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An Investigation of Organic Dye-Coloured Nacreous Pigments

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ABSTRACT

The preparation of some coloured mica-titanium dioxide nacreous pigments has been investigated. The results showed that some mordant and direct dyes were the preferred precursor materials. The effects of reaction conditions, such as temperature, pH and reaction time, on the quality of the coloured nacreous pigments were also studied.

1 INTRODUCTION

Organic dye-coloured mica-titanium dioxide nacreous pigments have both the brightness of nacreous pigments and the brilliant colour of organic dyes or pigments. They are prepared by precipitating organic dyes or pigments on mica-titanium dioxide. The application of this kind of pigment assists in solving many of the problems apparent in classical pigment technology through the mechanical mixing of titanium dioxide-coated mica with dyes or pigments. Moreover, they are brilliantly coloured and less toxic than the equivalent metal ion-coloured nacreous pigments.[1] Although attention has been given to certain specific systems, such as acid dye and direct dye-coloured mica-titanium dioxide, as outlined in several patents[2–4] and papers,[5] there are still no systematic and comprehensive reports on organic dye-coloured nacreous pigments.

In this paper, nacreous pigments coloured with acid dyes, mordant dyes and direct dyes were prepared. The effects of the reaction conditions on the quality of the pigments were studied. The application of dye-coloured nacreous pigments and their characterisation are also discussed.

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2 EXPERIMENTAL

2.1 One-step technology

Titanium dioxide-coated mica (3 g) was dispersed in 30 ml of distilled water; 6 ml of an aqueous solution based on 0·5 g dye dissolved in 100 ml water was mixed with the suspension. Ten millilitres of an aqueous solution of 5 g $AlCl_3$ in 100 ml water was added dropwise over 45 min while stirring, with simultaneous addition an aqueous solution of 5% (w/w) of NaOH to maintain the pH at 6–7. The suspension was filtered, washed and dried after the reaction.

2.2 Two-step technology

Titanium dioxide-coated mica (3 g) was dispersed in 30 ml of distilled water. Twenty millilitres of aq. solution of $AlCl_3$ (5%) were added. The pH was adjusted to 8 with 5% aq. NaOH. Of the aluminum hydroxide-coated nacreous pigment thus obtained, 3 g was dispersed in 80 ml of distilled water and 7 ml of 0·5% aq. dye solution was added. The pH was adjusted to 6–7 with 5% aq. NaOH, and reaction continued at room temperature for 30 min.

2.3 Determination of dye-uptake

The maximum wavelength of absorption for the dye solution was determined spectrophotometrically and calibrations between the dye concentration and absorbance established.

The filtrates from the filtering and washing stages were acquired and their absorbance at the maximum wavelength determined with a 721-Type spectrophotometer. The dye-uptake was calculated according to the calibrations mentioned above.

2.4 Application of screen printing pastes containing coloured-nacreous pigment formulations

The organic dye-coloured nacreous pigments were formulated into standard screen-printing pastes. These were then used in the colouring of cotton fibres.

3 RESULTS AND DISCUSSION

3.1 Colouring method with dyes

The one-step and two-step technologies of preparing organic dye-coloured nacreous pigment were used. In the former, aluminum chloride was

TABLE 1
Dye-uptake Using $AlCl_3$ and $CaCl_2$

Metal compound	*CI Mordant Orange 6*		*CI Direct Red 80*		*CI Direct Blue 80*	
	E	*Dye-uptake (%)*	*E*	*Dye-uptake (%)*	*E*	*Dye-uptake (%)*
$AlCl_3$	0·019	98·6	0·032	99·2	0·013	99·8
$CaCl_2$	0·321	80·0	0·560	74·0	0·459	74·9

added simultaneously with dye solution. Then, many more 'active sites' of aluminum hydroxide were created than could react with dye. In the latter case, the process was more easily controlled because the precipitating of aluminum hydroxide and dye were carried out separately. Thus, both of the technologies proved to be feasible.

Although both aluminum chloride and calcium chloride have been reported as being effective laking agents, the results of experiments with CI Mordant Orange 6, CI Direct Red 80 and CI Direct Blue 86 showed that the former is better, because it gives higher dye-uptakes, as shown in Table 1.

3.2 Influence of dyes

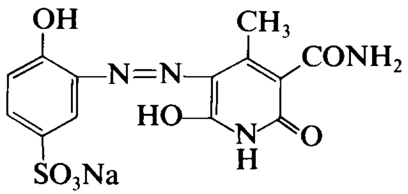
Because of the presence of sulfo groups and of carboxylic groups, one might be tempted to conclude that the acid dyes could be transformed into insoluble lakes when laking reagents were added. CI Acid Yellow 36, CI Acid Red 35, CI Acid Red 52, CI Acid Blue 1, CI Acid Blue 7 and CI Solvent Green 7 were chosen for the preparation of the coloured nacreous pigments. However, none of these gave successful products, since effective bonding was not achieved.

CI Mordant Orange 6(II), CI Mordant Red 9(IV), CI Mordant Red 15(V), CI Mordant Blue 1(VI) and two other dyes containing the pyridone group (I, III) were also used. It was found that all the dyes had potential chelating groups such as hydroxy, amino, carboxylic and azo groups in their molecules.

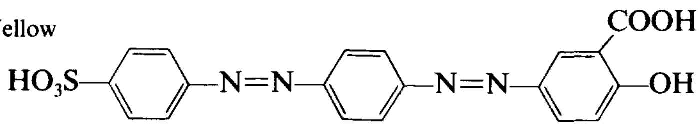
These can form 'dye-aluminum ion-titanium dioxide-coated mica' linkings with the help of complex formation between the dyes, aluminum hydroxide and nacreous pigments. This linking was so firm that extremely little dye leakage or migration occurred after fixation.

Direct dyes are large and planar molecules, and consequently provide large Van der Waals forces in their interactions.

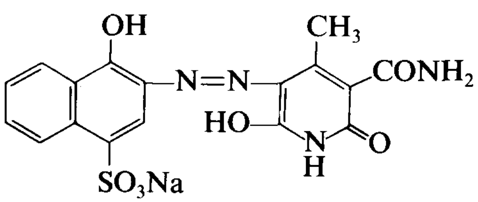
The products formed from both CI Direct Red 80(VII) and CI Direct Blue 86(VIII) proved that they gave firm associations with mica-titanium dioxide.



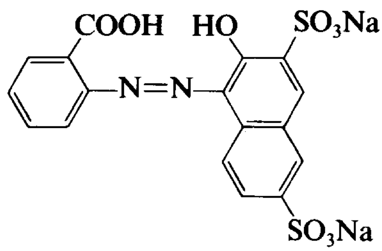
I. Mordant Yellow



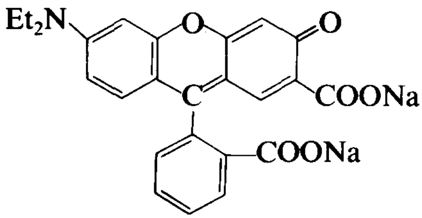
II. CI Mordant Orange 6



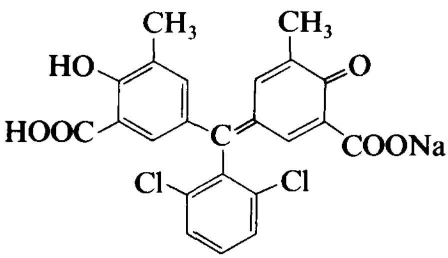
III. Mordant Red



IV. CI Mordant Red 9



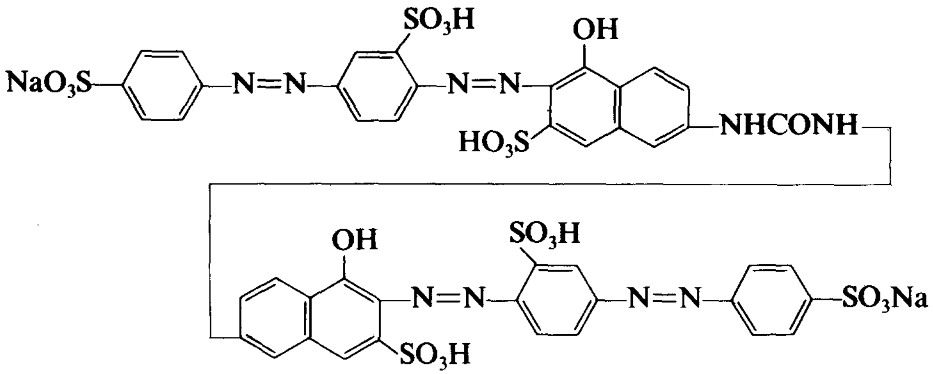
V. CI Mordant Red 15



VI. CI Mordant Blue 1

TABLE 2
Variation in Dye-uptake with pH value

pH	*Dye II*		*Dye VII*		*Dye VIII*	
	E	*Dye-uptake (%)*	*E*	*Dye-uptake (%)*	*E*	*Dye-uptake (%)*
5	0·130	91·7	0·525	75·7	0·480	73·7
6	0·019	98·6	0·032	99·2	0·013	99·8
7	0·075	95·1	0·074	98·1	0·050	99·3
8	0·181	88·6	0·045	98·9	0·036	99·5
9	0·372	76·9	0·570	73·4	0·520	71·4



VII. CI Direct Red 80

$[CuPC]$—$(SO_3Na)_2$

VIII. CI Direct Blue 86

3.3 Factors influencing colour enhancement

3.3.1 Influence of pH value

The pH value of the total medium was found to be a key factor with respect to the preparation of each coloured pigment. Its effects on dye-uptake can be deduced from Table 2 and Fig. 1.

The results show the extent of dye precipitation decreases at both high and low pH values. Figure 1 indicates that the dye-uptake is the highest at pH 6 for CI Mordant Orange 6, and at pH from 6 to 8 for CI Direct Red 80 and CI Direct Blue 86.

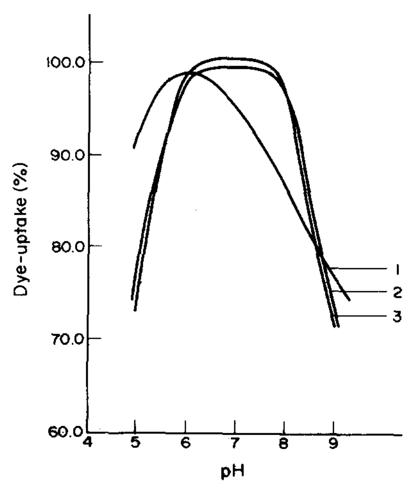


Fig. 1. Relation between dye-uptake and pH value: 1. Dye II, 2. Dye VII, 3. Dye VIII.

TABLE 3
Dye-uptake at Different Temperatures

Temperature (°C)	*Dye II*		*Dye VII*		*Dye VIII*	
	E	*Dye-uptake (%)*	*E*	*Dye-uptake (%)*	*E*	*Dye-uptake (%)*
25	0·019	98·6	0·032	99·2	0·013	99·8
55	0·334	79·1	0·435	80·3	0·220	88·3
90	0·550	66·0	0·614	71·1	0·590	67·4

3.3.2 Influence of temperature

Table 3 and Fig. 2 show the influence of temperature on the colouring reaction. The dye-uptake of all the three dyes decreases with increase in the reaction temperature. Thus, it is recommended that the coloured pigments should be prepared at room temperature.

3.3.3 Dyeing time

The experimental results of reactions carried out for different reaction times are shown in Table 4 and Fig. 3. It is apparent that a reaction time of 30 min is optimal. It was observed that the dye composite precipitated to no greater extent over longer reaction times.

3.3.4 The amount of aluminum chloride used

Irrespective of whether the 'one-step' or 'two-step' technology approach was used, it was found that any drift away from the optimum aluminum

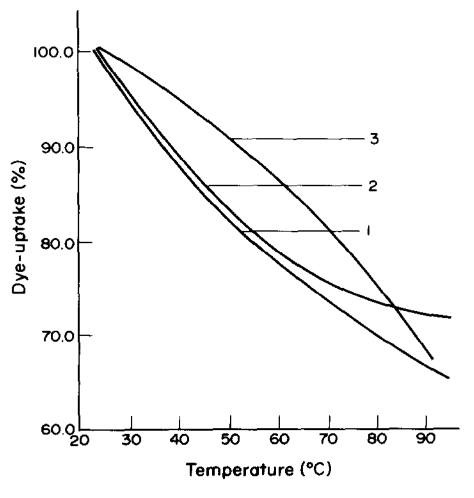


Fig. 2. Relation between dye-uptake and temperature: 1. Dye II, 2. Dye VII, 3. Dye VIII.

TABLE 4
Dye-uptake at Different Reaction Times

Reaction time (min)	Dye II		Dye VII		Dye VIII	
	E	Dye-uptake (%)	E	Dye-uptake (%)	E	Dye-uptake (%)
10	0·301	81·1	0·337	85·1	0·200	89·4
20	0·120	93·1	0·170	93·7	0·122	98·3
30	0·019	98·6	0·032	99·2	0·013	99·8
60	0·019	98·6	0·030	99·3	0·011	99·8

TABLE 5
Dye-uptake at Different Amounts of $AlCl_3$

Amount of 5% $AlCl_3$ (wt %)	Brightness	E	Dye-uptake (%)
10	Excellent	0·290	84·3
20	Excellent	0·013	99·8
30	Poor	0·575	68·3

chloride content (20%) was harmful to the coloured pigment produced (Table 5).

Similar experiments were carried out using the 'one-step' technology approach with CI Mordant Red 9, CI Mordant Red 15 and CI Mordant Blue 1. The preferred pH, reaction temperature and amount of aluminum chloride used were pH 6–7, room temperature and 16·7%, respectively.

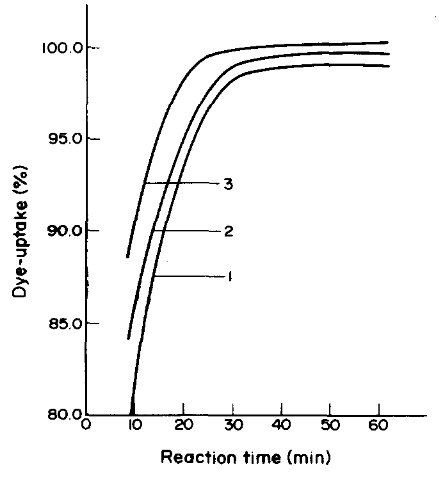


Fig. 3. Relation between dye-uptake and reaction time: 1. Dye II, 2. Dye VII, 3. Dye VIII.

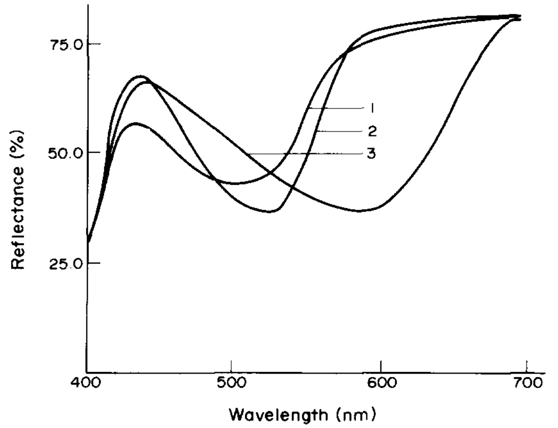


Fig. 4. Reflectance curves of dyed samples, 1. CI Mordant Red 9 Dye IV, 2. CI Mordant Red 15 Dye V, 3. CI Mordant Blue 1 Dye VI.

3.4 Application and characterisation

The organic dye-coloured nacreous pigments were applied as screen printing pastes for the printing of cotton fabrics. The printing characteristics for samples based on CI Mordant Red 9(IV), CI Mordant Red 15 (V) and CI Mordant Blue 1(VI) were determined. The reflectance curves of the prints are shown in Fig. 4.

4 CONCLUSIONS

Mordant dyes and direct dyes can be used to prepare organic dye-coloured nacreous pigments. Both the 'one-step' and 'two-step' results described gave products of good quality. Aluminum chloride was shown to be the best laking agent.

The colouring of titanium dioxide-coated mica should be carried out at pH 6–7, 25°C and with a reaction time of 30 min. The optimum amounts of aluminum chloride used were 16·7% and 20·0% (based on mica-titanium dioxide pigment) for the 'one-step' and 'two-step' approaches respectively. The pigments produced gave pearlescent effects.

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