The effect of dye particles on the rub fastness of naphthol dyes

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The effect of dye particles on the rub fastness of naphthol dyes has been investigated from the kinetic viewpoint. A measure of the rub fastness properties can be given by the rate constant and/or the equilibrium constant of a reversible first-order reaction. The presence of granular dye particles increases these constants and lowers the rub fastness. On the other hand, needle-shaped dye particles have little effect on these constants and do not lower the rub fastness.

INTRODUCTION

Dyeings from naphthol dyes tend to suffer from poor rub fastness. This defect is caused by the surface precipitation of dye particles that do not adhere well to textile fabrics. However, at the fundamental level relatively little is known about the effect of dye particles on the rub fastness.

The physical properties of solid particles vary with their size and shape, i.e. the particle size affects the characteristics of packing, optics and adhesion. In previous papers [1-4] the rub fastness of iron oxide particles on cotton fabrics was found to be affected by the size, shape and aggregation of the particles.

In the present paper the rubbing-off behaviour of naphthol dyes is investigated from the kinetic viewpoint and the effect of dye particles on the rub fastness is discussed.

EXPERIMENTAL

Materials

Plain cotton fabric was used in this study. The coupling component employed was Naphthol AS (CI Azoic Coupling Component 2) together with the diazo compounds Orange GC, Red 3GL, Brown RR, Blue BB and Green BB (CI Azoic Diazo Components 2, 9, 15, 20 and 118 respectively).

Methods

Dyeing was carried out according to a conventional method using a wetting agent, caustic soda, formaldehyde for Naphthol AS, which was coupled with three to seven times its own weight of diazo salt. Dyed fabrics were washed in cold water three times in a washing machine. Concentration of Orange GC, Red 3GL, Brown RR, Blue BB and Green BB on the dyed fabrics was determined by extraction with pyridine at 70°C followed colorimetric analysis at 520, 530, 555, 580 and 600 nm respectively.

Dry rubbing tests were conducted by the same method as described previously [5]. The amount of dye that stained the white fabric was determined by measuring the reflectance and comparing the value obtained from a standard calibration curve, as defined by Eqn 1:

$$f = \frac{(1-R_x)^2}{2R_x} - \frac{(1-R_0)^2}{2R_0} \quad (1)$$

where R_x and R_0 are the reflectances of the stained white cloth and the original respectively. The quantity f is linearly related to dye content as shown in Figure 1. Such a straight line was obtained with each dyeing.

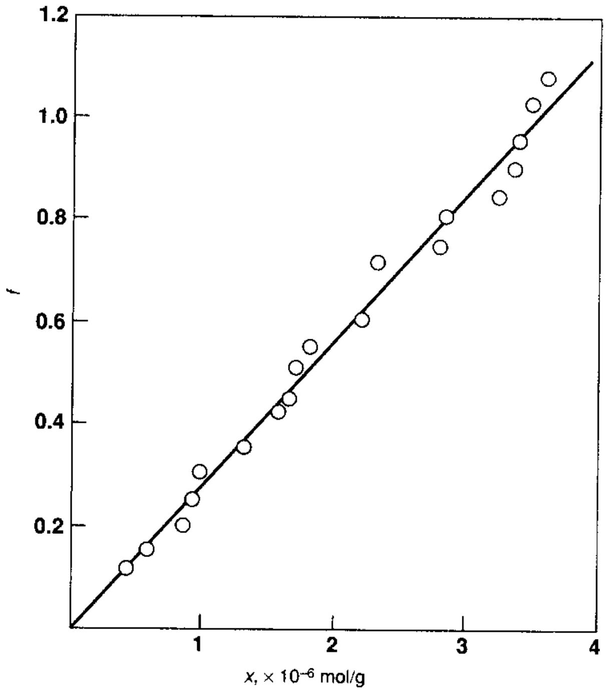

Figure 1 Calibration curve of f against dye content (x) for Green BB

Dye particles on the dyed fabrics or the stained white cloth were observed by means of a scanning electron microscope with magnifications of 3000 to 10 000.

RESULTS AND DISCUSSION

A measure of rub fastness

Rub fastness can be assessed in terms of the amount of dye transferred from a dyed fabric to a white fabric during the testing procedure. It has been proved that the rubbing-off behaviour of every kind of dye can be treated as a reversible first-order reaction [5,6]. So far in the work in this laboratory a measure of the kinetic properties of the rubbing process has been given by three constants: the rate constant k_1 of transfer of dye from dyed fabric to white fabric, the rate constant k_{-1} of the reverse process, and the equilibrium constant K (k_1/k_{-1}).

When the dye removal process conforms to a reversible first-order reaction, Eqn 2 should hold [5,7]:

$$\frac{dx}{dt} = (k_1 + k_{-1})\left[\frac{k_1 A}{k_1 + k_{-1}} - (x - F)\right] \quad (2)$$

where A, x and F are respectively the initial dye concentration on the dyed fabric, the amount of dye transferred from dyed fabric to white fabric after t rubs and a constant indicating the initial condition. The constant F has been discussed previously [5], and its value was very low in the present work.

Letting m equal $k_1A/(k_1 + k_{-1})$, substituting m into Eqn 2 and integrating yields Eqn 3:

$$\ln\left(\frac{m}{m-(x-F)}\right) = (k_1 + k_{-1})t + C \quad (3)$$

where C is zero because $x = F$ at $t = 0$.

By letting $k_1 + k_{-1} = k$ Eqn 4 can be written:

$$\ln[m-(x-F)] = \ln m - kt \quad (4)$$

which shows that a plot of $\ln[m - (x - F)]$ against t should be linear with a slope of $-k$ and an intercept at $\ln m$. To determine k from this plot m must be known, and it can be obtained by a trial and error method as shown previously [5]. A plot of $\ln[m - (x - F)]$ against t is shown in Figure 2. A linear relationship exists between the two for all the samples used in this work. Therefore the removal of naphthol dyes can be treated as a reversible first-order reaction. The rate constants and the equilibrium constant can be obtained from Eqns 5–7:

$$k_1 = \frac{mk}{A} \quad (5)$$

$$k_{-1} = k - k_1 \quad (6)$$

$$K = k_1/k_{-1} \quad (7)$$

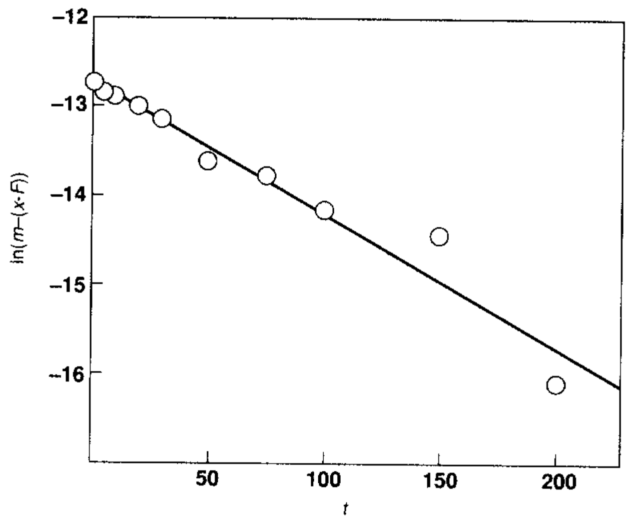

Figure 2 Relationship between $\ln[m - (x - F)]$ and t for Green BB

Dye particles

The surfaces of dyed fabrics were observed by means of scanning electron microscopy and are shown in Figures 3–5, in which the medium to deep dyeings are compared with the pale one. These micrographs indicate that many dye particles about 0.1–3 μm in diameter were present on the surfaces of the medium and deep dyeings, while few were present on the pale dyeing.

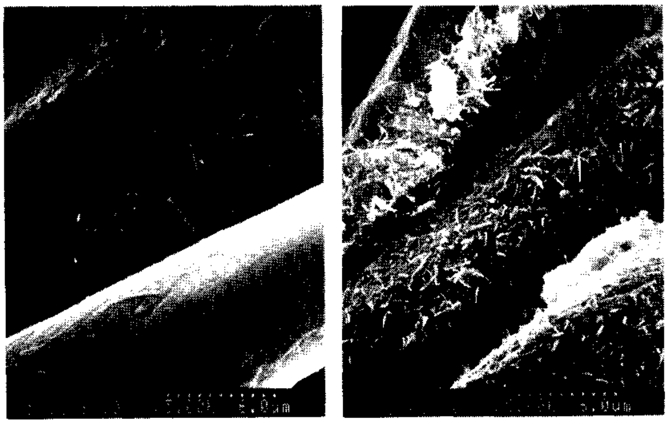

Figure 3 Comparison of dye particles on cotton fabric dyed with Blue BB between pale (left: 1.79×10^{-5} mol/g dye) and deep (right: 7.77×10^{-5} mol/g dye) dyeings

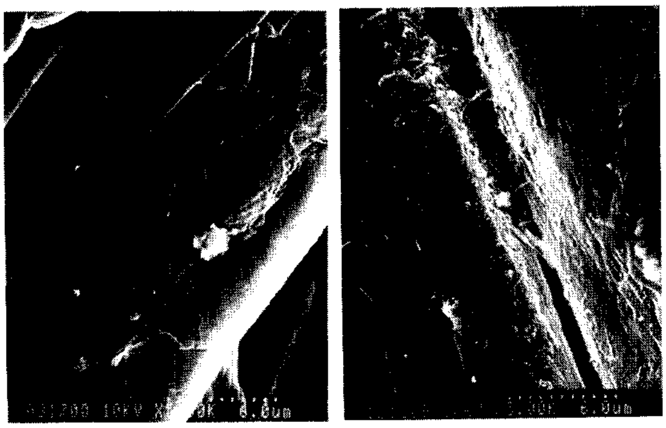

Figure 4 Comparison of dye particles on cotton fabric dyed with Red 3GL between pale (left: 1.89×10^{-5} mol/g dye) and medium-depth (right: 3.68×10^{-5} mol/g dye) dyeings

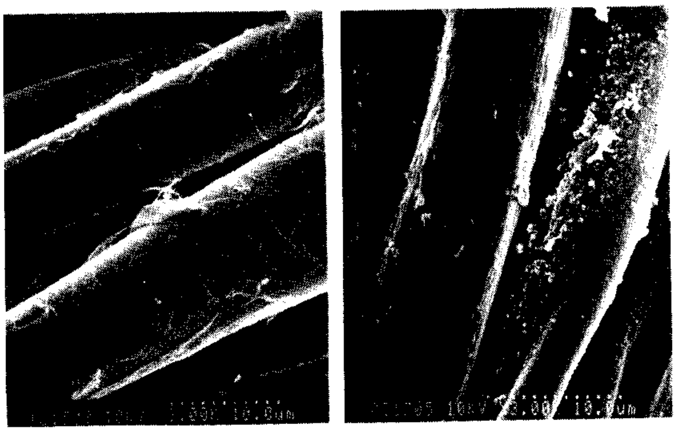

Figure 5 Comparison of dye particles on cotton fabric dyed with Green BB between pale (left: 2.08×10^{-5} mol/g dye) and deep (right: 6.34×10^{-5} mol/g dye) dyeings

The size and the shape of the particles were variable, but granular dye particles were mainly observed, except with Blue BB. Small dye particles, as shown in Figure 4, were observed on the medium-depth dyeings with most dyes. Large granular dye particles were present on the deep dyeings with Green BB (Figure 5). With Blue BB numerous needle-shaped dye particles were observed (Figure 3), and this shape was confirmed on the stained white fabric at a magnification of 10 000 × (Figure 6).

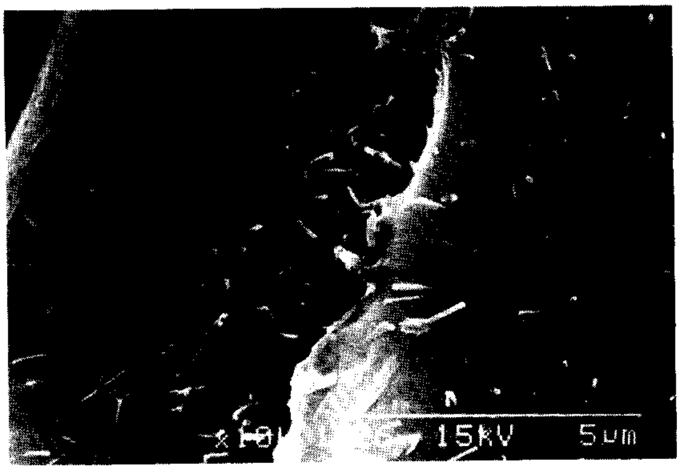

Figure 6 Dye particles on white cloth stained with Blue BB; dye content (x) 9.57×10^{-7} mol/g, number of rubs (t) 200, applied weight (W) 400 g

Effect of dye particles on amount of dye removed by rubbing

The ratio between the amount of dye removed by rubbing (x) and the initial dye concentration on the dyed fabric (A) is plotted against the number of rubs (t) in Figures 7–9. (Examples of the ratio between F and A are also given as the intercepts on the ordinate in Figures 7–9.)

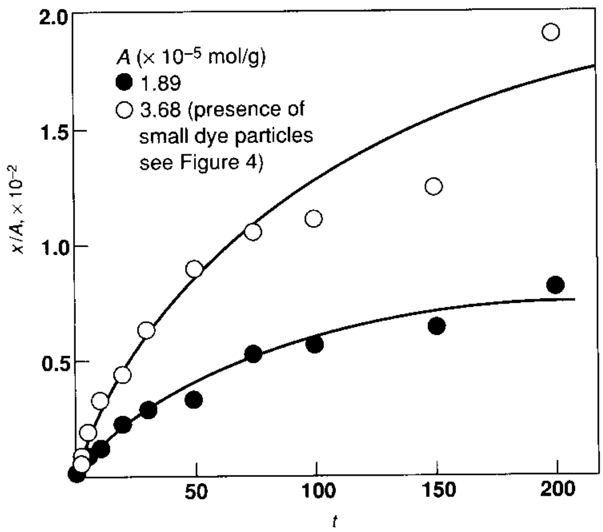

Figure 7 Effect of small dye particles on x/A against t curve for Red 3GL with 400 g applied weight

By rearranging Eqn 3, x and x/A can be expressed by Eqns 8 and 9 respectively:

$$x = \frac{k_1 A}{k}\left[1 - \exp(-kt)\right] + F \tag{8}$$

$$\frac{x}{A} = \frac{k_1}{k}\left[1 - \exp(-kt)\right] + \frac{F}{A} \tag{9}$$

Although x is proportional to A (Eqn 8), the value of $[(x/A) - (F/A)]$ is independent of A (Eqn 9). When F/A is very small, x/A is virtually independent of A. In this work F/A was very small, as shown by the intercepts on the

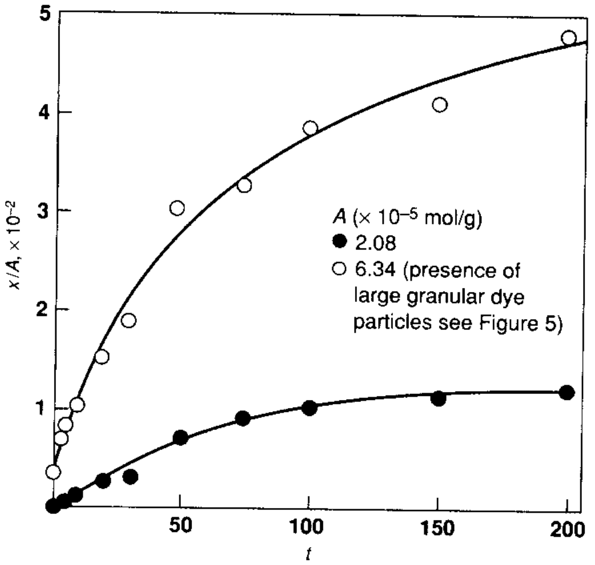

Figure 8 Effect of large granular dye particles on x/A against t curve for Green BB with 400 g applied weight

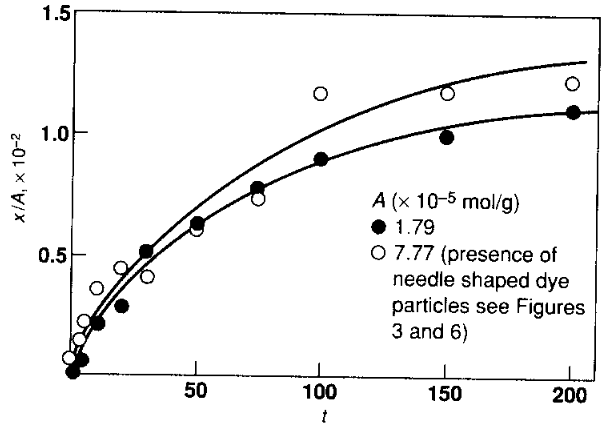

Figure 9 Effect of needle-shaped dye particles on x/A against t curve for Blue BB with 400 g applied weight

ordinate of x/A against t in Figures 7–9. Therefore x/A should be independent of A. In the case of naphthol dyes the value of x/A generally increases as the value of A rises, as shown in Figure 7. This must be attributed to the presence of dye particles. And there is a considerable increase in the value of x/A as large granular particles increase on the dyeings (Figure 8). With Blue BB the value of x/A increased only slightly as A increased (Figure 9), although numerous dye particles could be observed (Figure 3).

The removal of dye particles was assumed to be influenced by their coming into contact with the fibre surface. Granular particles have a small contacting surface, while with the needle-shaped particles this surface is considerably larger. Therefore the needle-shaped dye particles are more difficult to remove by rubbing.

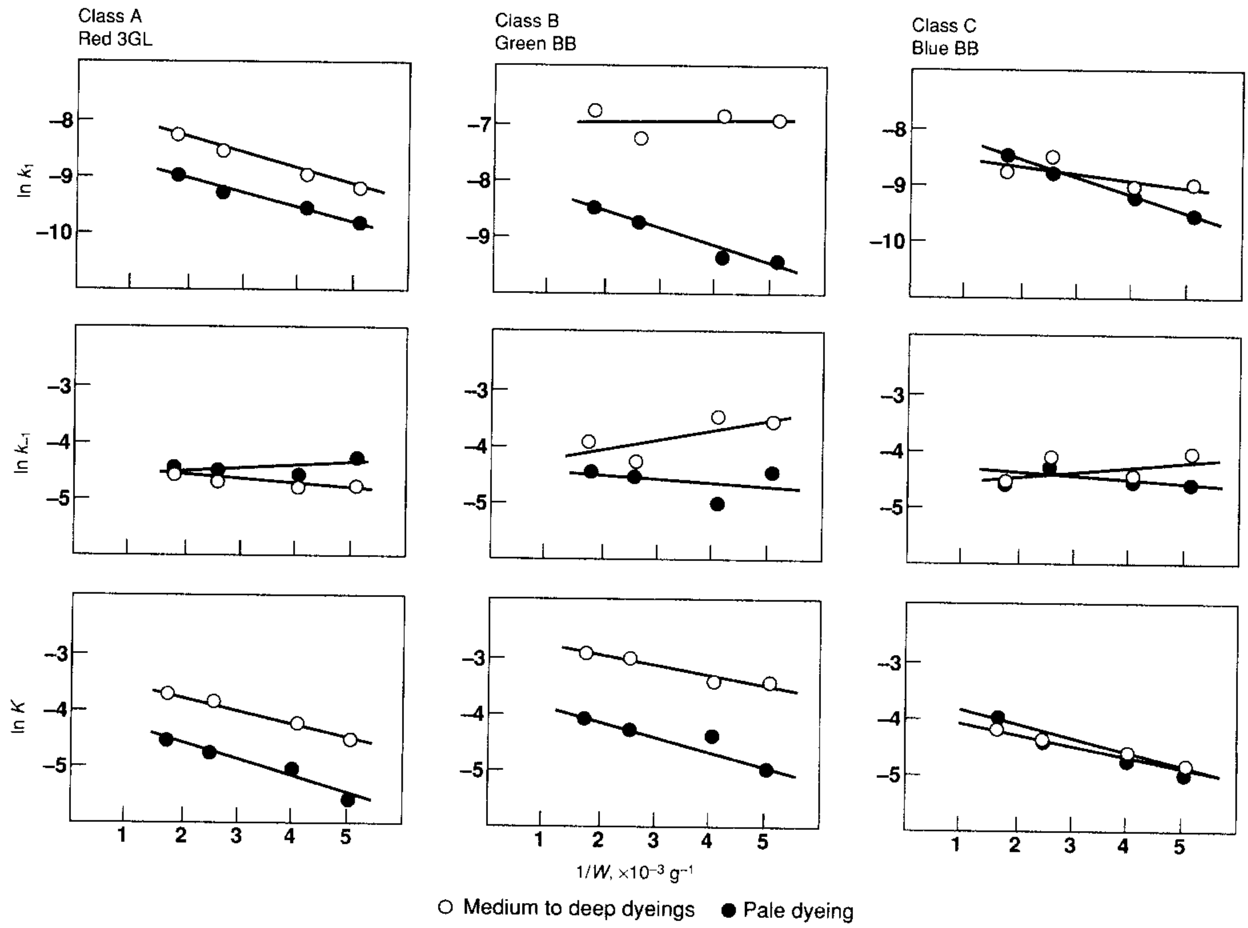

Figure 10 Effect of weight (W) and dye particles on rate constants (k_1, k_{-1}) and equilibrium constant (K) for Red 3GL, Green BB and Blue BB (for key see Figures 7, 8 and 9 respectively)

Effect of dye particles on rate constants and equilibrium constant

The rate constants and the equilibrium constant for each of the dyeings were obtained and their logarithms plotted against the reciprocal weight applied ($1/W$) on the white fabric in Figure 10; a linear relationship generally existed between the two. Here the medium to deep dyeings are compared with the pale dyeing.

The effect of dye particles on these constants can be divided into three types as shown in Figure 10. Class A is the most common, in which the presence of dye particles increases the values of k_1 and K, whilst not affecting k_{-1}. The weight dependence of the three constants hardly varies with the presence of dye particles, i.e. regardless of the presence of dye particles, the slopes of the straight lines obtained by plotting $\ln k_1$ and $\ln K$ against $1/W$ were about 200–300 and those obtained by plotting $\ln k_{-1}$ against $1/W$ were below 100. In this work almost all dyeings belong to this class.

Large granular particles present on the surface of the dyeings fall into class B, as with deep dyeings with Green BB. The behaviour of this class is similar to that of class A except for the weight dependence of k_1.

Class C covers the case of Blue BB. Here the presence of dye particles does not affect the constants k_1, k_{-1} and K. It is assumed that such needle-shaped dye particles have little effect on the rub fastness.

CONCLUSION

The effect of dye particles on the rub fastness of naphthol dyes has been investigated from the kinetic viewpoint. The kinetics of the rubbing process can be described by the rate constants k_1 and k_{-1} and the equilibrium constant K in terms of a reversible first-order reaction.

Numerous dye particles of about 0.1 to 3μm in diameter were observed on the surface of medium to deep dyeings by means of scanning electron microscopy. The presence of dye particles affected k_1 and K, but not k_{-1}. The effect of dye particles on k_1 and K can be divided into three types. The presence of granular dye particles increases the constants and lowers the rub fastness. Almost all dyeings used in this work show such behaviour (class A). This behaviour was promoted with the increase in the size of the particles (class B). On the other hand, needle-shaped dye particles hardly affect these constants at all, and do not lower the rub fastness (class C). It is assumed that needle-shaped dye particles are not substantially removed by rubbing because their surface area in contact with fibres is comparatively large.

If the presence of dye particles cannot be avoided, to improve rub fastness it is recommended that the size of the dye particles is kept as small as possible. The formation of needle-shaped particles also improves rub fastness.

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