Dyes and Pigments, Vol. 38, No. 4, pp. 185–193, 1998

Printed in Great Britain
PII: S0143-7208(97)00090-0
0143-7208/98 $19.00 + 0.00

The Effects of Mixed Coupling on the Properties of C.I. Pigment Yellow 12

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(Received 15 April 1997; accepted 29 August 1997)

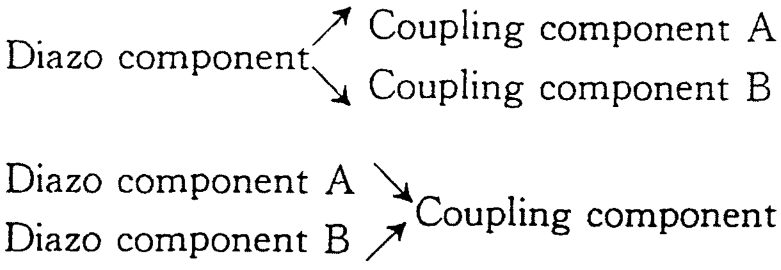
ABSTRACT

The influence of mixed coupling on the properties of C.I. Pigment Yellow 12 is studied. Carboxy and sulfo derivatives of acetoacetanilide were used as the second modifying coupling components. The results showed that the state of the crystal and particle size changed; the pigment flowability and dispersibility in non-polar solvents decreased due to the introduction of polar groups. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: C.I. pigment yellow 12, mixed coupling, sulto derivative, carboxy derivative.

INTRODUCTION

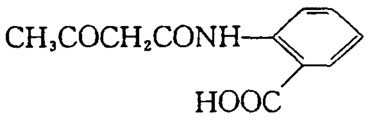
Mixed coupling is currently one of the most important methods of pigment modification. One diazo component coupled with two or more coupling components, or two or more diazo components coupled with one coupling component, are the two methods of mixed coupling, as illustrated by the following:



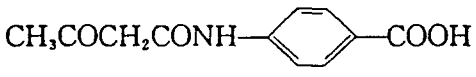
Azo pigments prepared through mixed coupling have the properties of a 'pigment alloy', such properties being different from those of a 'mechanical mixture'. The process is also referred to as 'solid solution of pigment'. Mixed coupling can change some characteristics of the pigment crystals and inhibit their growth. It can also modify the surface properties, particle size and distribution of the pigment [1,2].

Some data has been reported on the application of this technique to diarylide yellow pigments such as C.I. Pigment Yellows 12, 13, 14 and 83; they describe different derivatives of the coupling components which are used as the second modifying coupling components [3–7]. More detailed investigations on the influences of mixed coupling on pigment properties have not been fully reported.

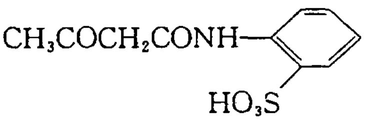
In this paper, carboxy and sulfo derivatives of acetoacetanilide were used as the second coupling components in the preparation of modified C.I. Pigment Yellow 12; the derivatives used were MCC-I—IV:



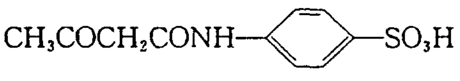
(MCC- I)



(MCC- II)



(MCC-III)



(MCC-IV)

The effects of mixed coupling on the crystal form of the pigment, and the particle size and distribution, polarity, and flowability were also studied.

EXPERIMENTAL

Preparation of C.I. Pigment Yellow 12 through mixed coupling

By conventional methods, 3.5 g (0.01 mol) 3,3′-dichlorobenzidine was diazotized; 0.0194 mol acetoacetanilide and 0.0006 mol of its carboxy derivative were dissolved in a solution of 1 g sodium hydroxide in 25 ml water, and the pH of the mixture was adjusted to pH 6.5 with 25% aq acetic acid (1:3). The diazonium salt solution of 3,3′-dichlorobenzidine was added dropwise until the end of coupling reaction, when the suspension did not show colour development with either the diazonium salt R-salt (disodium salt of 2-hydroxy-3,6-naphthalenedisulfonic acid). After filtering, washing and drying, the modified pigment prepared through mixed coupling was obtained.

Pigments modified with 5 or 10% carboxy derivative and 0.5, 1.0 and 2.0% sulfo derivative were prepared using the same method.

Determination of pigment properties

Flowability was determined according to the Chinese National Criterion, GB 1719–79 [8]. In this method, 0.3 g modified pigment was milled with 1 ml resin to prepare the oil ink, the appropriate amount of which was pressed between two glass plate with a weight of 200 g. The diameter of the round ink flat was used to determine the flowability of pigments (the higher the pigment flowability, the higher the ink flat).

Contact angle was calculated on the basis of the formulae:

$$\theta = 2\mathrm{arctg}(h/r) \qquad \theta < 90^\circ \tag{1}$$

$$= 90^\circ + \arcsin(h/r - 1) \quad \theta \geqslant 90^\circ \tag{2}$$

in which h and r, measured through JJC–1 type contact angle instrument, are the height and maximum level of the water drop on plate of pigment.

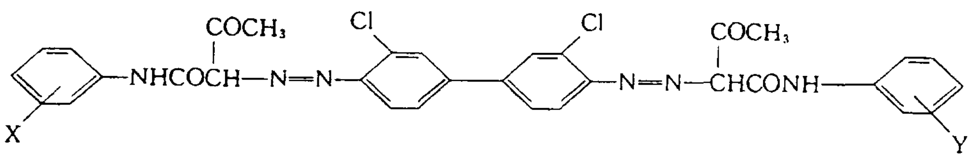
Modified pigments were dispersed in water using ultrasonics to prepare a 1% suspension; 1 ml of this was injected into an LKY–1 type particle diameter measuring instrument. After calculation, particle distribution curves and average particle diameters were obtained.

An S-450 scanning electron microscope and a CN-2308 type X-ray diffractometer were used to determine particle shape and crystal form of the pigment, respectively.

RESULTS AND DISCUSSION

Effects of mixed coupling on pigment crystal

The pigment prepared through the mixed coupling was a solid solution of C.I. Pigment Yellow 12 and its carboxy or sulfo derivatives and its composition can be expressed by the following structural formula.



C.I. Pigment Yellow 12: $X = Y = \mathrm{H}$
Pigment a: $X = Y = \mathrm{COOH}$ or $\mathrm{SO_3H}$
Pigment b: $X = \mathrm{COOH}$ or $\mathrm{SO_3H}$, $Y = \mathrm{H}$

The crystal form of this kind of 'pigment alloy' was different from that of C.I. Pigment Yellow 12, and changed with the variation of derivative addition. The X-ray diffraction patterns of the parent and modified pigments using ortho-carboxy acetoacetanilide (MCC–I) as the second coupling component are shown in Fig. 1.

Curve 1 shows the diffraction pattern of the ortho-biscarboxy derivative of C.I. Pigment Yellow 12, which was obtained through coupling of ortho-carboxy acetoacetanilide with the diazo salt of 3,3′-dichlorobenzidine. Its crystallinity was low and had only two diffraction peaks at 2θ angle 10.1° and 25.5°. Modified pigments showed three diffraction peaks at 2θ angle 10.3° to 12.5°,

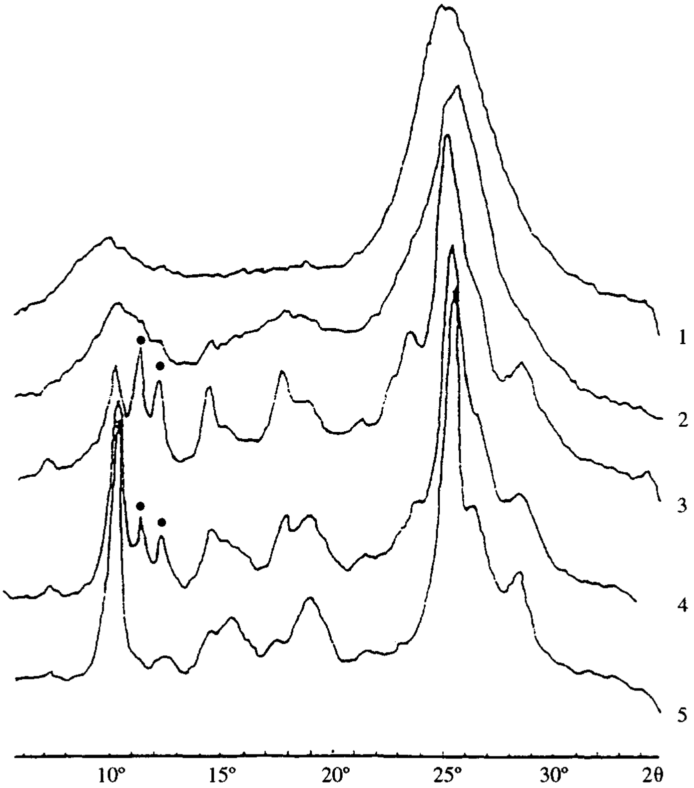


Fig. 1. X-ray diffraction pattern of pigments, 1. Bicarboxy derivative of C.I. Pigment Yellow 12 (pigment $a : x = y = \mathrm{COOH}$); 2. MCC-I 10%; 3. MCC-I 5%; 4. MCC-I 3%; 5. C.I. Pigment Yellow 12.

which indicates the emergence of a new crystal phase. The diffraction curve of the pigment containing 3% derivative was similar to that of C.I. Pigment Yellow 12, although they were not completely the same. When the amount of modifying coupling agent was increased to 10%, the pigment crystal was similar to that of the biscarboxy derivative of the parent pigment.

The addition of derivatives made the system more heterogeneous, with decrease of the crystallization energy. The nucleation rate therefore increased, and consequently there was insufficient time for the nuclei to grow intactly. Thus, a crypto-crystal, or even a non-crystalline form could be obtained, and their X-ray diffraction peaks are flow, or not apparent [9].

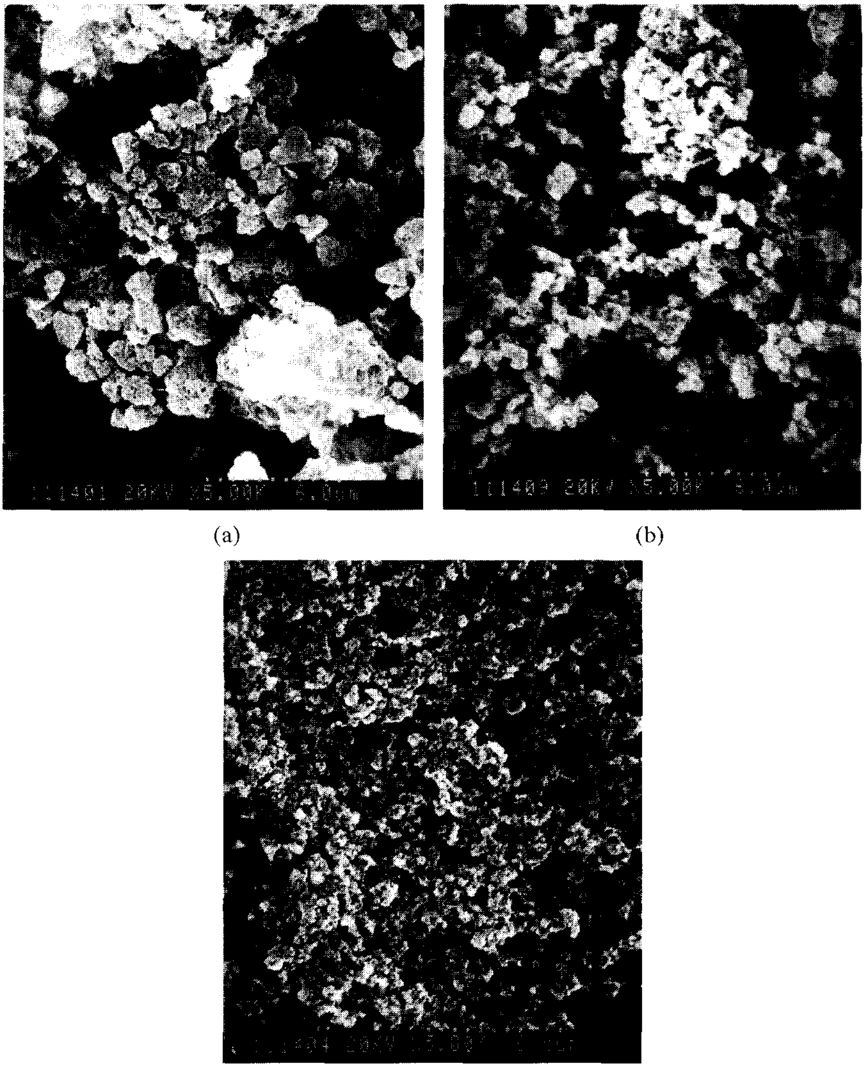
Effects of mixed coupling on particle shape

The experimental results showed that the technique of mixed coupling could accelerate the production of nucleus and change the growth state of the pigment crystal. The particle shapes of modified pigments using ortho-acetoacetamide benzene sulfonic acid (MCC-III) as the second coupling component are shown in Fig. 2.

After addition of the second coupling component, the particle diameter of the pigment decreased, and when the amount of modifying agent rose to 2.0%, the particles were very small. Nucleation and crystal growth were the two steps of crystallization, both of which were influenced by the mixed coupling process, which promoted the formation of nucleus, retarded the growing of crystals and resulted in a declining of particle size. The particle size distribution curves (Fig. 3) show the average particle diameter of the parent pigment to be about 1 μm, while that of the mixed coupled pigments were less than 0.75 μm. Moreover, most of particles were smaller than 0.5 μm when the addition of MCC-III was raised to 2.0%. All of the distribution curves of the modified pigments were higher and narrower than those of C.I. Pigment Yellow 12.

As a result of the decrease of particle size, the pigment flowability varied. The flowability of pigments prepared through mixed coupling with ortho- and para-acetoacetamide benzene sulfonic acid (MCC-III and IV) are listed in Table 1.

Figure 4 shows that the flowability decreased with increase of addition of the derivatives and decreases to less than 18.0 mm when 2.0% of modifying coupling component was used, while that of the parent pigment was 20.8 mm. Although the addition of the two different derivatives were the same, the pigments prepared from the ortho sulfo derivative (MCC-III) had smaller particle size and lower flowability than those from the para-derivative (MCC-IV). The variation of flowability was due to the increase of



(a) (b) (c)

Fig. 2. Particle shape of pigments. (a) C.I. Pigment Yellow 12; (b) MCC-III addition 0.5%; (c) MCC-III addition 2.0%.

specific interfacial area and oil absorption caused by the decreasing particle diameter; it was also interrelated with pigment polarity.

Effects of mixed coupling on wettability of pigments

The introduction of polar substituents into the pigment molecular influences particle polarity, wettability, and hence its compatibility with water. The

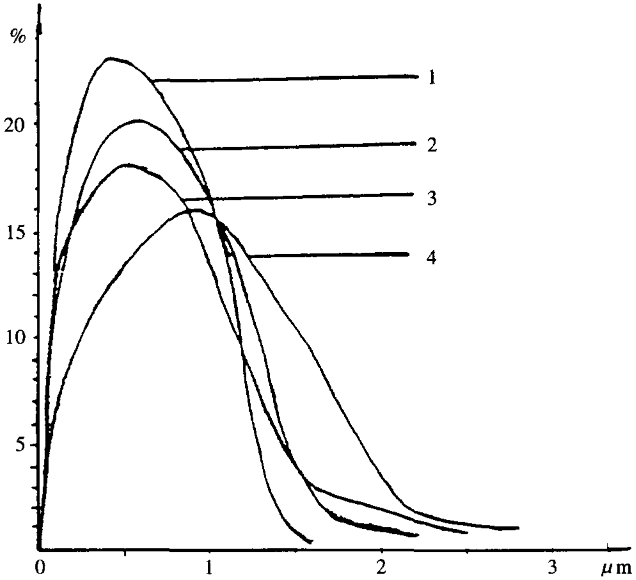


Fig. 3. Particle size distribution of pigments. 1. MCC-III 2.0%; 2. MCC-III 1.0%; 3. MCC-III 0.5%; 4. C.I. Pigment Yellow 12.

TABLE 1
Effect of Mixed Coupling on Flowability of Pigments

Derivative	*Flowability of pigments (mm)*			
	0	*0.5%*	*1.0%*	*2.0%*
MCC-III	20.8	19.6	17.9	17.3
MCC-IV	20.8	19.9	18.8	17.5

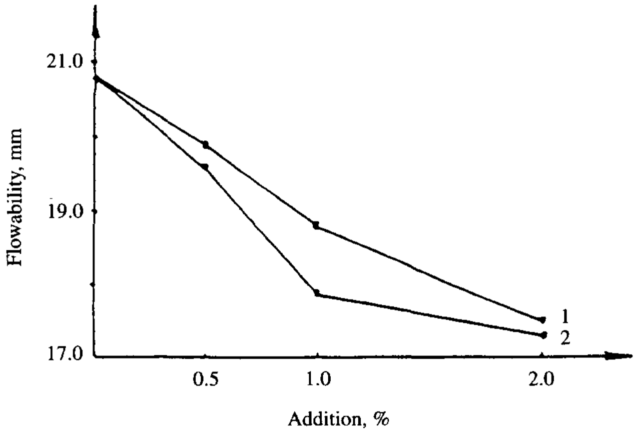


Fig. 4. Flowability of pigments versus addition of derivatives. 1. MCC-III; 2. MCC-IV.

contact angles with water of pigments prepared through mixed coupling with different amounts of derivatives are listed in Table 2.

Figure 5 clearly indicates the changing of contact angle, and shows that the contact angle of mixed coupled pigments with water is lower than that of C.I. Pigment Yellow 12, and decreases with increase of derivative addition. One reason for the decrease of contact angle is that the pigment tends to be wetted by solvent, in order to reduce its high surface free energy caused by the smallness of the particle. An alternative reason is the enhancing of the compatibility of the pigment with water, as the result of introducing sulfo groups consequent increase in pigment polarity.

On the other hand, the pigment was more difficult to be 'wetted' by an organic solvent. It was known that wetting is an indispensable condition of dispersing. A stable dispersion cannot be obtained if the pigment is not well wetted. Thus, the dispersion degree in non-polar media of the modified pigments made through this technique was low.

TABLE 2
Effect of Mixed Coupling on Contact Angle of Pigments

Derivative	*Contact angle of pigment (degree)*			
	0	*0.5%*	*1.0%*	*2.0%*
MCC-III	96.3	94.6	92.9	89.8
MCC-IV	96.3	95.0	92.7	88.8

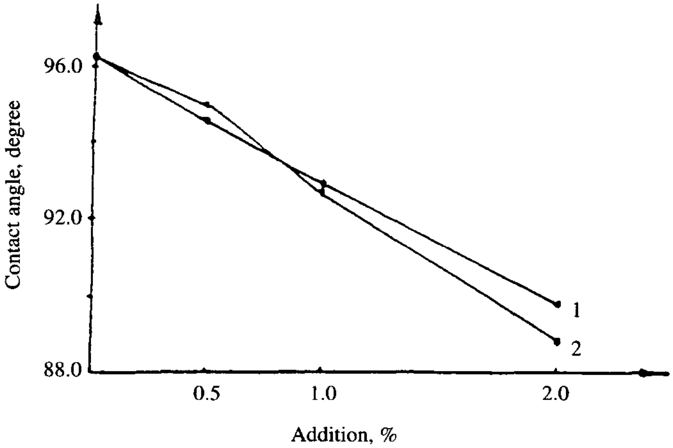


Fig. 5. Contact angle of pigments with water versus addition of derivatives. 1. MCC-III; 2. MCC-IV.

CONCLUSION

The technique of mixed coupling changes the crystal shape and results in new diffraction peaks. The crystallinity decreased when the addition of the second coupling component rose to a certain extent. Pigments prepared through this technique had small particle size, narrow particle size distribution curve, and low flowability. The introduction of a sulfo group made the wetting of the pigment by polar solvents easy, and its dispersion in non-polar solvents more difficult.

REFERENCES

1. Dongzhi, L. and Shengwu, R., *Dyestuff Industry*, 1992, **29**(6), 15.
2. Dongzhi, L. and Shengwu, R., *Dyestuff Industry*, 1990, **27**(3), 8.
3. Chunlong, Z., Proceedings of National Symposium on Organic Pigment, China, 1994, p. 22.
4. ICI, British Patent, No. 1 139 294, 1966.
5. ICI, British Patent, No. 972 805, 1964.
6. Takahiro, Y. and Kenji, K., JP 01 193 364, 1989.
7. Hays, B. G. and Stanaback, R. S., US Patent No. 4 648 907, 1987.
8. Haerbin Paint Factory, GB 1719-79, China, 1979.
9. Zhenpei, W., Zhichao, Z. and Zhonghe, L., *Crystallography*, Construction Industry Publishing House of China, Beijing, 1986, p. 25.