

## 1991 Intersectional Technical Paper Competition

## Effects of Dye Substantivity in Dyeing Cotton with Reactive Dyes

In dyeing cotton with fiber reactive dyes, the addition of alkali to the dyebath not only promotes formation of the covalent bond between the dye and the cellulose but also causes hydrolysis of the reactive group of the dye. Unfixed hydrolyzed dye remaining in the fabric after the dyeing process must be removed by washing, otherwise the optimal fastness to washing and crocking of the final fabric will not be realized. The batch dyeing process thus consists of three stages:

• The migration phase. In this first stage, the cotton is treated with dye solution in the presence of salt at about pH 6, but little reaction with the cellulose occurs. The dye is free to migrate from the more heavily to the lightly dyed areas of

the material. The dyebath exhaustion at the end of this phase is called the primary exhaustion.

• The fixation phase. This begins when alkali is added to the dyebath to raise the pH to the point where the dissociated hydroxyl groups of the cellulose begin to react with the dye. Migration of the fixed dye is impossible. During this stage, more dye is absorbed from the solution and reacts with the cellulose. The exhaustion of the dyebath at the end of the process is called the secondary or final exhaustion.

• The washing phase. Once dyeing is completed, the material is washed several times to remove unfixed dye. The fixation is calculated using a simple mass balance based on the total amount of dye added to the initial dyebath, the amount remaining in the final bath and the amount removed by washing.

The primary and final dyebath exhaustion and the fixation yield are defined as follows:

$$\begin{aligned} \% \text{ Exhaustion} \\ = 100 \times (C_i - C_f) / C_i \end{aligned}$$

where  $C_i$  = initial concentration of dye (g/L) and  $C_f$  = final concentration of dye (g/L).

$$\begin{aligned} \% \text{ Fixation} \\ = 100 \times (M_i - M_f - M_w) / M_i \end{aligned}$$

where  $M_i$  = mass of dye in the initial dyebath (g),  $M_f$  = mass of dye in the final dyebath (g) and  $M_w$  = mass of dye removed by washing (g).

The primary dyebath exhaustion, and the ease with which unfixed dye can be removed by washing after dyeing, depend on the substantivity of the reactive dye, or of its hydrolysis product, for the cotton. In general, the two forms have almost identical substantivities. Many of the early reactive dyes for cotton were, by design, dyes of low substantivity whose chemical structures resembled low molecular weight acid dyes rather than the more complex direct dyes. It was not possible, however, to provide a complete range of colors, including navy blues for example, without introducing at least some dyes which had substantially higher substantivity for cotton. Some of the newer bifunctional reactive dyes, such as those synthesized by coupling two monofunctional reactive dye molecules together, are also of increased substantivity.

In almost any range of commercial reactive dyes, there is a graduation of substantivity from very low to medium, or even quite high substantivity, particularly in the presence of salt. The dyer is thus faced with the problem of deciding how severe the washing conditions should be for removal of unfixed dye from the material since he must decrease the residual amount to the level that his client is satisfied with the fastness properties of the final product. To achieve the best product quality, the dyer can wash the goods repeatedly, consuming more hot water than may be absolutely necessary. On the other hand, from the point of view of cost and productivity, it is important to keep hot water consumption to a minimum.

The problem of dyeing on shade with trichromatic mixtures of reactive dyes is also related to the substantivity of the dyes. The best color control results by using dyes which all have the same reactive group, and which also have comparable rates of dye absorption and fixation. The dyer then only needs to be concerned about the gradual development of the depth of the particular shade. When using dyes of quite different reactivity or substantivity towards the cellulose, there will be pronounced color changes during the dyeing operation, as well as the usual build up in depth. This makes color matching very difficult.

This project was developed in response to these practical problems related to the substantivity of reactive dyes. The objective was to examine how the substantivity of these dyes influences dyeing with trichromatic mixtures, and the ease with which unfixed dye can be washed off the cotton after dyeing is completed. It was also decided that it would be valuable to have some simple laboratory test which the dyer might use to evaluate the substantivity of reactive dyes. The results of such a test might be used to select dyes for dyeing in combination and also for establishing more or less severe washing conditions, and thus contribute to energy savings where this is possible.

#### Experimental Techniques

For paper chromatography of the dyes, a solution of dye (1.00 g/L) was prepared in aqueous NaOH solution (1.00 g/L). The

#### ABSTRACT

Fiber reactive dyes for cotton were shown to vary widely in their substantivity for the fiber. Substantivity also depended on dyebath temperature and salt concentration, as expected. The relative substantivities of the hydrolyzed forms of the reactive dyes were assessed in the laboratory by means of a simple, quick and inexpensive paper chromatography test. Correlation of the substantivity of the dye with the amount removed from the cotton under various washing conditions indicated that it should be possible to select higher or lower washing temperatures based on the substantivity of the dye to be removed. In addition, the paper chromatography test was useful for quick selection of dyes of about the same substantivity. Mixtures of such dyes dyed cotton with little change in hue during the dyeing process; dyes of different substantivity gave pronounced color changes.

#### Key Terms

Dyeing Cotton  
Fiber Reactive Dyes  
Paper Chromatography  
Reactive Dyes  
Reactive Groups  
Substantivity

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solution was allowed to stand for several days to ensure that the reactive groups of the dyes were hydrolyzed and then neutralized to pH 6 with acetic acid. Small volumes of the dye solutions were then spotted onto a small piece (2 × 4 in.) of Whatman #1 filter paper. After drying, the papers were developed by standing them in a shallow pool of solvent in a closed jar and the chromatograms developed by the ascending technique (1,2). The developing solvents used were 2-propanol/water/acetic acid (18:17:1 by volume) and

2-propanol/water/concentrated aqueous ammonia (9:8:1 by volume).

All analyses of dye solutions were performed using standard spectrophotometric techniques (3). Transmission measurements were carried out using a Diano Match Scan II double beam reflectance spectrophotometer with matched 1.00 cm glass cuvettes. To ensure that the dye in the solution always had the same environment, and thus did not undergo changes in extinction coefficient, samples of the dye-bath to be analyzed were mixed with phosphate buffer solution (0.10M Na<sub>2</sub>HPO<sub>4</sub> × 7H<sub>2</sub>O, 0.10 M KH<sub>2</sub>PO<sub>4</sub>) and diluted by a factor of five (4). Dye concen-

trations were determined by absorbance measurements at the wavelength of maximum absorption and calculation from the slope of the Beer-Lambert calibration graph prepared using dye solutions containing the same amount of phosphate buffer.

The material used was a bleached cotton jersey knit (163 g/m<sup>2</sup>). The reactive dyes were applied at a depth of 1.00% owf at temperatures, and salt and alkali concentrations, according to the recommendations of the manufacturers (see Table I). All dyeings were carried out in sealed stainless steel pots using a Zeltex Polycolor laboratory dyeing machine equipped with a Sedo PC 1000 microprocessor controller. In all cases, a liquor-to-goods ratio of 20:1 was used (5.00 g cotton plus 100 mL dye solution). The alkali was added in the form of powdered sodium carbonate, or a very small volume of concentrated sodium hydroxide solution. After dyeing, the cotton was washed six times in clean water, for 5 min. at 30C and then for 15 min. at temperatures of 60, 60, 100, 100 and 60C using a 16:1 liquor ratio.

In trials to measure the exhaustion of the hydrolyzed forms of the dyes, stock solutions were prepared as described for paper chromatography. The dye bath exhaustion after 60 min. was measured for 1.00% owf dyeings carried out at either 30, 50, 75 or 100C, in the presence of either 0, 10, 20 or 30 g/L salt using a 20:1 liquor ratio.

In tests of dyeings using washing conditions of increasing severity, dyeings at a 1.00% owf strength were prepared using the conditions given in Table I. For each dye, three dyeings were prepared, and one sample of each was submitted to one of the three washing procedures. These consisted of five-15 min. washes at a 16:1 liquor ratio using the following temperatures:

- Wash =1: 30, 30, 60, 60, and 60C.
- Wash =2: 30, 60, 60, 100, and 60C.
- Wash =3: 30, 60, 100, 100, and 60C.

To evaluate the efficiency of these procedures, the final air dried dyeings were again washed for 15 min. at the boil, using the same liquor ratio, and the amount of extracted dye was measured.

Dyeings with mixtures of reactive dyes, to test for the constancy of the hue during the process, were carried out in a Benz pilot scale jet dyeing machine using the dyeing method starting at 50C and adding alkali at 80C (see Table I). Samples of dyed cotton were cut at five min. intervals after the addition of the alkali. These were well washed in hot water and dried at room temperature. The CIELAB color co-ordinates were measured using the Diano Match Scan II reflectance spectrophotometer.

### Dye Selection

All the reactive dyes were commercial samples used as received from the manu-

Table I. Dyeing Conditions for the Exhaustion and Fixation Data

Dye	Dyeing Temp (C)	Salt Conc. (g/L)	Na <sub>2</sub> CO <sub>3</sub> Conc. (g/L)	Time of Migration (min.)	Time of Fixation (min.)
1	40	50	5 <sup>a</sup> + 0.5 NaOH <sup>a</sup>	30	15 <sup>a</sup> 45 <sup>a</sup>
2	30	40	10	40	60
3	45	30	10	30	60
4	30	40	10	30	60
5	50-80 <sup>b</sup>	20	15	40 <sup>b</sup>	45 <sup>b</sup>
6	50-80 <sup>b</sup>	40	15	40 <sup>b</sup>	45 <sup>b</sup>
7	30	40	10	30	60
8	40	40	10	40	60
9	50-80 <sup>b</sup>	20	15	40 <sup>b</sup>	45 <sup>b</sup>

<sup>a</sup>Fixation with soda ash for 15 min. followed by NaOH for 45 min. <sup>b</sup>50C/10 min. plus salt. 50-80C/30 min., add alkali. fixation at 80C/45 min.

Table II. Commercial Names of Dyes Used in the Study

Code Number <sup>a</sup>	Commercial Name, C.I. Name	Type <sup>b</sup>
<b>Dyes Studied in Detail</b>		
1	Remazol Yellow R	VS
2	Procion Blue MX-R, Blue 4	DCT
3	Levafix Brilliant Blue E-B, Blue 29	DCC
4	Procion Blue MX-7RX, Blue 161	DCT
5	Cibacron Red C-2G, Red 228	MFT-VS
6	Cibacron Yellow C-R, Yellow 168	MFT-VS
7	Procion Turquoise MX-G, Blue 140	DCT
8	Drimarene Navy Blue K-2B, Blue 193	DFCP
9	Procion Red HE-7B, Red 141	MCT-MCT
<b>Other Dyes Used</b>		
10	Remazol Navy Blue RGB	
11	Procion Red MX-5B, Red 2	DCT
12	Drimarene Brilliant Red K-4BL, Red 147	DFCP
13	Procion Yellow MX-3R	DCT
14	Procion Yellow HE-6R	MCT
15	Basilen Yellow E-3R, Yellow 3	MCT
16	Levafix Yellow E-2RA	DCC
<b>Dyes Used in Mixtures for Dyeing Cotton</b>		
17	Remazol Brilliant Blue R spec., Blue 19	VS
18	Remazol Yellow 3RS	
19	Remazol Brilliant Blue RBC	
20	Procion Brilliant Red H-EGXL	MCT-MCT
21	Procion Blue H-EGN, Blue 198	MCT-MCT
22	Procion Yellow H-E4R, Yellow 84	MCT-MCT
23	Procion Turquoise H-A, Blue 71	MCT
24	Procion Yellow H-EXL	MCT-MCT

<sup>a</sup>In the text, all dyes will be referred to by this code number. <sup>b</sup>VS = vinyl sulfone, MCT = monochlorotriazine, DCT = dichlorotriazine, DCC = dichloroquinoline, DFCP = difluorochloropyrimidine and MFT = monofluorotriazine.

facturers. Early in the project, some difficulties were encountered with dyes whose extinction coefficients were found to vary with change in the salt concentration or the pH of the solution. Such problems have been observed before (5). Some dyes were also found to be unstable in boiling water. Dyes exhibiting the presence of two colored components, with different substantivities based on paper chromatography tests, were avoided. Because of the need to have reliable exhaustion data as a measure of dye substantivity, most of the dyes selected for study were those which passed a specially developed screening test. This is described in another paper (4).

The list in Table II gives the commercial names of the dyes used in this study, and, where known, the nature of the reactive group and their Colour Index Name (6); e.g., C.I. Reactive Blue 4.

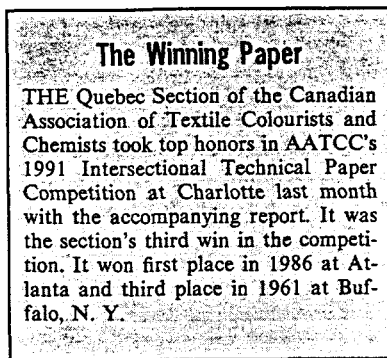
Dyes 1 and 9 were found to be mixtures. These dyes were included because of their low and high substantivity for cotton, respectively. After completion of the dyeing trials, solutions of Dye 8 were found to be unstable on heating at 90C in the presence of salt and alkali. Data for this dye are included but the fixation yield and washing data will be less reliable than for the other dyes.

#### Paper Chromatography Of Hydrolyzed Dyes

The paper chromatography characteristics of 50 reactive dyes were examined by the ascending technique using the two different developing solvents. About 25% of these dyes contained significant amounts of a second colored component of different  $R_F$  value. For 16 of the dyes, the  $R_F$  value was measured at least three times and the mean value calculated. The  $R_F$  value is the distance the dye spot travels from the origin ( $x$ ) divided by the distance traveled by the solvent front ( $y$ ), as shown in Fig. 1. It was calculated as a percentage.

$$R_F = (100 \times x) / y$$

The standard deviation of the three or four measurements was  $\pm 1.9\%$ . Fig. 2 shows the relationship between the  $R_F$  values in the two solvents (aqueous propanol/ammonia and aqueous propanol/acetic acid) for the selected dyes. Both solvents gave a wide range of  $R_F$  values showing the considerable variations of the substantivities of the dyes examined. Previous studies (1) have shown that paper chromatography  $R_F$  values correlate well with the substantivity of various types of dyes for cotton. This test therefore provides a rapid and inexpensive means of assessing the relative substantivity of reactive dyes for cotton. In general, the value of  $R_F$  in the propanol/ammonia solvent was higher. This is probably a consequence of the lower substantivity of the anionic dyes for cellulose in an alkaline environment (7).



#### Dyebath Exhaustion And Fixation Yields

In the initial dyeing trials, the primary and final dyebath exhaustion and the fixation yield were measured for a number of different reactive dyes using dyeing procedures derived from the dye manufacturer's literature. A resume of the dyeing conditions is given in Table I and the results are in Table III.

The wide range of primary exhaustion values showed that the dyes selected did have the desired range of substantivity for cotton. Some of the fixation yields were disappointingly low, particularly for the dichloro- and monofluoro-triazine reactive dyes. This was probably a consequence of the loss of reactive capability due to extended storage. These results do not indicate poor quality of certain products since the dyeing methods were not optimized.

The data shown in Fig. 3 confirmed that the primary exhaustion of the reactive dyes was directly related to the paper chromatography  $R_F$  values. High  $R_F$  values were obtained for dyes of low substantivity. Unfortunately, Dyes 1 through 5 all gave low primary exhaustion values, with little variation, despite fairly large differences in  $R_F$  values in the two different developing solvents.

Despite the wide range of fixation yields obtained in the dyeing trials, and the rather low values for some dyes, all but two of the final dyeings contained about 10-12 mg (0.20-0.24% owf) of extractable unfixed dye compared to the initial amount of 50.0 mg (1.00% owf). These amounts were larger than calculated from the difference

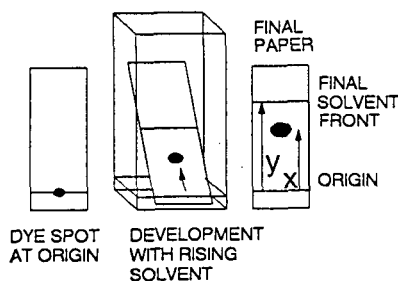


Fig. 1. Paper chromatography.

between the final exhaustion and the fixation yield. This was because the transfer of varying amounts of dyebath solution into the first wash bath was unavoidable in order to avoid loss of dye.

#### Washing Off Unfixed Dyes

After dyeing, unfixed dye was extracted from the cotton in a series of six washings with clean water: one wash at 30C for 5 min. and five 15-min. washes at 60C, 60C, 100C, 100C and 60C. The data on washing off of the unfixed dyes are shown in the histogram in Fig. 4.

Examination of Fig. 4 shows two trends related to the substantivity of the dye. In general, for the dyes of lower substantivity for cotton (Dyes 1-5), large amounts of unfixed dye were extracted in the first two washing processes (30C/5min. and 60C/15 min.), very small amounts being removed in the final wash (60C/15 min.). For these dyes, each successive wash removed less dye than the previous one. Although Dye 2 had a somewhat different profile, it is a dye of low substantivity and the complete washing cycle resulted in a very small amount of residual unfixed dye in the fabric. For the other dyes (Dyes 6-9), the washing profiles were quite different. Relatively less dye was extracted in the initial cold wash and higher washing temperatures (60 and 100C) were necessary to remove the bulk of the unfixed dye.

In the case of the most substantive dye (Dye 9), the final wash at 60C still removed a considerable proportion of unfixed dye. It was tempting to consider that this was a direct consequence of the high substantivity of this dye for cotton fibers but other factors must be considered.

Firstly, it is always possible that some color is being removed in washing because of instability of the dye-fiber bond under the washing conditions. This is not likely to be too important in this case since by the time the fabric has already been washed five times in water, the pH would corre-

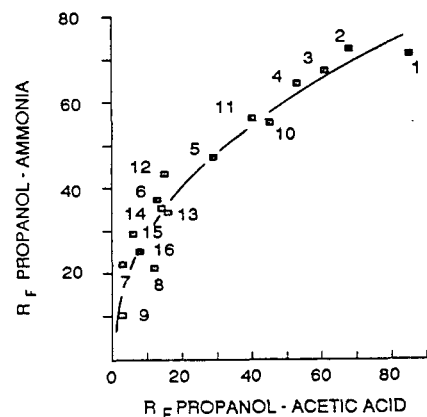


Fig. 2. Relation between the  $R_F$  values of the hydrolyzed reactive dyes in the two different developing solvents. Dyes are numbered using the codes in Table II.

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spend closely to that of maximum dye-fiber bond stability (8).

Secondly, in this case, the analysis is less precise. Dye 9 contained two colored components of differing substantivity. During the course of the washing cycle, the absorption spectra of the wash solution changed, the two absorption maxima at 510 and 540 nm shifting to 520 and 557 nm. The dye was found to be thermally stable under the washing conditions and the change in spectrum was attributed to extraction of different proportions of the two colored components. Despite the fact that this introduced some imprecision into the analysis, it appears that the difficulty

of removal of the unfixed form of Dye 9 is a consequence of its high substantivity for cotton. This dye was, in fact, selected because of this.

In order to examine the relation between the ease of removal of unfixed dye and the substantivity, as expressed by the paper chromatography  $R_F$  values, the amount of dye removed in a particular washing process was divided by the total amount removed from the fabric in this and all subsequent washing steps. This parameter was called the washing ratio. Washing ratio =  $100 \times$  Dye removed in the  $n^{th}$  wash divided by Dye removed in the  $n^{th}$  and subsequent washes.

The data in Fig. 5 show some interesting trends. As the temperature of the washing process increased, the value of the washing ratio increased, the effect being more pronounced for dyes of higher substantivity. At washing temperatures of 30 and 60C, there was a definite influence of the substantivity of the unfixed dye on the ease of its extraction from the cotton. The more substantive dyes, of low  $R_F$  value, were more difficult to wash out. For washings at

Table III. Measurements of Dyebath Exhaustion and Fixation Yield

Dye	Primary Exhaustion	Final Exhaustion	Fixation Yield
1	5.7%	60.5%	45.7%
2	11.1	60.5	40.4
3	12.3	66.7	56.1
4	9.9	41.7	27.2
5	10.7	33.7	31.8
6	37.8	71.0	56.7
7	26.5	53.7	23.1
8	47.6	88.9	72.5
9	70.2	86.3	66.5

100C, all the dyes were extracted with equal facility. Data presented later in the paper clearly illustrated that at the boil, in the absence of salt, the hydrolyzed forms of all the dyes studied, except Dye 7, have very low substantivity for cotton. Thus, the definitive method for removal of unfixed reactive dyes from cotton is to wash at as high a temperature as possible, once the salt has been rinsed from the fabric. This of course increases production costs and it would be desirable to reach a compromise between the need for effective removal of unfixed dye and the cost of the hot water to realize this.

### Substantivity of Hydrolyzed Reactive Dyes

Additional data on the substantivity of the hydrolyzed forms of the dyes were obtained in a series of dyeing trials carried out at different temperatures and salt concentrations. The baths contained 1% of the dye and dyeing was carried out for 60 min. using a 20:1 liquor ratio. After dyeing, the exhaustion of the dyebath was determined. In Fig. 6, note that the upper series of five graphs has a 0-20% exhaustion scale, while the lower series has a 0-80% scale.

The hydrolyzed forms of Dyes 1, 3 and 4 were of low substantivity, had maximum exhaustion dyeing temperatures below

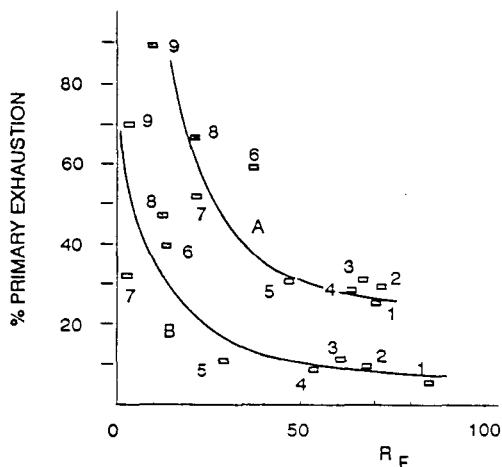


Fig. 3. Relations between the primary exhaustion of the reactive dyes and the paper chromatography  $R_F$  values. A: developing solvent is propanol/ammonia. This curve is displaced by +20% on the y axis. B: developing solvent is propanol/acetic acid.

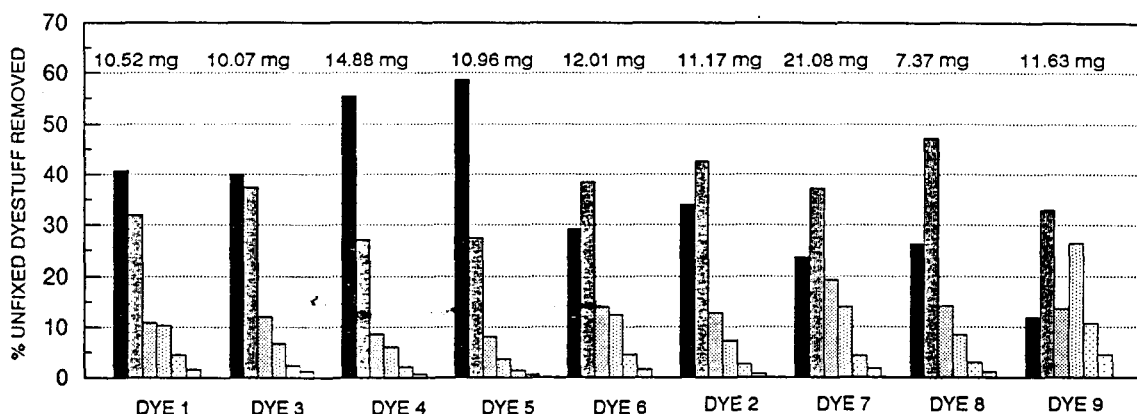


Fig. 4. Amounts of unfixed dye removed in the six washings after dyeing. The total amount of extracted dye is given above the bars for each dye. For each dye, the heights of the bars from left to right indicate the amount of dye removed, relative to the total extracted dye, in each successive washing process at 30, 60, 60, 100, 100 and 60C.

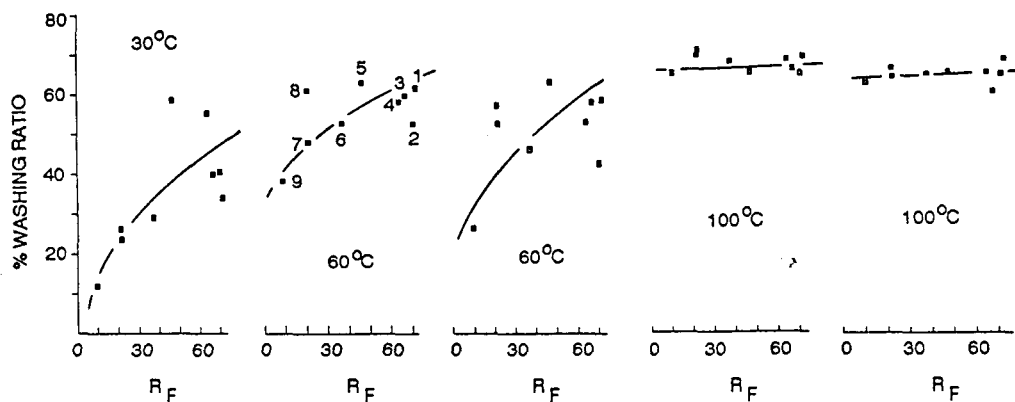


Fig. 5. Values of the washing ratio for the first five-washing process as a function of the  $R_F$  value for the propanol/ammonia solvent. The washing temperature is given on each graph. The dyes are identified by their numbers in the second graph from the left.

30°C, and were not particularly sensitive to the addition of salt. Dyes 2 and 5 were also of low substantivity but, as the salt concentration was increased, maximum dye bath exhaustion occurred at higher temperatures. Such behavior is more typical of direct dyes and can be interpreted in terms of the effect of salt in promoting dye aggregation in the fiber, rather than in the solution (9). The hydrolyzed forms of the remaining dyes (Dyes 6-9) all behaved like direct dyes. Their substantivity for cotton

was much higher and was much increased in the presence of salt. The temperature of maximum exhaustion was always above 40°C. The maxima in the profiles would be explained by the opposing tendencies of salt, which promotes greater dye aggregation in the fiber and thus higher substantivity, and of increasing temperature, which causes deaggregation of the dye in both phases, but less effectively in the fiber than in solution below 40-50°C.

The profiles for Dyes 7 and 9 are of

particular interest. Dye 7 is a copper phthalocyanine dye. These types are well known to aggregate in solution (10) and higher dyeing temperatures give more monomolecular dye, which is free to diffuse into the cotton fibers. For Dye 9 at 30°C, addition of salt initially increases the dye bath exhaustion, but further amounts of salt suppress it. Dye 9 thus behaves like a highly substantive direct dye, for which addition of salt increases the substantivity by promoting aggregation of the dye in the

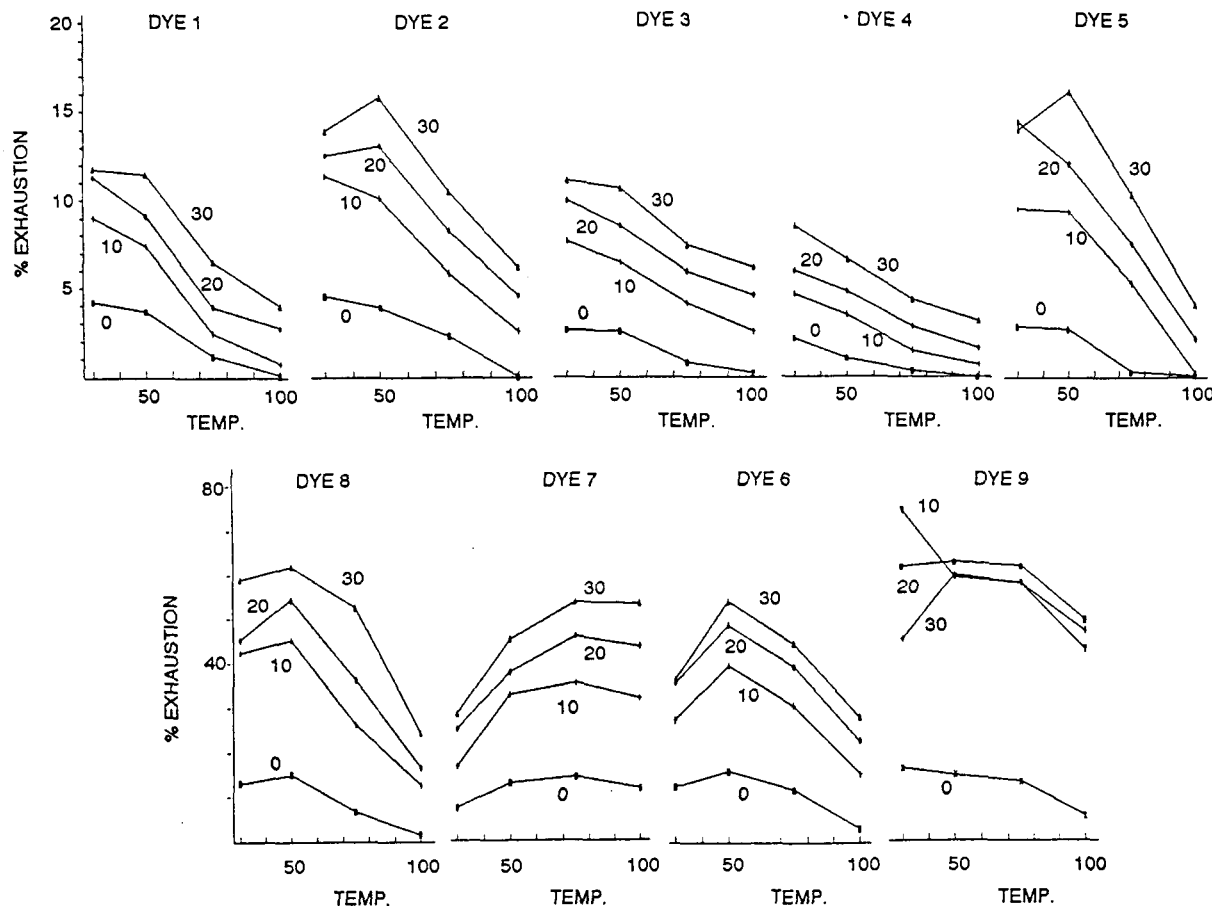


Fig. 6. Data on exhaustion of hydrolyzed reactive dyes at different salt concentrations and different temperatures. Salt concentrations are shown in g/L.

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cotton. At higher salt concentrations, the formation of larger dye aggregates in solution gives less and less monomolecular dye in the bath. Absorption of dye by diffusion thus becomes more and more restricted.

### Washing Off of Hydrolyzed Dyes

The objective of this part of the study was to examine the washing off characteristics of reactive dyes of quite different substantivity for cotton using conditions which would be classed as mild, medium and severe. It was hoped that dyes of low substantivity would be effectively eliminated from the fabric using a mild washing procedure, those of medium substantivity by washing of medium severity and the most highly substantive dyes by a rigorous washing procedure.

The dyes chosen for this study were Dyes 1, 6 and 9. A 1.00% owf dyeing of each dye was submitted to each of the three washing operations, of increasing severity, as described in the experimental section. The results are shown in Fig. 7.

The results were similar to those shown in Fig. 4. Increasing the severity of the washing operations from Wash #1 to Wash #3 increased the amount of unfixed dye removed from the cotton. The reproducibility of the procedures was good, as shown by the constant amounts of dye removed for samples containing the same amount of unfixed dye and which received

the same treatments. In general, the amount of dye removed in the first wash was greater than indicated in Fig. 4 because, in this series of washing trials, the first wash was for 15 rather than 5 minutes. This explains, for example, the difference in profile for Dye 6 between Figs. 4 and 7.

After the washing test, each sample was air dried. Additional unfixed dye was then extracted from the sample by treatment with boiling water for 15 min. using a 20:1 liquor ratio. The mass of extracted dye was determined by absorption spectrophotometry. The results are also given in Fig. 7.

For these samples, 0.5 mg of residual unfixed dye in the cotton corresponds to 0.01% dye owf. If this were considered to be an acceptable maximum level to achieve the fastness properties consistent with customer satisfaction, it was easily surpassed using the procedure for Wash #1 for Dye 1. For Dye 2, of higher substantivity, even Wash #2 was borderline, and Wash #3 was necessary to leave less than 0.5 mg unfixed dye in the cotton. For the most substantive dye (Dye 9), even Wash #3 did not meet the requirement of less than 0.5 mg residual dye and even more severe washing conditions would be required to meet this standard.

Although time only permitted examination of three dyes, these preliminary results did show that it would be possible to select more or less severe washing conditions based on an examination of dye substantivity for cotton using either the primary exhaustion or an  $R_F$  value.

### Dyeing with Mixtures of Dyes

Dyeing trials on cotton were carried out in which dyes were pre-selected to have either very similar or different substantivity for the cotton based on the measurement of paper chromatography  $R_F$  values. All the dyeings were performed on a pilot scale jet dyeing machine using the dyeing method starting at 50C and adding alkali

**Table IV. Data for Dyeings Using Mixtures of Reactive Dyes**

Combination	Dyes	Dye	$R_F^a$
A	18	0.73% <sup>b</sup>	42%
	19	0.18	51
B	18	0.82	42
	17	0.15	94
C	20	0.25	9
	21	0.16	4
D	22	0.62	6
	9	0.17	3
	23	0.19	10
	24	0.52	22

<sup>a</sup> $R_F$  values in aqueous propanol/ammonia.  
<sup>b</sup>owf.

at 80C (Table I). Table IV gives the dye recipes and the paper chromatography  $R_F$  values of the dyes selected. During the dyeing process, after the addition of alkali to initiate fixation, samples of the cotton were removed at 5 min. intervals over the course of 1 hr. These were washed in hot water, air dried, and then the CIELAB color co-ordinates  $a^*$  and  $b^*$  were measured. In the first trial, a mixture of Dyes 18 and 19 was used. The points for the values of  $a^*$  and  $b^*$ , corresponding to different times after addition of the alkali to the bath, all clustered together (Fig. 8, A), presumably because of the high rate of fixation of these dyes under the dyeing conditions.

When using Dyes 17 and 18, a similar shade was obtained, but in this case the dyeing became gradually yellower during dyeing. This could be a consequence of the higher reactivity of the less substantive blue dye (Dye 17). Also, it must be remembered that vinyl sulphone reactive dyes present a special case. The substantivity of the hydrolyzed dye as measured by the  $R_F$  value may not correspond to that of the vinyl sulphone. For this mixture, the connection of the points for  $a^*$  and  $b^*$  gave

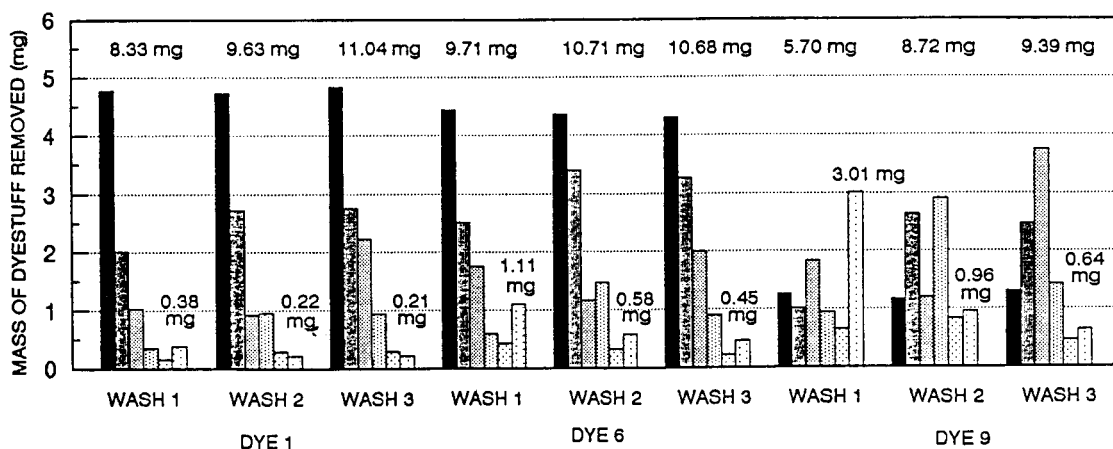


Fig. 7. Amounts of unfixed dye removed from dyed cotton fabric using three washing procedures with different temperature regimes. The total amount of dye removed by each complete washing procedure is given above the bars for each dye. The last bar on the right for each dye is printed over the last bar. Each dyed sample was washed in clean water for 15 minutes using the multiples of temperatures designated as Wash #1, #2 and #3.

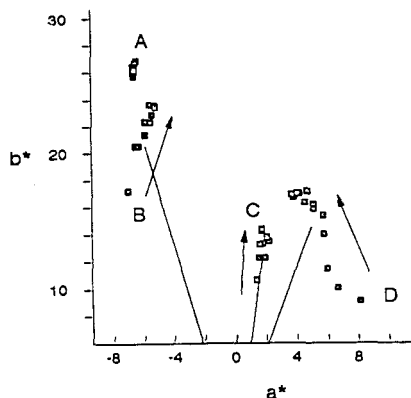


Fig. 8. Variation of CIELAB  $a^*$  and  $b^*$  values during the course of dyeing with various combinations of reactive dyes on cotton. See Table IV for legend. Arrows indicate increase in dyeing time. The lines are lines of constant hue.

a line cutting across the line of constant hue originating at  $a^* = 0$ ,  $b^* = 0$ , as shown in Fig. 8, B. If dyeing is to occur with little change in hue, a plot of  $b^*$  versus  $a^*$  should give a line from the origin out to the highest absolute values of  $a^*$  and  $b^*$ .

This behavior is shown for the trial with Dyes 20, 21 and 22. This combination gave a tan color which gradually became deeper during dyeing but was always on shade (Fig. 8, C). For a similar shade obtained using Dyes 9, 23 and 24, the initial dyeings were much too red because of the high substantivity and reactivity of Dye 9. During the operation, the dyeings gradually became deeper and yellower as the less substantive components were absorbed, but the line connecting the points for  $a^*$  and  $b^*$  as dyeing proceeded were spread out, curved and they cut across the line of constant hue in the color space (Fig. 8, D). This type of behavior would make accurate color matching almost impossible.

These initial dyeing trials with mixtures of dyes indicated that paper chromatography could be valuable for selecting dyes of comparable substantivity to obtain dyeings which develop with constant hue. Of course, such control of the dyeing process is aided if the dyes are also of comparable reactivity towards the fiber.

#### Conclusions

The substantivity of reactive dyes for cotton influenced the ease with which the unfixed dye could be removed from the fabric after dyeing, the lower substantivity dyes being removed in larger amounts under milder conditions. Although only a limited number of dyes have been examined, it seems that washing temperatures could be selected to be lower for less substantive dyes, and higher for more substantive dyes. In this respect, the paper chromatography test was most useful in providing a quick and inexpensive measure of the substantivity of the dye. This test would also allow rapid selection of

dyes, to be used in combination, which would dye cotton with little change in hue as the depth of the dyeing gradually develops. This would give the dyer much more control in color matching. Future studies should confirm these initial results.

#### Committee Members

The paper was presented in Charlotte by Michel Hehlen of Sandoz Canada Inc. Other committee members included Camil Tremblay, chairman, Hoechst Canada Inc.; Christian Langlois, Intech PEM Inc.; Arthur D. Broadbent, Yawen Qu, Siamak Jamshidi-Barzi and Mahmoud Feiz of the Université de Sherbrooke. Mahmoud Feiz is on leave from Isfahan University of Technology, Iran.

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#### References

- (1) Sramek, J., *Analytical Chemistry of Synthetic Dyes*; Edited by K. Vankataraman; Wiley-Interscience, New York, 1977, p57.
- (2) Sherma, J. and G. Zweig, *Paper Chromatography and Electrophoresis, Vol. II, Paper Chromatography*; Academic Press, New York, 1971.
- (3) Strobel, H. A. and W. R. Heineman, *Chemical Instrumentation: A Systematic Approach*, 3rd Edition, Wiley-Interscience, New York, 1989.
- (4) Qu, Y. and S. Jamshidi-Barzi, *Book of Papers: AATCC International Conference & Exhibition*, Charlotte, October 1991, p30.
- (5) Garland, C. E., *Analytical Chemistry of Synthetic Dyes*; Edited by K. Venkataraman; Wiley-Interscience, New York, 1977; p149.
- (6) *Colour Index*, Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists, Third Edition, 1971.
- (7) Burkinshaw, S. M., *The Chemistry and Application of Dyes*; Edited by D. R. Waring and G. Hallas; Plenum Press, New York, 1990, 0277.
- (8) Senn, R. C. and H. Zollinger, *Helvetica Chimica Acta*, Vol. 46, No. 3, 1963, p781.
- (9) Giles, C. H., *The Theory of Coloration of Textiles*; Edited by C. L. Bird and W. S. Boston; Dyers Company Publications Trust, Society of Dyers and Colourists, Bradford, England, 1975, p86.
- (10) Datyner, A. and M. T. Pailthorpe, *Journal of Colloidal and Interfacial Science*, Vol. 76, No. 2, August 1980, p557.

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