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Part I: Dyeing from a Non-Homogeneous System

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ABSTRACT

A laboratory method for dyeing basic dyeable acrylic fibres from a "charged" perchloroethylene dyebath is aescribed. Conventional basic (cationic) dyes were used and the charge consisted of water, lauryl monoethanolamide and a quaternary ammonium compound. The appearance, handle and fastness properties of the solvent dyed samples, at least for single shades, were found not to differ from those samples dyed by a conventional aqueous method.

KEY WORDS

Acrylic (polyacrylonitrile) fibres — cationic dyes — perchloroethylene — retarder — lauryl monoethanolamide — sodium dodecylbenzene sulphonate — solvent dyeing.

INTRODUCTION

The solvent processing of textiles has long been an established technology, especially with respect to solvent finishing procedures such as solvent scouring, milling and shrinkproofing[1−3]. The possible rationalisation of dyeing and finishing procedures in organic solvent media has therefore led to an increased rate of research in the field of, more specifically, dyeing from solvents.

The advantage of dyeing from solvents may be classified as being either of an economic, socio-economic or of a technical nature[4]. The most quoted advantages are the following: solving the problem of effluent disposal, lower energy consumption for heating purposes and the shortening of processing cycles. The most popular solvent for dyeing purposes, today, is perchloroethylene. This choice is based mainly on physico-chemical considerations which have been enumerated by Mecheels[5] and Ritter[6].

Dyeing acrylonitrile based fibres with conventional cationic dyes from a perchloroethylene system requires a polar co-solvent to dissolve the dye and to provide a reaction medium whereby fixation may take place. In this respect the ionic dyeing textile fibres such as wool, nylon and acrylics exhibit a common requirement. It has been shown that the solvent/tenside/water system described by Mecheels[5] may be effectively adapted to dye cotton[7] and wool[8] on laboratory scale, using mainly reactive dyes. This paper, therefore, deals with the modification

and adaptation of the existing charge systems for the dyeing of acrylic fibres with conventional cationic dyestuffs.

The main problem in applying cationic dyes to acrylic fibres has long been recognised to be the need to ensure an even and uniform absorption of the dye by the fibre, since levelling of cationic dyes at 100°C is poor. Level dyeing, therefore, entails a strict control of temperature, and the use of suitable cationic or anionic retarding compounds. A commercial example of such an auxiliary is Ciba Retarder A[9], which is a cationic alkyl ammonium compound[10].

There are systems available whereby acrylic fibres may be dyed from a homogeneous perchloroethylene system using solvent-soluble cationic dyes. Some aspects of dyeing from such a homogeneous liquor will be dealt with in a subsequent paper.

EXPERIMENTAL

Untreated, 100% acrylic fibre (Orlon type 42) was used throughout the investigations. The fabric parameters were the following:

Structure	:	Punto-di-Roma
Yarn linear density	:	24,5 tex
Stitch density	:	14 courses x 15 wales per cm^2
Structural Cell Stitch Length (SCSL)	:	2,82 cm

Samples (5 g) of the above material were dyed in stainless steel capsules (300 ml capacity) in a Linitest Laboratory Dyeing apparatus. The required amount of lauryl monoethanolamide (LEA) and/or sodium dodecylbenzene sulphonate (SDBS) was dissolved in heated perchloroethylene (200 ml) after which the required amount of water or Ciba Retarder A, or both, was pipetted into the flask. This was followed by the addition of the required amount of dye powder. All additions were made while maintaining a rapid stirring rate, with suitable time intervals (2—3 min) between additions of chemicals, and finally entering the undyed samples. Dyeing was commenced at 60°C and the dye liquor was kept at this temperature for 5 minutes. Then the temperature was raised to 75°C over 10 minutes and to 100°C over another 40 minutes. Dyeing was continued at 100°C for the appropriate time.

Cooling was carried out at a rate not exceeding 1°C/min until the temperature was well below the glass transition point of the fibres (approximately 80°C).

Comparative aqueous dyeings were performed on 5 g samples in the Linitest apparatus. The dyebath contained the following —

x% dye

7,5% Na_2SO_4

1% $(NH_4)O_2CCH_3$

Acetic acid to pH 4—5

Liquor-to-goods ratio : 20:1

(All amounts are expressed as percentages on mass of goods).

The rates of heating and cooling were the same as those for the solvent dyeings, except that the total dyeing time was 1½ hours at 100°C.

Reflectance measurements of the dyed samples were carried out on a Beckman DB spectrophotometer fitted with a reflectance measurement unit. The wavelength of minimum reflectance was determined by scanning the visible spectrum from 380 to 750 nm at 10 nm intervals. Values obtained as % reflectance (means of at least 6 readings, both sides of the sample) were transformed to K/S-values by using the Kubelka-Munk equation and the appropriate numerical tables[11], and regarding the reflectance of a magnesium oxide disc as 100%[12].

The amount of dye on the fibre (and hence the bath exhaustion) was determined by the following method:

Samples of dyed fibre (0,1 g) were dissolved in 10 ml of dimethyl formamide, and the solution centrifuged at 17 000 r.p.m. for 1 hour. The dye concentrations were then determined by using standard spectrophotometric methods.

The chromaticity coordinates (x and y) and the tristimulus ratios $\frac{X}{Y}$, Y and $\frac{Z}{Y}$ were determined using the Harrison Shirley Digital Colorimeter[13].

The dyed samples were tested for fastness to washing (ISO 3), alkaline perspiration and light[14].

RESULTS AND DISCUSSION

A qualitative visual judgement of the relative degrees of exhaustion may be made by comparing the reflectance characteristics of the solvent and aqueous dyed samples at a given wavelength. It was, however, established that the ratio of the Kubelka-Munk (KM) functions is more useful, since reflectance-dye concentration curves are not linearly related[11, 12]. Thus, if F_{sw} designates the Kubelka-Munk Reflectance Ratio, then:

$$F_{sw} = \frac{[K/S]_s - [K/S]_o}{[K/S]_w - [K/S]_o}, \text{ where}$$

$[K/S]_s$ = K.M. function of the solvent dyed sample

$[K/S]_w$ = K.M. function of the aqueous dyed sample

$[K/S]_o$ = K.M. function of the undyed substrate.

The value for the undyed substrate, $[K/S]_o$, is small and may be disregarded.

In Fig. 1 it is shown that the minimum amount of water in the dyebath required for a level dyeing and maximum exhaustion is a function of the depth of shade. The samples were dyed with varying amounts of water and dye and those samples dyed unlevel due to poor dye solubilisation and substrate wetting were discarded. The minimum amount of water (% on mass of fibre) is shown as a non-linear function of the dye concentration in the bath. The initial steep slope of

the curve may be attributed to the first 10–12% of the charge being required to both wet out the fibres and to solubilise the dye, while further increases in the amount of dye in the bath requires proportionately smaller additions of water. At this stage, the water probably only functions to solubilise the increasing dye additions, the fibres having been saturated with the aqueous dye charge. Although it appears that 25% water (o.m.f.) is sufficient to produce acceptable results, experience has shown that a charge composition of 30–50% water (o.m.f.) proves more beneficial from a practical point of view.

It was also observed that the dissolving of the dye at the start of the dye cycle is beneficial, but no essential to produce level dyeings. This may be due to the fact that not all the water droplets in the solvent bath are absorbed by the fibre as is the case when dyeing wool from the charged system. An increase in the temperature will then solubilise the dye sufficiently in the water remaining in the emulsion. This will only hold true if azeotropic distillation is compensated for when dyeing on bulk scale, or provided the free volume above the dye liquor is small enough to become saturated with azeotrope before all the water is lost from the liquor.
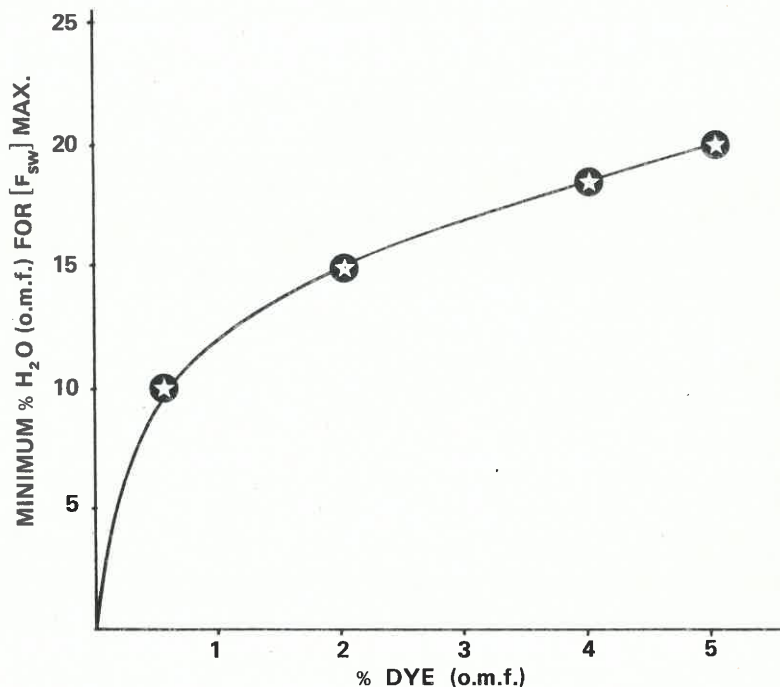

FIGURE 1

The relationship between % Dye (o.m.f.) and minimum amount of water required for a level dyeing (Dyestuff : C.I. Basic Blue 73)

Fig. 2 shows the effect of anionic emulsifying agents on the degree of bath exhaustion. All three basic dyes (C.I. Basic Orange 37, C.I. Basic Red 44 and C.I. Basic Blue 73) exhibit an exponential decrease in the reflectance ratio with increasing emulsifier concentration, suggesting a blocking mechanism between dye cation and emulsifier anion. This can be expected due to the strongly anionic nature of sodium dodecylbenzene sulphonate and this phenomenon is also known in conventional aqueous dyeing systems[15]. Similar results were also obtained for the Aerosol anionic surfactants, such as sodium dioctyl sulphosuccinate. A possible mechanism could be the dye-tensile complex being more soluble in the perchloro-ethylene, resulting in a decrease in the partition coefficient between fibre and dye liquor with an increase in emulsifier concentration. These surfactants should therefore not be present in the solvent dyebath.

The amount of emulsion stabilizer (lauryl monoethanolamide) did not have a significant effect on bath exhaustion. This is shown in Fig. 3. The slight decrease in F_{sw} with increasing concentration of LEA may be considered as not significant, probably due to its nonionic nature as compared to the strongly anionic nature of SDBS. Up to 5% (o.m.f.) LEA may therefore be used safely without fear of colour
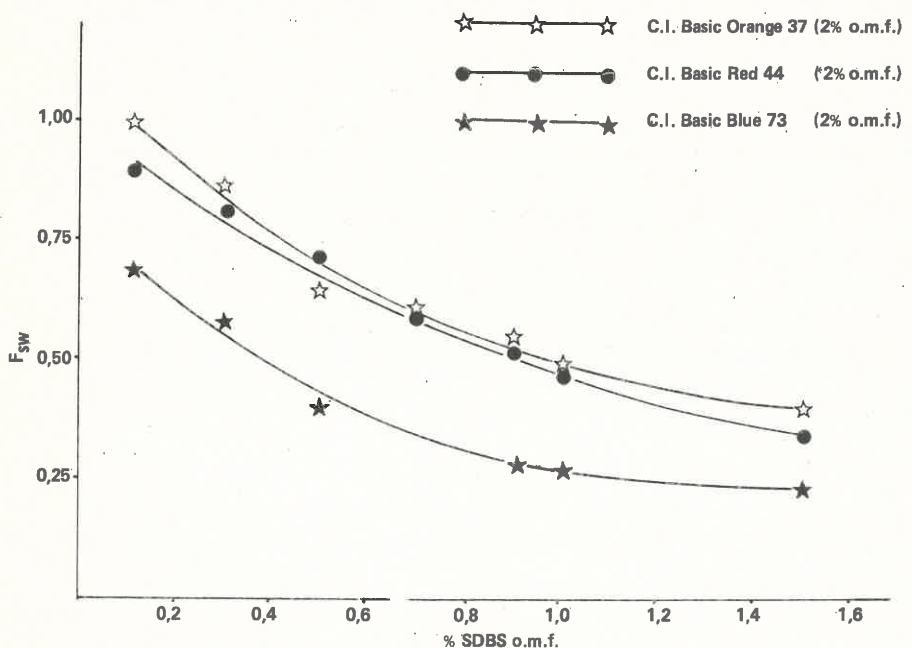

FIGURE 2

The relationship between % emulsifier (sodium dodecylbenzene sulphonate — SDBS, o.m.f.) and F_{sw} (50% H_2O o.m.f., 5% LEA o.m.f.; 1 hour at 100°C)

loss due to an increase in the perchloroethylene solubility of dye-tenside complex.

Preliminary experiments indicated that a quaternary ammonium compound of the general formula $R_3 N^{\oplus} X^{\ominus}$ (example: Ciba Retarder A) could effectively be used in conjunction with 5% (o.m.f.) LEA to produce level dyeings from a well exhausted bath. A minimum of 3% (o.m.f.) Retarder A was found to be sufficient to produce both a levelling effect as well as a sufficient degree of emulsion stability during the dyeing cycle. Up to 5% (o.m.f.) of the alkyl ammonium salt was used successfully without adverse effects on bath exhaustion, but such excessive amounts should be avoided for reasons of economy. Fig. 4 shows a typical exhaustion curve for a conventional cationic dye applied from such a charge system. It can be seen that virtually 100% bath exhaustion can be obtained after dyeing for approximately 5 minutes at 96—98°C.

Data relating to the colour measurement of samples dyed with 11 selected cationic dyes, applied according to both solvent and aqueous dyeing methods, are shown in Table I. Subsequent to colour measurement, all the samples were judged by a panel of 3 independent observers. No change in hue between the samples from each system, dyed with the same dyestuff, could be observed. It was, therefore, assumed that the variations in $\dfrac{X}{Y}$ and $\dfrac{Z}{Y}$ (which indicates a shift towards redder or
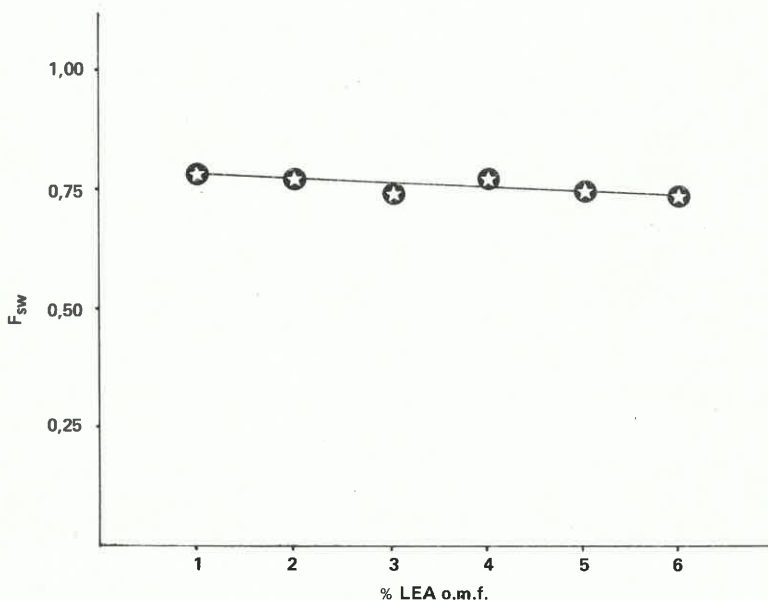

FIGURE 3

The relationship between % emulsion stabilizer (lauryl monoethanolamide — LEA, o.m.f.) and F_{sw} (50% H_2O o.m.f., 2% C.I. Basic Blue 73 o.m.f., 1 hour at 100°C)

bluer[16]), are not of significance. It can also be seen that larger variations occurred in the respective Y (i.e. brightness) values. The respective brightness values for C.I. Basic Orange 37, C.I. Basic Yellow 13 and C.I. Basic Red 27 are slightly higher from the solvent system than from the aqueous system. This does not necessarily imply a deeper shade (i.e. better exhaustion) from the aqueous system, but it would rather imply that these dyeings appear brighter than the corresponding aqueous dyeings.

The fastness properties of the selected dyestuffs, applied from both aqueous as well as solvent systems, are given in Table II. No significant variations were found, and it may therefore be considered that, with respect to colour value and fastness properties, similar dyeings in single shades may be produced from either the aqueous or the solvent dyeing system.

It was established that the normal rules of cationic dye selection and combination does not necessarily hold for charged solvent systems. In Table III, the colour data for a series of mixture dyeings are given. The three dyes used in admixtures, viz. C.I. Basic Blue 3, C.I. Basic Red 46 and C.I. Basic Yellow 45 are compatible in aqueous dyeing systems. For dyeings IV and VI a higher rate of absorption of the blue component from the charge was found. This is indicated by the increase in
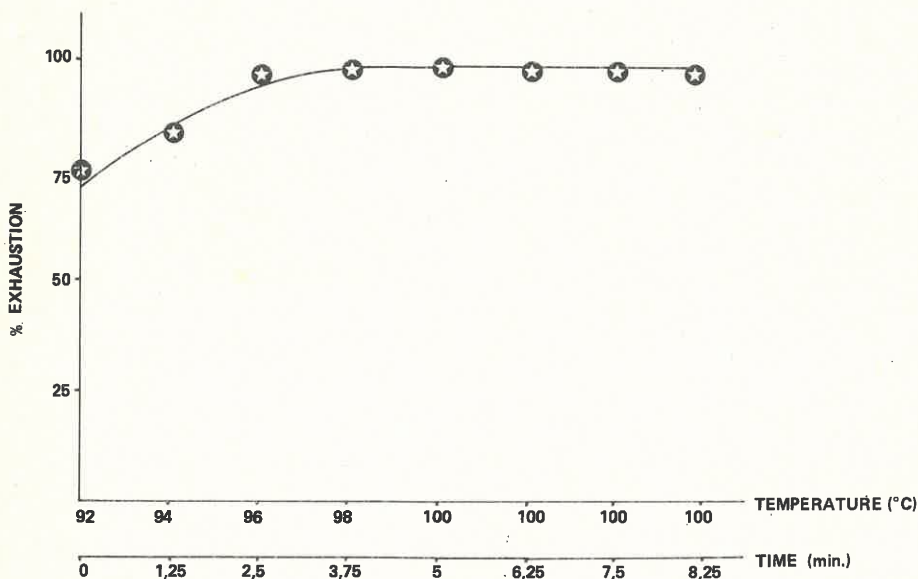

FIGURE 4

The sorption characteristics of C.I. Basic Blue 3 from a charged solvent system (perchloroethylene) containing 2% dye (o.m.f.), 5% LEA (o.m.f.), 3% Ciba Retarder A (o.m.f.), and 50% H_2O (o.m.f.)

TABLE I

COMPARATIVE COLOUR MEASUREMENT DATA OF COMMERCIAL CATIONIC DYES APPLIED FROM CHARGED SOLVENT- AND AQUEOUS SYSTEMS

| DYESTUFF (C.I. BASIC) | SOLVENT SYSTEM (5% LEA, 30% H_2O, 3% RETARDER A o.m.f., 2% DYE; 10 min at 100°C) | | | | | AQUEOUS SYSTEM (2% DYE o.m.f.; 90 min at 100°C) | | | | |
| | Chromaticity Co-ordinates | | Brightness | Tristimulus Ratios | | Chromaticity Co-ordinates | | Brightness | Tristimulus Ratios | |
	x	y	Y	$\frac{X}{Y}$	$\frac{Z}{Y}$	x	y	Y	$\frac{X}{Y}$	$\frac{Z}{Y}$
Blue 73	0,1827	0,1694	7,70	1,0724	3,7766	0,1577	0,1773	8,33	1,0532	3,536
Red 44	0,5854	0,3134	5,83	1,8559	0,3053	0,5796	0,3156	6,33	1,8252	0,315
Blue 3	0,1673	0,1781	3,82	0,9335	3,6256	0,1639	0,1720	3,79	0,9481	3,809
Violet 30	0,5377	0,2854	3,55	1,8693	0,5955	0,5272	0,2834	3,59	1,8436	0,645
Orange 38	0,6120	0,3490	15,03	1,7423	0,0989	0,6048	0,3498	14,11	1,7323	0,110
Yellow 13	0,4254	0,5051	64,78	0,8574	0,1292	0,4250	0,5110	63,63	0,8270	0,1171
Violet 31	0,3697	0,2240	1,86	1,6378	1,769	0,3649	0,2249	1,94	1,6116	0,771
Brown 13	0,5864	0,3447	8,48	1,6899	0,1854	0,5835	0,3449	7,78	1,6810	1,1933
Red 27	0,5914	0,2877	18,54	2,0435	0,4064	0,5901	0,2879	17,45	2,0381	0,4083
Orange 37	0,5528	0,4092	26,57	1,3428	0,0822	0,5510	0,4094	26,24	1,3365	0,0865
Sandocryl Navy B-RL)	0,280	0,2431	1,35	1,1416	0,9149	0,2726	0,2549	1,30	1,0794	1,789

TABLE II

COMPARATIVE FASTNESS PROPERTIES OF COMMERCIAL CATIONIC DYES APPLIED FROM CHARGED SOLVENT AND AQUEOUS SYSTEMS

DYESTUFF (C.I. BASIC)	SOLVENT SYSTEM (5% LEA, 30% H₂O, 3% RETARDER A, 2% DYE o.m.f.; 10 min at 100°C)							AQUEOUS SYSTEM (2% DYE o.m.f.; 90 min at 100°C)						
	Light	WASHING			PERSPIRATION			Light	WASHING			PERSPIRATION		
		Change in Shade	Staining Wool	Staining Acrylic	Change in Shade	Staining Wool	Staining Acrylic		Change in Shade	Staining Wool	Staining Acrylic	Change in Shade	Staining Wool	Staining Acrylic
Blue 73	7–8	4–5	5	4–5	4–5	5	4–5	5–6	5	5	4–5	5	5	4–5
Red 44	8	5	5	5	4	3	3–4	7	5	5	5	5	2	2–3
Blue 3	7	5	5	4–5	5	3	4–5	6–7	4–5	5	5	4–5	3	5
Violet 30	8	5	5	4–5	4–5	3	3	7–8	5	5	4–5	4–5	4	4
Orange 38	8	5	4–5	5	5	3–4	5	7–8	5	5	5	5	3–4	4
Yellow 13	8	4–5	4–5	5	5	3	4–5	8	4–5	5	5	5	4	5
Violet 31	8	5	5	4–5	5	5	4–5	8	5	5	4–5	5	5	4–5
Brown 13	7–8	5	4–5	5	4	2–3	3–4	8	5	5	4–5	4	2–3	3
Red 27	4	4	5	5	4–5	5	5		5	5	5	5	5	5
Orange 37	7–8	5	5	3	5	3	5	7–8	4–5	5	5	4–5	3	5
Sandocryl Navy B-RL)	7	4–5	5	4–5	4–5	3	4	7	5	5	4–5	4–5	4	4–5

TABLE III

COMPARATIVE COLOUR MEASUREMENT DATA FOR MIXTURE DYEINGS FROM AQUEOUS AND SOLVENT SYSTEMS (5% LEA, 3% CIBA RETARDER A, 40% H_2O o.m.f.)

Experiments	DYE COMBINATIONS (% o.m.f.)			AQUEOUS SYSTEM					SOLVENT SYSTEM				
	C.I. Basic Red 46	C.I. Basic Blue 3	C.I. Basic Yellow 45	x	y	Y	$\frac{X}{Y}$	$\frac{Z}{Y}$	x	y	Y	$\frac{X}{Y}$	$\frac{Z}{Y}$
I	1	0	0	0,5728	0,2737	10,85	11,9532	0,4667	0,5890	0,2984	12,12	1,9774	0,3885
II	0	1	0	0,1636	0,1981	7,10	0,8286	3,2435	0,1603	0,1931	7,36	0,8321	3,3529
III	0	0	1	0,4684	0,4890	50,66	0,9590	0,0939	0,4598	0,4974	54,43	0,9237	0,0874
IV	0,5	0,5	0	0,2796	0,1775	2,55	1,5825	3,0690	0,2707	0,1656	2,55	1,6365	3,4245
V	0,5	0	0,5	0,5875	0,3311	13,29	1,7758	0,2558	0,5949	0,3297	15,06	1,8060	0,2386
VI	0	0,5	0,5	0,2195	0,4749	10,36	0,4646	0,6503	0,2125	0,4392	9,46	0,4852	0,8003
VII	0,33	0,33	0,33	0,3388	0,2889	4,01	1,1736	1,2996			UNLEVEL		

the $\frac{Z}{Y}$ values compared with the values for the aqueous dyed samples. When all three dyes were used together with a trichromatic dyeing (dyeing VII) the differential absorption characteristics predominated to such an extent that level dyeing became impossible.

SUMMARY AND CONCLUSIONS

It was established that basic-dyeable acrylic fibres can be dyed successfully to a single shade from a charged perchloroethylene system, the charge consisting of 30%–50% o.m.f. water, 5% o.m.f. lauryl monoethanolamide and 3% o.m.f. of a quaternary alkyl ammonium salt. Dyeing time was only 5 minutes at 98–100°C, resulting in a bath exhaustion in excess of 95%. The dyeings had similar wet- and light fastness properties to those obtained from a conventional aqueous system.

ACKNOWLEDGEMENT

THE USE OF PROPRIETARY NAMES

The use of proprietary names for some chemicals used in this investigation does not imply a bias for or discrimination against any given manufacturer. Other brands may be as good or even better.

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