Dyes and Pigments 44 (2000) 75–80

Modification study involving a Naphthol as red pigment

Fei Xuening [a,*], Zhang Tianyong [b], Zhou Chunlong [b]

[a] Department of Basic Science, Tianjin Institute of Urban Construction, Tianjin 300381, PR China
[b] Department of Applied Chemistry, College of Chemical Engineering, Tianjin University, Tianjin 300072, PR China

Received 30 September 1998; accepted 8 February 1999

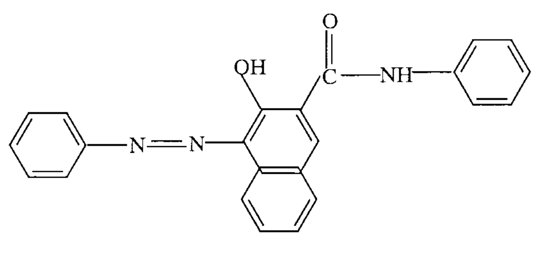
Abstract

This paper is concerned with the modification study on a Naphthol red pigment (known in China as 808 Scarlet) synthesized by coupling aniline with Naphthol AS, on the surface of inorganic cores. We also report the use of Tobias acid to modify the aniline in the coupling step, producing a mixed coupling. As the size of the inorganic core decreases, surfaces of silica gel are fully covered with coupling component, and the resultant coated pigment is made by the naphthol coupling component reacting with the diazonium component on the inorganic core surface. The results of these experiments show that the resistance to heat, color strength, shade and dispersing stability (in aqueous media) of the modified pigment made by the "coated core" method and the mixing coupling technique are all increased. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Coated pigment; Mixed coupling; Silica gel; Surface modification; 808 Scarlet pigment

1. Introduction

The naphthol red organic pigment (808 Scarlet) made from aniline and Naphthol AS is used in the coloration of coatings, leather and emulsion paints and has high color strength, good covering power, base and acid-resistance. But some application properties of this red pigment do not satisfy current requirements. We have found that the organic coated pigments made by organic pigment encapsulation on the surface of inert inorganic cores have not only organic pigment properties such as high color strength and excellent shade but also reflect typical inorganic pigment performance of good resistance to heat and high covering power [1]. In addition, with inert inorganic cores being used in the organic pigment encapsulation process, the production cost of the pigment is decreased [2]. This paper deals with the technology of coated pigment preparation made by coating 808 Scarlet on silica gel particles. Pigment properties such as covering power and resistance to heat have been improved. Moreover, a modification of 808 Scarlet made by mixed coupling technology with Tobias acid was prepared [3,4], and certain properties of the modified pigment were clearly enhanced.



808 Scarlet

* Corresponding author. Fax: + +086022 23618897.

0143-7208/99/$ - see front matter
PII: S0143-7208(99)00072-8

2. Experimental

2.1. Preparation of benzenediazonium chloride

A mixture of aniline (0.015 mol), water (50 cm^3) and HCl (30%, 4.2 ml) was kept at 3–5°C, then aqueous $NaNO_2$ (30%) was added dropwise to the mixture until diazotization was complete. The reaction was then stirred for 30 min.

2.2. Preparation of the coated pigment [5]

A mixture of Naphthol AS (0.015 mol), sulphonated castor oil (0.75 g) and NaOH (3.5 ml^3, NaOH) was heated to effect complete solution. Silica gel (1.4 g) with mean diameter of 80–100 μm was mixed with alcohol (5 cm^3) and then milled for 2 h in a ball mill. The silica gel suspension was mixed with the Naphthol AS solution and milling was continued for 2 h. The diazonium compound was added dropwise to the silica gel/coupling component mixture, until all the Naphthol was consumed and the pH was adjusted to neutral at 40°C in 0.5 h. The mixture was kept at 70°C for 1 h, filtered, washed and dried.

2.3. Preparation of the Naphthol AS solution

A mixture of sulphonated castor oil (0.75 g) NaOH (20%, 3.5 cm^3) and water (50 ml) was heated to 80°C. Naphthol AS (0.015 mol) was added with stirring and the transparent solution was adjusted to 60 ml with water. The resultant solution was stirred for 30 min before use in the coupling step.

2.4. Preparation of diazonium salt of Tobias acid

The diazonium salt of Tobias acid was obtained according to the method described in Section 2.1.

2.5. Modification of 808 Scarlet

A basic solution of Naphthol AS (0.015 mol, 60 ml) was coupled with benzenediazonium chloride (0.015 mol). To this mixture, the diazonium salt of Tobias acid (TA) (1.77×10^{-4}, 5.3×10^{-4}, 8.8×10^{-4}, or 12.4×10^{-4} mol) was added, and the reaction was stirred as a basic solution of Naphthol AS was added. Stirring was continued until all the diazonium salt was consumed. Laking agent (calcium chloride) was added and stirring was continued for 0.5 h, keeping the temperature at 80–90°C for 30–60 min. The filtered product was washed with warm water until the filtrate was neutral, and dried.

2.6. Determination of properties of modified pigments

The shade and color strength of the pigments were determined according to Chinese National Standards GB 1864–80,1719–79 and 1708–79. The measurement of the dispersing extent (DE) of pigments was carried out according to the literature [6]. The crystalline form of the pigment was measured using an X-ray powder diffraction analyzer (Rigaku, 2038 type, made in Japan).

3. Results and discussion

3.1. Modification study on coated technology for 808 Scarlet

When a basic solution of Naphthol AS was milled with a silica gel suspension, molecules of Naphthol AS were adsorbed on the surfaces of silica gel particles. Addition of the diazonium salt produced azo pigment on the surfaces of silica gel particles. It is well known that silica gel has free surface area and many pores on its surface. Silica gel particles consist of SiO_2 tetrahedra, and has a slightly irregular three-dimensional construction, similar to a spheroid. The surface of silica gel has -OH and -O- groups, as illustrated in Fig. 1.

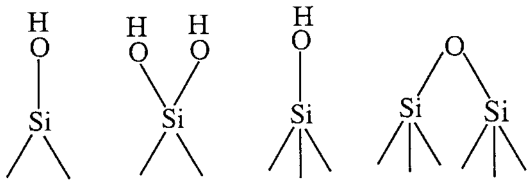


Fig. 1. Functional groups on the silica gel surface.

Fig. 2 shows hydrogen bonding between silica gel and Naphthol AS molecules. Attached Naphthol AS molecules react to form the coated pigment. The smaller the silica gel particle size, the more active the absorption points on the gel's surface, and the more organic pigment molecules formed and adsorbed.

X-ray powder diffraction patterns of 808 Scarlet, silica gel and the coated pigment were determined. Fig. 3 shows that the 2θ diffraction angles of the encapsulated pigment with silica gel cores are nearly the same as the diffraction angles of 808 Scarlet. Differences involve the intensities for the two 2θ diffraction angles at 29° and 31°, which are slightly weaker for the coated pigment. Also, the characteristic peaks of silica gel molecules which form the cores of the organic coated pigment disappear in the X-ray diffraction curves of the coated pigment. On the basis of these observations, we conclude that the surface of the inorganic core is fully encapsulated.

3.2. *Applicable properties of coated pigment*

The transparency, shade, color strength and flowability of the coated pigment were determined, and the results are listed in Table 1. From Table 1, we can see that the shade, transparency and flowability of the coated pigment are the same as the uncoated standard, and the color strength of the coated pigment is higher than the uncoated standard.

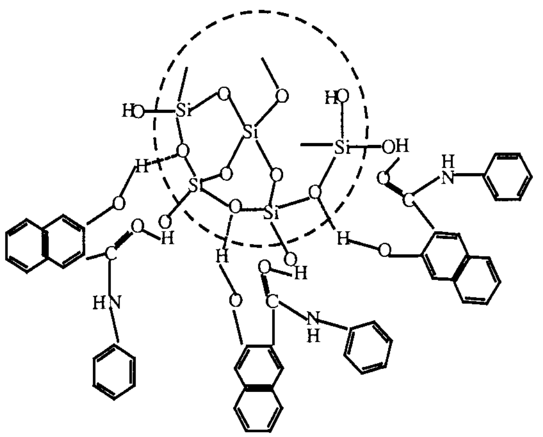


Fig. 2. Diagram for the adsorption of Naphthol AS on silica gel.

To check the heat resistance of the coated pigment, differential thermal analysis (DTA) of the coated pigment and uncoated 808 Scarlet were compared, as shown in Fig. 4. As can be seen, the melting point of the coated pigment (249°C) is slightly higher than that of the uncoated 808 Scarlet pigment (245°C). Multiple hydrogen bonding points between organic pigment and inorganic core would account for the increased melting point. Additional experiments show that the color strength of 808 Scarlet begins to decrease at 176°C. together with a change in pigment shade. However, the shade of the coated pigment does not change until 215°C, confirming that it has improved thermal stability.

Experimental results also show that the coated pigment has not only higher thermal stability, but also an improved dispersibility in aqueous media as shown in Fig. 5. After the hydrogen bond is

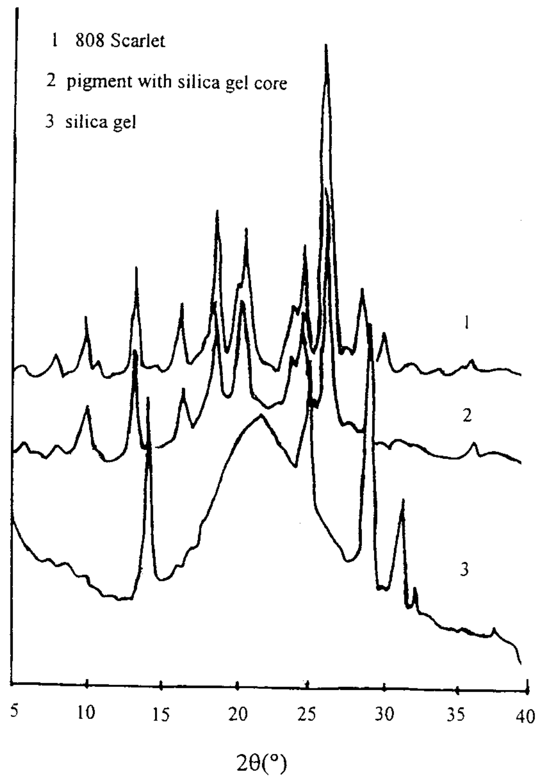


Fig. 3. The X-ray diffraction curves for the silica gel coated pigment.

Table 1
Applicable properties of the coated pigment

Item	Comparison	Requirement	Experimental results
Transparency	Compared with standard sample[a]	Slightly higher or same	Same
Shade	Compared with standard sample	Slightly higher or same	Bright red
Color strength	Compared with standard sample	⩾95%	104%
Flowability (mm)	Compared with standard sample	31 ± 2	29

[a] Standard sample is the commercial pigment 808 Scarlet.

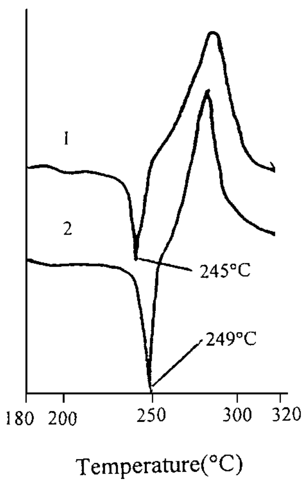


Fig. 4. The DTA curves of 808 Scarlet (1) and pigment with silica gel core (2).

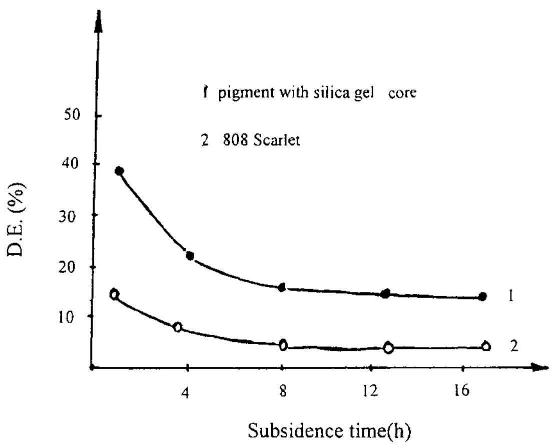


Fig. 5. The aqueous dispersing extent curves for the coated pigment (1) and 808 Scarlet (2).

formed between the organic pigment and the surface of silica gel particles, the surplus valences on the silica gel surface can combine with water molecules to form an electrical double layer. When the particle size of the inorganic core is small enough to make the force between coated pigment and water molecules higer than or similar to the force of gravity on the coated pigment, the latter exhibits good dispersibility.

These experimental results indicate that the physical properties of the coated pigment made from 808 Scarlet molecules by encapsulation on the surface of silica gel cores are superior to uncoated 808 Scarlet organic pigment. The ratio of inorganic core used is 25% of the coated pigment, making it possible to reduce production cost.

3.3. Modification of 808 Scarlet using mixed coupling technology

In this aspect of our study, Tobias acid was used as a second diazonium coupling component. The process is illustrated in Fig. 6.

3.3.1. Effect of the second diazo component on pigment properties

The shade, color strength and flowability of pigment modified with TA were studied, the results of which are shown in Table 2. When the second diazo component is used, color strength and pigment transparency are obviously increased, and the shade of the modified pigment becomes slightly bluish red. When the amount of TA added is 1%, the observed color strength is 109%, and the shade is bright bluish-red. The modified pigment is more bluish red in shade because of the

Table 2
The properties of 808 Scarlet modified by a second coupling

No.	Modifier	Amount of modifier ($mol \times 10^{-4}$)	Amount of Naphthol AS ($mol \times 10^{-2}$)	Hue[a]	Flowability (mm)	Color strength (%)
808 Scarlet	–	0	1.77	B	31	95
2-1	TA	1.77	1.75	BB	35	109
2-2	TA	5.3	1.71	BB	23	108
2-3	TA	8.8	1.68	BBB	21	–
2-4	TA	12.4	1.64	BBB	20	–

[a] B: slightly blue; BB: fairly blue; BBB: dark blue.

extended conjugation afforded by TA. TA can also effect crystal growth in the modified pigment and can prevent pigment particles from aggregating. In aqueous media, there is an electrical double layer around the surface of the modified pigment particle. The repulsion between two particles increases as they approach each other. Since aggregation decreases the overall size of pigment particle, flowability also decreases.

3.3.2. Particle size distribution and X-ray diffraction

Physical properties of modified pigments are closely related to their particle size and crystal form. Particle size distribution of modified pigments incorporating 1, 3, 5 and 7% of TA were determined. By adding TA, the particle size of modified pigments becomes smaller. This is advantageous to the crystal core of the pigment which is quickly formed and retards further crystal growth. Under the experimental conditions, the rate of crystal core formation is faster than the rate of further crystal growth. The mean diameter of 808 Scarlet particles is 1.33 μm. The mean diameters of the modified pigments containing 1, 3 and 5% of TA are 0.38, 0.82 and 1.30 μm, respectively. The mean diameter of the modified pigment containing 1% of TA is smaller than that of 808 Scarlet.

As the amount of added TA increases, the mean diameter of the resultant modified pigment gradually become large and approaches the size of the parent pigment particle, as shown in Table 3. This change of properties in a modified pigment is interrelated to its crystal form. From the X-ray diffraction curves we can observe that characteristic peaks of modified pigment incorporating 1% of the modifier differ from those of the parent pigment. The 2θ peak intensity at 10.20° of modified 808 Scarlet pigment becomes weak, but the peak at 28.40° is appreciably increased.

3.3.3. Thermal stability and dispersion stability of modified pigment

The DTA of 808 Scarlet modified by adding 1% of TA was determined, showing that both the melting point of modified pigment and the temperature of color change (200°C) are higher than 808 Scarlet.

The dispersion of modified pigment in aqueous media was now studied, with modified pigment incorporating 1 and 3% of TA, and was compared with the parent pigment. Our results indicate that

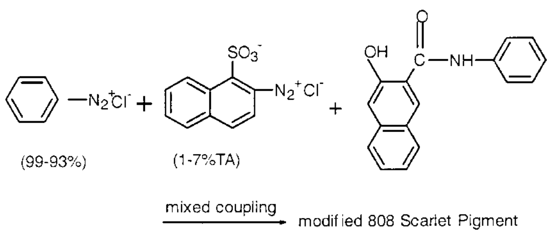


Fig. 6. Modification of 808 Scarlet via mixed coupling.

Table 3
The particle sizes of 808 Scarlet modified by mixed coupling

No.	Amount of TA (%)	$\bar{d}$ (μm)	< 0.5 μm (%)	< 1.5 μm (%)
1	0	1.33	9.4	55.2
2	1	0.38	60.9	73
3	3	0.82	32.2	43.8
4	5	1.30	31.2	40.5

dispersion of modified pigment was improved in aqueous media. As the amount of sulphonic groups increases on the surface of modified pigment, so does the electric charge on the surface, as the double electrical layer on the surface of modified pigment is easily formed. This is advantageous in effecting dispersion of the modified pigment. Both aggregation and flocculation of the modified pigment can be prevented because the particles of modified pigment become smaller.

4. Conclusion

Both organic encapsulation on a silica gel core with mixed coupling with Tobias Acid can be used for enhancement of 808 Scarlet pigment. Experimental results show that 808 Scarlet pigment encapsulated about silica gel particles not only has a higher thermal stability but also improved dispersibility in aqueous media. TA can be used as a second mixed coupling component to modify of 808 Scarlet pigment. When the amount of TA added is 1%, color strength and heat-resistance are superior to 808 Scarlet pigment, and the shade is bluish-red. The ratio of the smaller to larger particles in the product is also higher. X-ray diffraction experiments indicate that the crystal form of the encapsulated pigment differs from that of 808 Scarlet.

References

[1] Nobuoka S. Shikizai Kyokaishi 1987;60(12):653–60.
[2] Mita Industrial Co., JP 59,86,662, 1984.
[3] ACY, JP 81,116,753, 1980.
[4] Dainippon Ink Chemical Industry Co., EP 2,021,906, 1988.
[5] Liu Hongzhuang, CN 1,073,463, 1993.
[6] Tianyong Z, Chunlong Z, Dyes and Pigments 1997;35(2): 123–30.