dry PYPs powder which had been dried for 24 h was measured by a Laser granularity analyzer respectively.

2.2.3. Complete settlement analysis. 1.0 g of the sample was dispersed in 20.0 ml deionize water with the aid of ultrasonic vibration at room temperature for 30 min, then 5.0 ml of the solution was taken in the measuring cylinder. The settling time was recorded by a stopwatch, the beginning time was when
the solution was static after ultrasonic vibration, and the ending time was when the components were completely precipitated.

3. Results and Discussion

3.1. NaOH treatment of yellow pigments
Though the solubility of NaOH in water at 20 °C is 109g/100ml, the concentration of NaOH can be up to 52%. When the concentration of NaOH was above 40%, PYP40 and PYP50 would agglomerate and could not be filtered. In this research, just PYP10, PYP20, PYP30 were prepared and filtered. The coupling agent KH550 was also used to treat PYP10 in order to prepare PYP10-KH550.

3.2. Microscope particle size analysis

![Microscope images of PYPs in deionized water.](image)

**Figure 1.** Microscope (200times) images of PYPs in deionized water.

The microscope images (200 times) of wet particles of PYPs particles in deionized water were shown in Fig.1 and the average size of particles were calculated from Fig.1 then listed in Table 2.

| Sample          | Particle size (μm) |
|-----------------|--------------------|
| YP0             | 35.5               |
| PYP10           | 30.7               |
| PYP20           | 24.8               |
| PYP30           | 19.4               |
| PYP10-KH550     | 21.7               |

**Table 2.** Particle size of PYPs calculated from microscope images
Figure 1 and Figure 2 show that the average particle size of PYPs decreases with the concentration of NaOH, it may be due to the surface modification effect of NaOH. When the hydroxyl groups of the surface of PYPs increased, the particle agglomeration was less and the average particle size of PYPs decreased.

Table 2 shows that the particle of PYP10-KH550 (21.7 μm) was 28.39% smaller than that of PYP10 (30.7 μm). This indicates that the particle of PYP10-KH550 was hard to be agglomerated because of the steric hindrance effect and lipophilic of KH550. The particle of PYP10-KH550 was larger than that of PYP30, the steric hindrance effect and lipophilic of KH550 could be simulated through the following equation.

Calculated and simulated from the Fig 2, the equation of concentration of NaOH to the particle size can be as following:

\[ Y = -0.542x + 35.73 \]

\[ R^2 = 0.9985 \]

Y: the particle size
X: the concentration of NaOH, 0 ≤ X ≤ 30

In this equation, if Y = 21.7 μm, X = 25.89; it means the PYP10-KH550 is similar to PYP25.89 (calculated); the effect of 10%NaOH+5%KH550 is similar to that of 25.89% NaOH.

Therefore, the order of particle size observed under the microscope at 200 times was: YP0 > PYP10 > PYP20 > PYP10-KH550 > PYP30.

3.3. Laser granularity analyzer analysis
The particle sizes of dry PYPs was measured by a laser granularity analyzer, and were listed in Table 3.

| Sample    | D50 particle size (μm) | D99 particle size (μm) |
|-----------|------------------------|------------------------|
| YP0       | 8.35                   | 24.89                  |
| PYP10     | 10.11                  | 29.97                  |
| PYP20     | 11.01                  | 35.37                  |
| PYP30     | 31.99                  | 174.81                 |
| PYP10-KH550 | 9.06                  | 26.98                  |

Table 3 shows that as the concentration of NaOH increased, the particle size of the dry powder of PYPs was larger. The reason may be the agglomeration of particle because of the hydroxyl dehydration
in the drying process of 24h. When the concentration of NaOH was 30%, the agglomeration effect was greatly enhanced and the D50 particle size of PYP30 was up to 31.99.

The order of particle size measurement by laser granularity analyzer was: PYP30> PYP20> PYP10> PYP10-KH550> YP0, the particle size of YP0 and PYP10-KH550 could maintain small because KH550 did not dehydrate. When the powder was dissolved in water, the particles were dispersed again, and this can be observed by microscope.

3.4. Stability analysis

The stability of PYPs was evaluated by investigated the solution’s complete settling time, the results were shown in Table 4. It can be seen in Table 4 that the settling time of PYPs increased with the concentration of NaOH.

| Table 4. The complete settling time of samples. |
|-----------------------------------------------|
| YP0   | PYP10 | PYP20 | PYP30 | PYP10-KH550 |
| Complete settling time (h) | 0.5 | 1.5 | 5.0 | 8.0 | 1.0 |

Because of the existence of the hydroxyl group on the surface of PYPs, the particles were hard to agglomerate. With the increasing of the hydroxyl group, the buoyancy of the particles increased, and the settling time was prolonged. For example, there was more hydroxyl groups on the surface of PYP30 than that of PYP20, the settling time of PYP30 was longer than PYP20.

The hydroxyl groups on the surface of PYPs improved the buoyancy of the particles, so the complete settling time of PYP10 and PYP10-KH550 were longer than that of YP0. And PYP10-KH550 was linked with the coupling agent which had three silanol groups that could connect to three yellow pigment particles at the same time, therefore the weight of the particles increased, and the settling time was shorter than that of PYP10.

It concluded that the order of stability and complete settling time was YP0< PYP10-KH550< PYP10<PYP20<PYP30.

4. Conclusion

Surface modification effect on particle size and stability of Yellow Pigment by NaOH and KH550 were investigated. The results showed that the particle size of wet PYPs decreased with the concentration of NaOH; the tendency was as the equation (Y=-0.542x+35.73) shown, and the particle size of wet PYP30 was smallest. After the PYPs were filtrated and dried, the particle size of dry powder increased with the concentration of NaOH. And the stability of PYPs increased with the concentration of NaOH and PYP30 has the best stability. Comparing with PYP10-KH550, PYP30 is better both in particle size and stability, which means PYP30 would be potential to be used in industry.

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