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An Investigation of Complex Modification of Benzidine Yellow G

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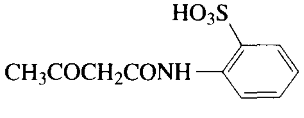
ABSTRACT

Benzidine Yellow G (C.I. Pigment Yellow 12) was successively modified through mixed coupling with sulfo derivatives of acetoacetanilide and fatty amines. The hydrocarbon chain of the fatty amine enclosed the polar sulfo groups, and properties such as flowability, wettability, and dispersibility were greatly improved after the pigment was treated with stearylamine. © 1998 Elsevier Science Ltd. All rights reserved

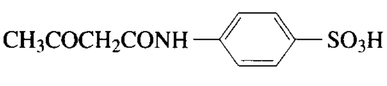
Keywords: C.I. Pigment Yellow 12, complex modification, mixed coupling, amine treatment.

1 INTRODUCTION

Mixed coupling is an important method to modify the properties of azo pigments, such as shade, color strength, transparency, particle size and distribution. It had been used in some azo yellow pigments, including C.I. Pigment Yellow 13, 14 and 83 [1,2]. In this paper, we prepared C.I. Pigment Yellow 12 with ortho- and para-acetoactamido benzene sulfonic acid (D–I and D–II) as the second coupling component (modifying component).



(D–I)



(D–II)

The results of property determinations showed that the particle diameter decreased, and the color strength and transparency increased visibly.

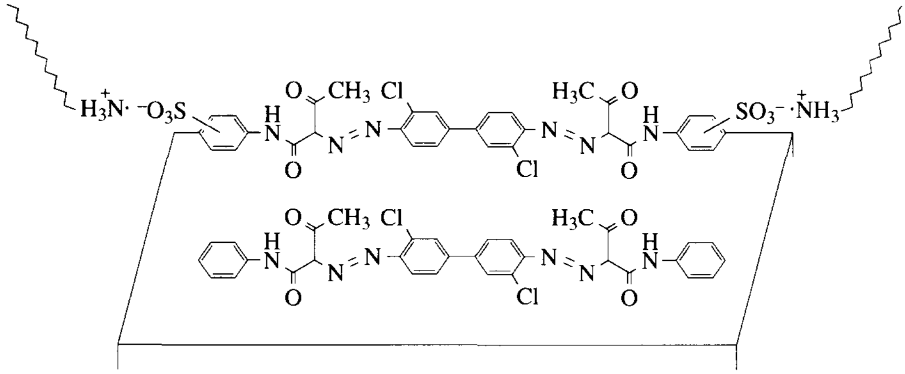


Fig. 1. Model of complex modification

However, the increase of the modified pigment polarity made its dispersabilities in non-polar organic solvent much more difficult.

On the other hand, we have previously obtained C.I. Pigment Yellow 12 with a high flowability and dispersibility in non-polar solvent through surface treatment with organic amines [3]. The amines however, tended to migrate from the particle surface in the course of use of the pigments.

As a result of this, complex modification, as illustrated in Fig. 1, was used. This method is similar to the surface treatment of quinacridone and phthalocyanine pigments and could be referred to as a 'two step modification' [4–6].

It resulted in a synergistic action of the sulfo group and the amine. Because of the similarity of chemical structure, modifying derivatives containing sulfo groups are readily and strongly adsorbed on the surface of the parent pigment. Stearylamine used in this paper combined on the pigment particles through an ionic bond between the quaternary cationic and sulfo groups according to the following reaction:

$$[\text{C.I.P.Y.12} \vdash \text{SO}_3^- + \text{R} - \text{NH}_3^+ \rightarrow [\text{C.I.P.Y.12} \vdash \text{SO}_3^-.{}^+\text{NH}_3 - \text{R} \qquad (1)$$

This type of chemical combination made the amine much more stable on the pigment surface than would physical adsorption.

2 EXPERIMENTAL

2.1 Pigment preparation

Acetoacetanilide [3.68 g (0.0198 mol)] was dissolved in 25 ml dilute sodium hydroxide. The diazonium solution of 3,3′-dichlorobenzidine was then added dropwise until the end point of coupling was observed. A solution of 0.05 g (0.0002 mol) of ortho- or para-acetoacetamido benzene sulfonic acid (D–I or D–II) was then added to the suspension, and the addition of diazonium salt continued in order to ensure that the second coupling component had fully reacted. After stirring for 20 min, an acetic acid solution of 0.06 g (0.0002 mol) of stearylamine was added. The suspension was then heated to 80°C and maintained at this temperature for 45–60 min. The product was then filtered, washed and dried to give the modified C.I. Pigment Yellow 12.

Flowability was measured according to GB 1719–79 [7], in which the appropriate amount of oil ink made from modified pigments was pressed between two glass plates with a weight of 200 g. The diameter of the round ink flat was used to determine the flowability of the pigments.

The contact angle was calculated on the basis of the formulae: $\theta = 2\,\mathrm{arctg}(h r^{-1})$ $\theta < 90°$, $\theta = 90° + \arcsin(h r^{-1})$ $\theta \geq 90°$ in which h and r are the height and maximum chord of water drop on plates of pigment, respectively, measured using a JJC-1 type contact angle instrument [8].

The dispersion degree was obtained according to the formula [9]: $D.D = (100 - T)\%$ in which T is the transmittance of the pigment suspension obtained from its dispersion in toluene; it was determined using a 751 G spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 Flowability of pigments

Pigments prepared through mixed coupling had low flowability because of their small particles and strong polarity. After treatment with stearylamine, their flowability was enhanced to a large extent and pigment transparency remained ideal. The flowability of pigments modified through mixed coupling and complex method is shown in Table 1.

Figure 2, obtained from Table 1, more clearly shows the change of pigment flowability after stearylamine treatment.

TABLE 1
Flowability of Pigments (mm)

Amount of derivatives and amine (%)	*Mixed coupling*		*Complex modification*	
	D–I	*D–II*	*D–I*	*D–II*
0	20.8	20.8	20.8	20.8
0.5	20.1	20.7	23.0	22.2
1.0	17.7	19.2	23.4	22.2
2.0	17.6	17.9	23.6	22.8

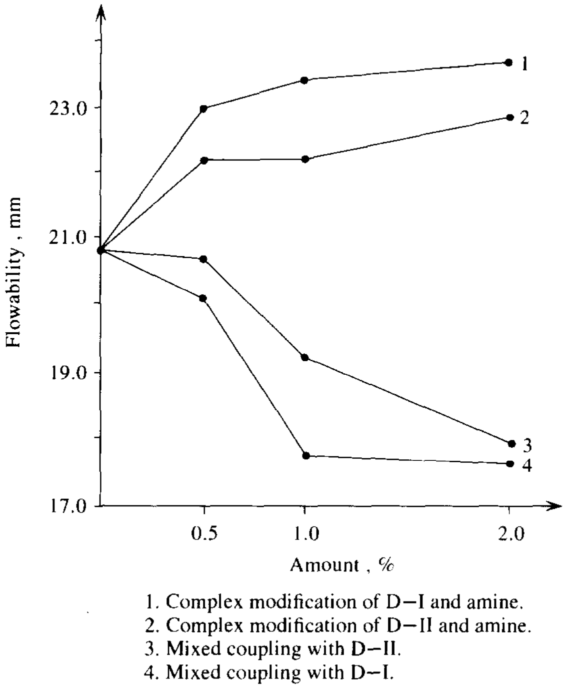


Fig. 2. Flowability of pigments vs amount of derivatives and amine.

The flowability of pigments modified through mixed coupling decreased with increase of the derivative addition, irrespective of whether the ortho- or para-derivative was used. After treatment with stearylamine, it increased greatly. Moreover, the more sulfo derivative and amine used, the higher was the flowability.

Because the ionic bond between steaylamine and the sulfo acetoacetanilde covered the polar group of the pigment, this resulted in a lowering of the polarity of the pigment, and its compatibility with the dispersion medium rose; the flowability then improved.

3.2 Dispersibility and wettability of pigments

The dispersibility of modified complex and of mixed coupling pigments is shown in Table 2.

In Table 2, pigments treated with amine can be seen to have a higher dispersibility, no matter how much derivative and amine was added. The long hydrocarbon chain of stearylamine covering on the pigments had a higher compatibility with the solvent. It could stretch out and depress the flocculation of pigment particles, as shown in Fig. 3. Thus, the pigment has a higher dispersion degree, and its suspension was more stable.

TABLE 2
Dispersion Degree of Pigments (%)

Amount of derivatives and amine (%)	*D–I*		*D–II*	
	Mixed coupling	*Complex modification*	*Mixed coupling*	*Complex modification*
0	19.7	19.7	19.7	19.7
0.5	38.7	48.7	23.1	48.2
1.0	35.9	63.9	20.9	43.4
2.0	29.3	39.0	21.2	47.2

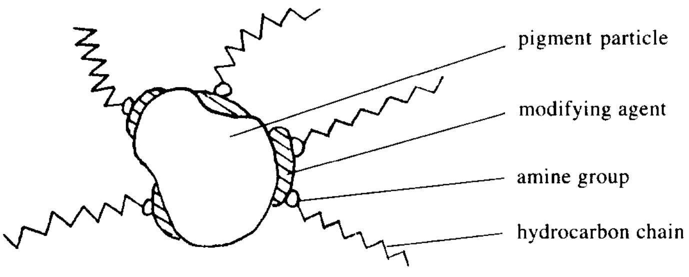


Fig. 3. The function of fatty amine.

The contact angle of the pigment with water could be used to measure its wettability. The bigger the contact angle, the more difficult was the wetting, and the pigment polarity was also lower, the dispersion in non-polar organic solvent was then easier. After formation of the ionic bond, the contact angle of the pigments changed to a large degree, as shown in Table 3 and Fig. 4.

Without amine treatment, the contact angle was small and declined when more sulfo derivative was added. After treatment with stearylamine, the wetting of the pigment by water was more difficult, and the contact angle became larger. As a result of the decrease in polarity, the pigment was more easily wetted by, and dispersed in, non-polar solvent.

TABLE 3
Contact Angle of Pigments with Water (degree)

Amount of derivatives and amine (%)	*Mixed coupling*		*Complex modification*	
	D–I	*D–II*	*D–I*	*D–II*
0	96.3	96.3	96.3	96.3
0.5	94.6	94.8	102.8	103.3
1.0	91.9	93.9	104.1	104.9
2.0	90.6	90.3	105.7	106.5

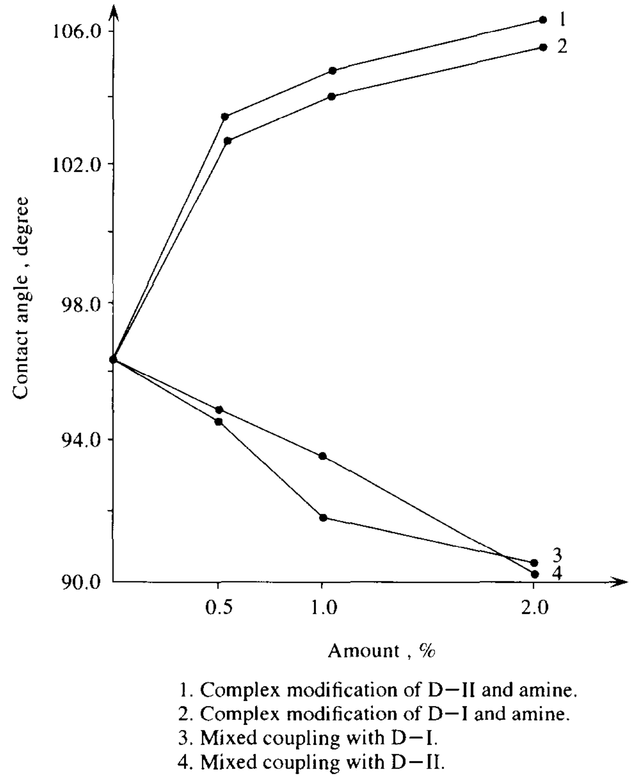


Fig. 4. Contact angle of pigments vs amount of derivatives and amine.

4 CONCLUSION

Mixed coupling with sulfo derivatives of acetoacetanilide modify the transparency of the pigment investigated. The flowability and contact angle with water was low. Complex modification of mixed coupling and stearylamine treatment gave a visible synergistic action. Both flowability and dispersibility in non-polar organic solvent were improved in maintaining the small particle size and high transparency of the pigment.

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