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Improved Fixation of Dyes on Polyamide Fibres. Part 1: Using 1,3,5-Triacroylamino-Hexahydro-*s*-Triazine as a Crosslinking Agent

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ABSTRACT

*The crosslinker 1,3,5-triacroylamino-hexahydro-*s*-triazine was synthesised and applied to nylon-6,6 fabric from a long liquor; its substantivity was found to be optimum at pH 8 but was rated as only moderate, approximately 30–40% of the agent being absorbed from boiling aqueous solutions when an initial amount of 3% omf was applied. Amino-alkyl dyes were prepared from reaction of existing chloro-triazinyl reactive dyes with ethylene diamine. The amino-alkyl group in these dyes behaved as an excellent nucleophile and could be crosslinked to the fibre amino groups using the above crosslinker to obtain covalently bound dyeings of excellent wet fastness.*

1 INTRODUCTION

In the late 1960s it was found that dyes with suitable nucleophilic functional groups could be indirectly bonded to cellulosic fibres by using crosslinking agents. The Basazol (BASF) dyes contained pendant aminosulphonyl groups and employed a polyfunctional crosslinking agent known as Fixing Agent P (1,3,5-triacroylamino-hexahydro-*s*-triazine, FAP), whose constitution is shown on the following page. The covalent fixation of certain nucleophile containing dyes on cotton fabrics with FAP has been studied.[1-3] It was shown that addition of the polyfunctional

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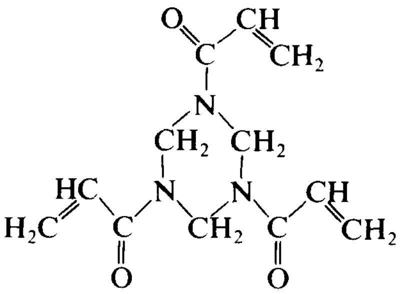
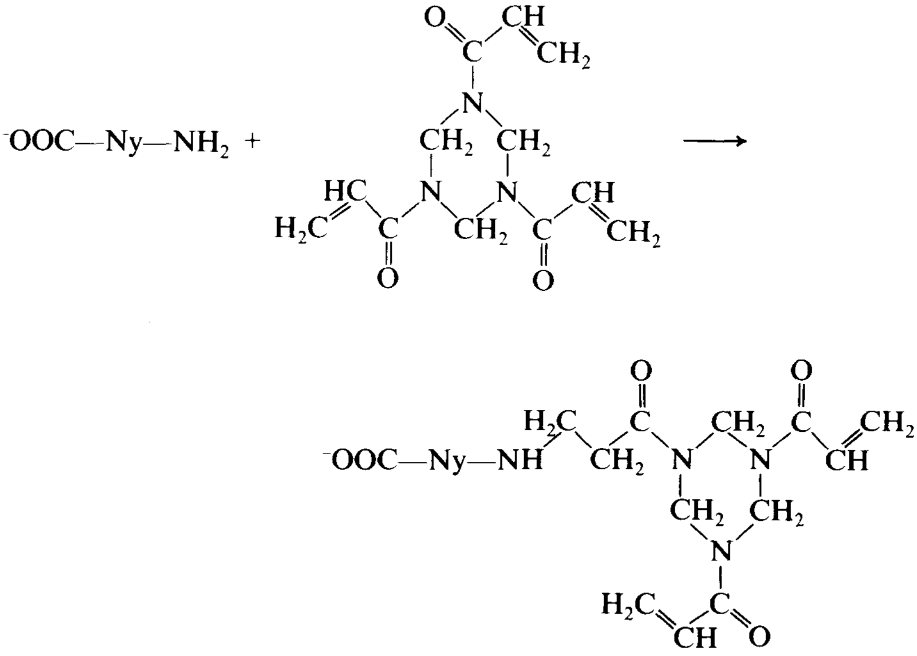


FAP

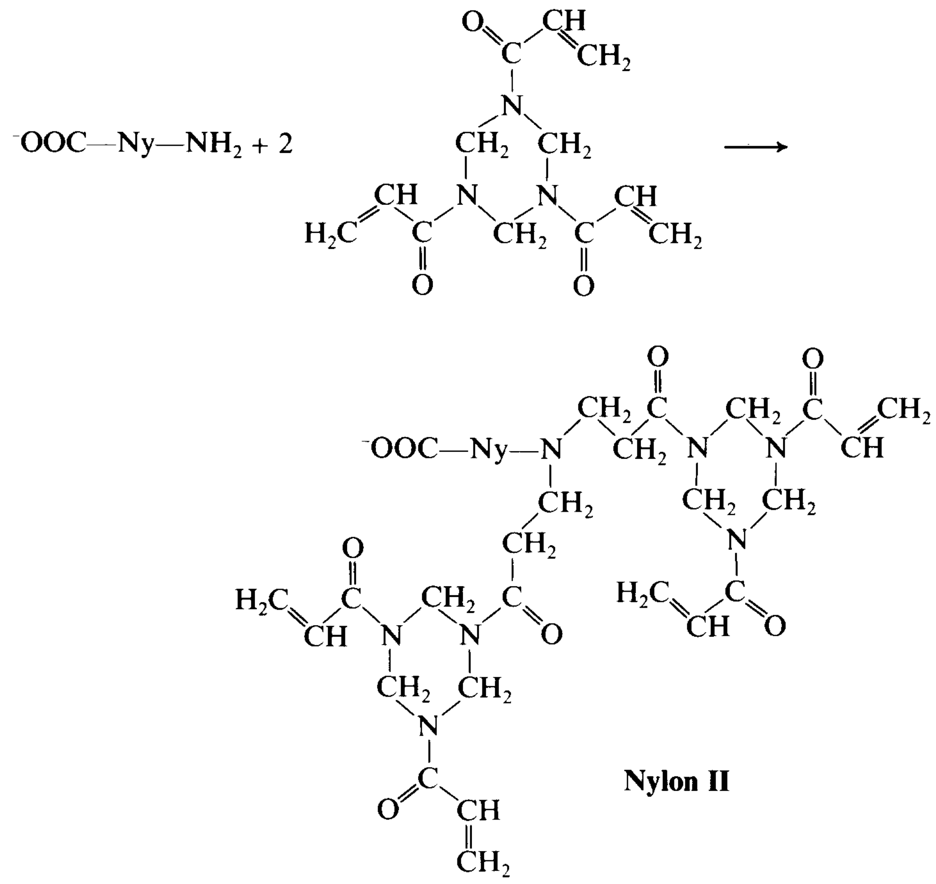
crosslinking agent did in fact cause an increase in colour yield and covalent fixation. In particular, BASF[1,2] employed dyes with pendant aryl-sulphonylamino residues which under alkaline conditions (>pH 10) were sufficiently nucleophilic to react with FAP during steaming. This system was therefore promoted for steam fixing amino-sulphonyl dyes to cellulosic fibres following application in printing or continuous dyeing systems.

The amino groups in synthetic polyamide (nylon) fibres may also serve



Nylon I

Scheme 1 1 : 1 Stoichiometry

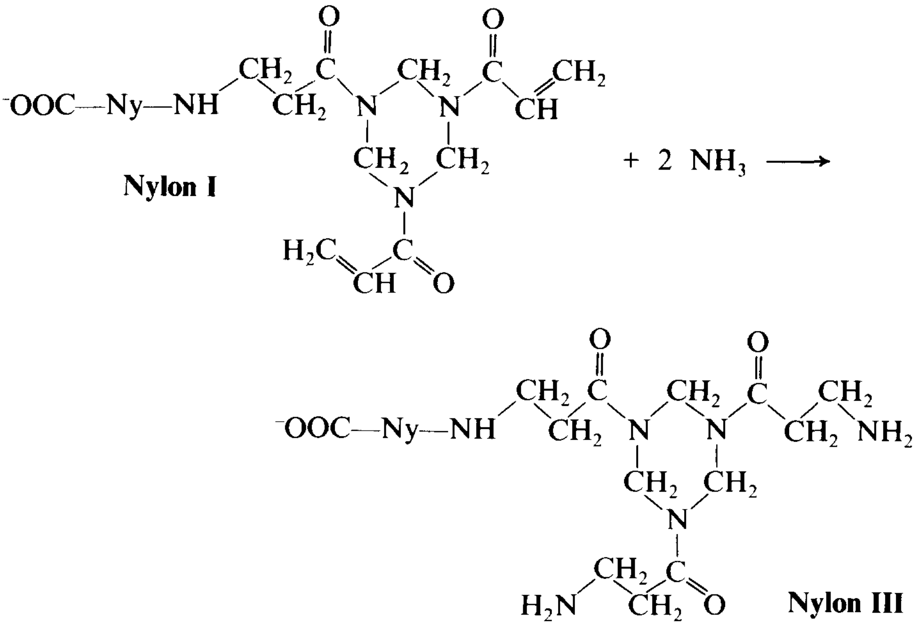


Scheme 2 1 : 2 Stoichiometry

as nucleophilic reactants in reactions with FAP and this research has thus investigated optimum conditions for effecting reaction between FAP and nylon. Additionally, FAP/ammonia can be employed for increasing the nucleophilic character of nylon to improve its dyeing properties with conventional reactive dyes. It is proposed that the crosslinking agent, FAP, reacts with nylon as shown in Schemes 1 and 2.

The above activated fibre will react readily with nucleophiles; the very simple reaction with ammonia may be represented as shown in Schemes 3 and 4.

Nylons I and II may be regarded as 'reactive' fibres capable of covalent reaction with nucleophilic dyes, whereas nylons III and IV may be regarded as amino nucleophile enriched fibres capable of more efficient reaction with conventional reactive dyes in comparison with untreated nylon which has relatively few primary amino groups.



Scheme 3

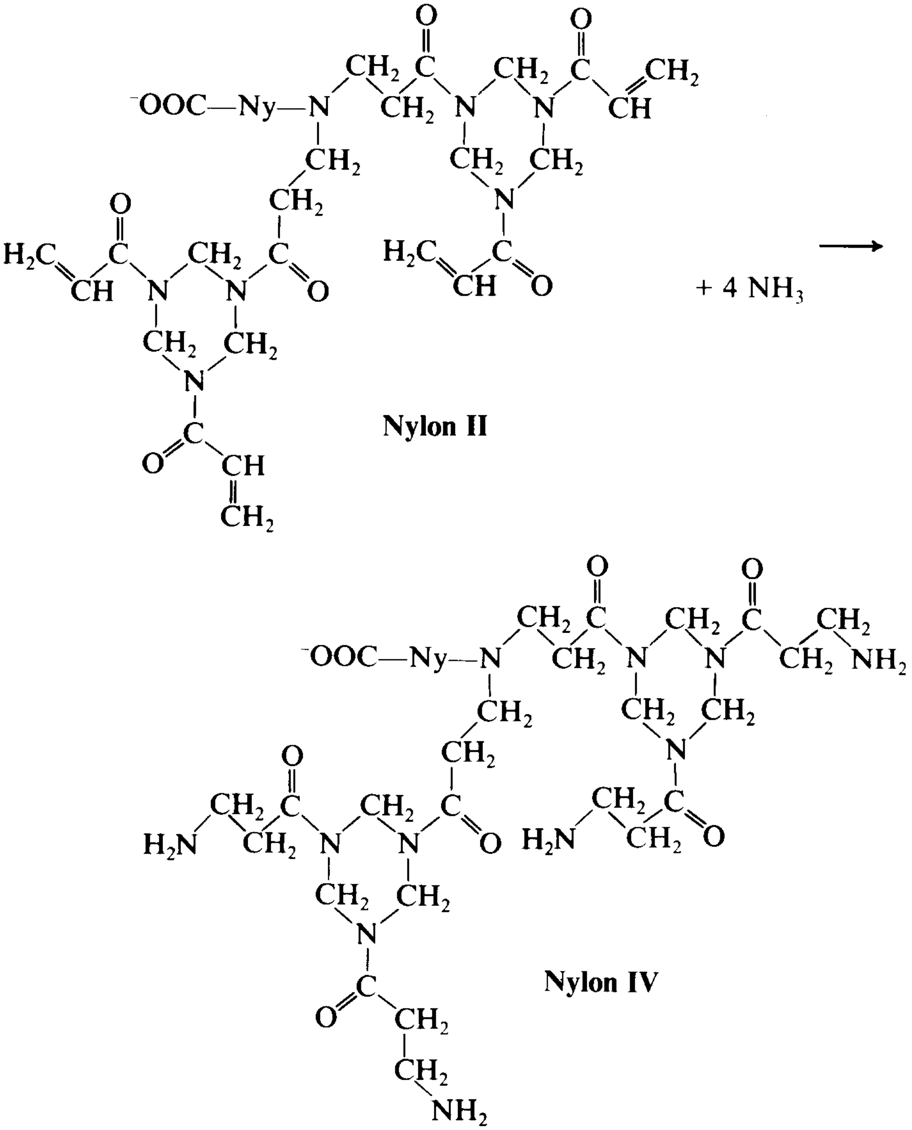
2 EXPERIMENTAL

2.1 Fibre

Scoured knitted nylon-6,6 fabric (78d/F20) (230·5 g m^{-2}) supplied by Dupont Fibres Division was employed in all experiments.

2.2 Synthesis of Fixing Agent P (1,3,5-triacroylamino-hexahydro-*s*-triazine), FAP

A solution of 16·37 ml acrylonitrile, 0·35 ml sulfuric acid and 50 ml carbon tetrachloride was brought to reflux. A solution of 16·50 ml acrylonitrile and 15·0 g *s*-trioxane dissolved in 50 ml carbon tetrachloride was then added dropwise with stirring over 25 min. The temperature was kept at 65°C. A white solid separated out before addition was complete. The mixture was then stirred and refluxed for 1 h. After cooling to room temperature over about 40 min, the white amorphous solid which precipitated was collected on a filter and washed with carbon tetrachloride and dried at 40°C. The reaction scheme is shown in Scheme 5.



Nylon II

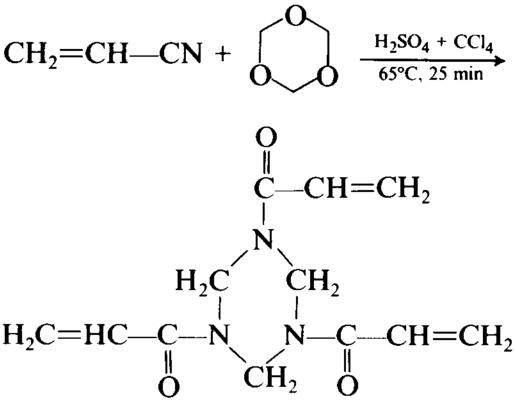
Nylon IV

Scheme 4

2.3 Synthesis of CI Reactive Red 3

This was carried out in four distinct steps:

(i) *Diazotisation.* A diazo solution was prepared in the usual way: orthanilic acid (0·05 mole) was dissolved in water (100 ml) and sodium carbonate was added to raise the pH value of the mixture



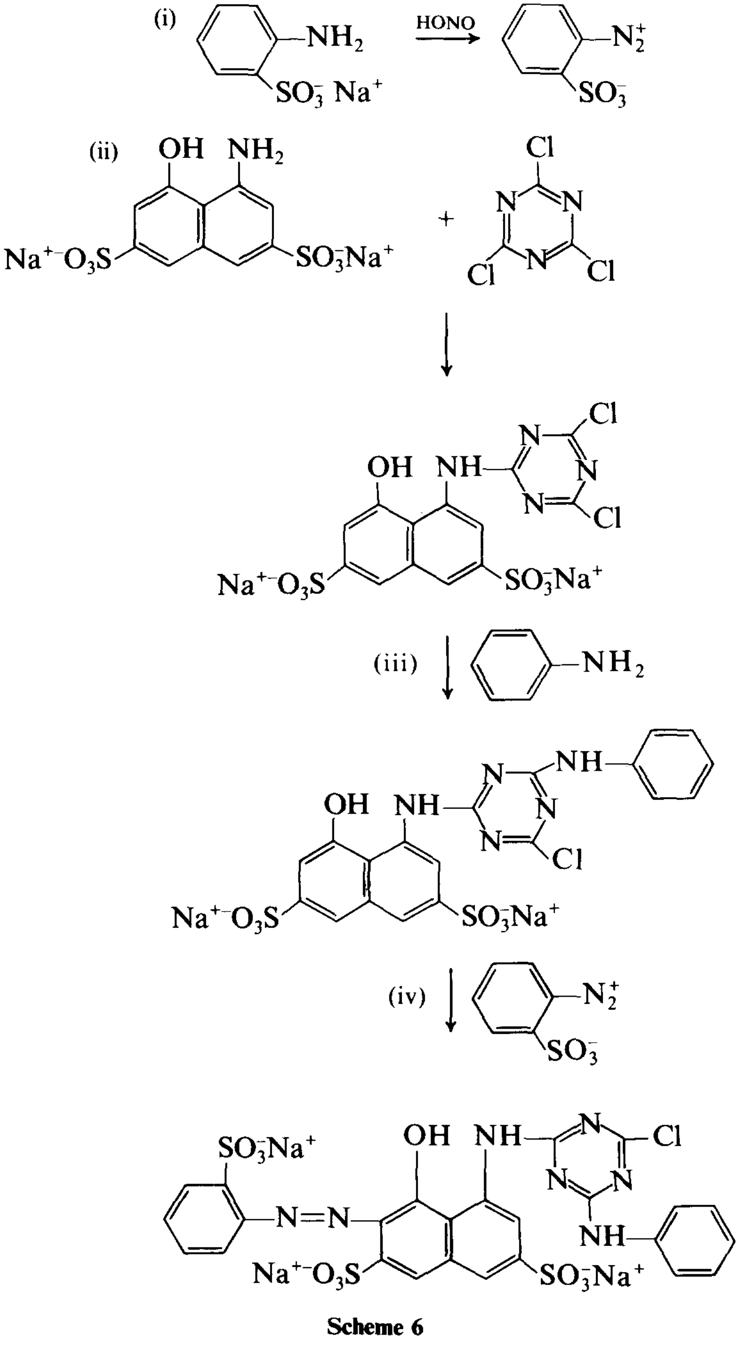
Scheme 5

to 5. The solution was then cooled to 0–4°C in an ice/salt bath and the pH value of the mixture adjusted to 2·5 with hydrogen chloride; a solution of sodium nitrite (0·05 mole) was added dropwise over 15 min. The temperature of the mixture did not rise above 4°C and its pH value remained at 2·5. The solution was stirred for a further 30 min.

(ii) *Condensation of H-acid with cyanuric chloride and subsequent reaction with aniline.* Cyanuric chloride (0·05 mole) was stirred with water (40 ml) and acetone (10 ml) and the solution was cooled to 0–4°C in an ice/salt bath. To the latter was added a neutral (pH 6·9) solution of 1-amino-8-naphthol-3,6-disulphonic acid (H-acid) (0·05 mole) in water (100 ml). The temperature of the mixture was kept below 4°C and its pH value remained below 3·5. The solution was stirred for a further 2 h and was then filtered prior to use in stage (iii).

(iii) *Conversion of dichloro-*s*-triazine to the monochloro-anilino-triazine.* Aniline (0·05 mole) was run into the above solution over 20 min, allowing the temperature to rise to 8°C. When the pH value of the solution had fallen to 4·5, sodium carbonate solution was added portionwise to raise the pH value to 6·7; the temperature was then slowly raised to room temperature when the pH value began to fall at a moderate rate. The temperature was kept constant at room temperature whilst further aqueous sodium carbonate was added in portions until the pH value remained at 6–7.

(iv) *Coupling and isolation.* The above solution was adjusted to pH 7, cooled to 4°C and the diazo salt of orthanilic acid added. Coupling to form the desired red dye was complete within 1 h. The dye was isolated by addition of 10 g sodium chloride per 100 ml solution; after being collected by filtration, it was dried at



Scheme 6

a conveniently low temperature (e.g. 40°C) in a vacuum drying oven.

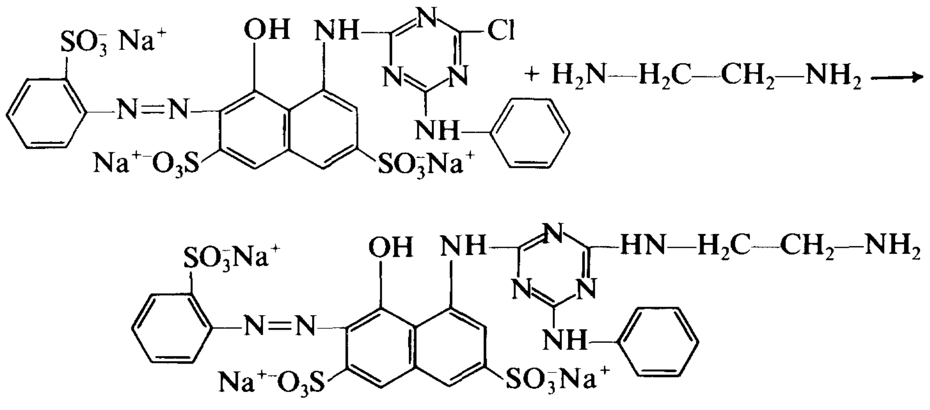
The overall reaction is shown in Scheme 6.

2.4 Synthesis of a sulphonated amino-ethyl anionic dye

A 50% (v/v) aqueous solution of ethylenediamine (50 ml) was stirred and heated to the boil on a stirrer–heater unit and a 5% (w/v) aqueous solution of CI Reactive Red 3 (50 ml) was added dropwise over 20 min. The mixture was then stirred and refluxed for a further 2 h, cooled to room temperature, and the pH value of the mixture was then adjusted to 10 with hydrochloric acid solution. The product was isolated at pH 10 by addition of 25 g of sodium thiocyanate (NaSCN) per 100 ml of solution; it was then collected by filtration and washed five times with 10% (w/v) aqueous sodium thiocyanate solution at pH 10. Finally, the dye was repeatedly washed with acetone to remove residual sodium thiocyanate (the product was shown to be free of the SCN IR band at 2168 cm^{-1}); the product was dried at 40°C. The reaction scheme may be written as in Scheme 7.

2.5 FAP treatment of nylon (formation of nylon I and II)

All treatments of nylon fibres with FAP were carried out in 100 ml sealed stainless steel dye pots housed in a Rotadyer machine at a liquor to goods ratio of 20 : 1. The treatment bath, which contained FAP and water, was set at the required pH value (pH 6–8). Treatment commenced at 20°C, the bath temperature was raised to the boil (2°C min^{-1}) and treatment continued at the boil for 1 h.



Scheme 7

2.6 FAP/NH_3 treatment of nylon (formation of nylon III and IV)

FAP treated nylon was treated in a solution containing 50 g l^{-1} of ammonia (d = 0·880). The treatment was carried out at the boil for 1 h in 100 ml sealed stainless steel dyepots, housed in a Rotadyer machine at a liquor to goods ratio of 20 : 1. The sample was then rinsed thoroughly in tap water and air dried.

2.7 Preparation of FAP dispersions

FAP was dispersed in water by using the anionic dispersing agent Matexil DA-AC (sulphonated naphthalene–formaldehyde condensate) (ICI) (FAP : DA-AC : water = 10 : 2 : 38). The mixture was dispersed for 36 h using a ball mill (laboratory milling machine at 180 revs min^{-1}).

2.8 Measurements of dye exhaustion

The uptake of dye was measured by sampling the dyebath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption of the dye using a UV/visible spectrophotometer (Kontron Uvikon 860). Dyebath exhaustion (E) was calculated using the following equation:

$$E(\%) = 100 \times (1 - A_1/A_0)$$

where A_0 and A_1 are absorbance of dye solution before and after the process, respectively.

2.9 Measurement of dye fixation

Measurement of the extent of dye–fibre covalent bonding or dye fixation was carried out by stripping any unfixed dye from the dyed material using a 25% (v/v) pyridine/water solution (100°C, LR = 20 : 1). The dyed fabric sample was repeatedly extracted with fresh pyridine/water solution for 3 min until all the unfixed dye had been stripped (a colourless extract was obtained). The combined extracts were collected and diluted to 1000 ml and then the solution absorbance measured spectrophotometrically at λ_{max}. Fixation (F) was expressed as the percentage of dye not removed from the dyed fibre by the extraction procedure.

An alternative use of the term ‘fixation’ is sometimes used, which in fact refers to the amount of original dye taken which is covalently bonded. This overall fixation efficiency (T) is related to F (exhausted dye fixed) by the equation:

$$\%T = (\%F \times \%E)/100$$

2.10 Dyeing method

All dyeings were carried out in 100 ml capacity sealed stainless steel dyepots, housed in a Rotadyer (John Jeffreys) laboratory dyeing machine, at a liquor to goods ratio of 20 : 1. The dyebath was set at the required pH value. Dyeing was commenced at 20°C, the temperature was raised to the boil over 40 min (2°C min^{-1}) and dyeing was continued at the boil for the required length of time.

2.11 IR analysis

2.11.1 IR/attenuated total internal reflectance (ATR) analysis of fabric materials

IR analysis of nylon fabric was carried out on a Perkin Elmer 1740 Infrared Fourier Transform Spectrometer using a vertical ATR pressure cell attachment.

2.11.2 Solids

IR analysis of CI Reactive Red 3 and the amino-ethyl anionic dye were carried out on a Perkin Elmer 1740 Fourier Transform Infrared Spectrometer. Samples were prepared by mixing 1 mg of the sample in 200 mg of potassium bromide (KBr).

2.12 HPLC analysis

The amino-ethyl anionic dye was analysed using a Varian 5000 Liquid Chromatograph using an Apex octadecyl C18 column. The mobile phase used in this analysis was a mixture of 50/50 (v/v) water/methanol, which also contained 0·001 mole of tetrabutylammonium bromide as an ion-pairing reagent and 0·5 ml l^{-1} of 20% (w/w) acetic acid and 0·5 ml l^{-1} of 5% (w/w) potassium hydroxide as a buffer.

2.13 Capillary electrophoresis analysis

A Dionex Capillary Electrophoresis System 1 was used for amino-ethyl anionic dye analysis. An uncoated silica capillary of internal diameter 75 μm and length 58 cm was used. Samples were introduced into the capillary by gravity injection: the sample vial was elevated by 50 mm for 10 s. The buffer employed was 10 mmole l^{-1} potassium dihydrogen phosphate at pH 9. Detection was by visible light absorbance at 540 nm (λ_{max} of the dye).[6,7]

3 RESULTS AND DISCUSSION

3.1 Analysis of the synthesised triacroylamino-hexahydro-triazine (FAP)

3.1.1 IR study of FAP

IR analysis of FAP was carried out (Perkin Elmer 1740 Infrared Fourier Transform Spectrometer) using the KBr disc method. The spectrum is shown in Fig. 1; the band at 1651 cm^{-1} is due to the C=O stretching vibration and the one at 1618 cm^{-1} is attributed to the C=C stretching vibration. This peak is weaker than the C=O band. The absorbances at 1463 and 1376 cm^{-1} are due to C—H deformation vibrations. Lack of absorbance between 1510 and 1570 cm^{-1} rules out the possibility of a monosubstituted amide. Moreover, the absorbance bands between 3100 and 3500 cm^{-1} are too weak to be due to —NH or —NH_2 stretching vibrations. Therefore, the amide must be disubstituted. This infrared spectrum is similar to that previously reported for this compound.[8]

3.1.2 Elemental analysis of FAP

Found: C, 55·90%, H, 6·00%; N, 16·75%. Calculated: C, 57·80%; H, 6·00%; N, 16·86%.

3.2 Effect of pH and temperature on uptake of FAP on nylon using UV absorbance

The standard plots for FAP concentration versus optical density at 250 nm were found to be linear, indicating that Beer's Law is obeyed. It was

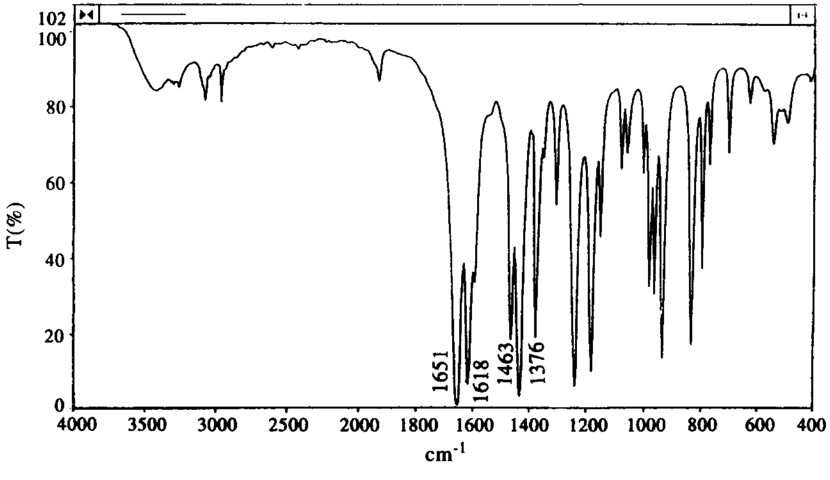


Fig. 1. FTIR spectrum of FAP solid.

TABLE 1
Effect of pH on the Uptake of FAP (3% omf)

pH	*FAP uptake (E (%))*	
	80°C	*100°C*
6	3·3	24·1
7	14·1	32·7
8	15·7	35·6
9	11·5	31·3

possible to follow the uptake of FAP on nylon-6,6 by taking a standard amount of solution from the bath prior to addition of the fabric and measuring its optical density, then removing similar solution samples at the end of the treatment process. UV absorbance measurements were made at 250 nm on these solution samples and the results, expressed in terms of % bath exhaustion, are shown in Table 1.

The uptake of FAP by nylon is clearly not a very efficient process and only fairly low levels of modification are possible by such a long liquor process. In other words, FAP shows low substantivity for nylon under these conditions. Application of this product to nylon by padding procedures may give more efficient uptake and subsequent reaction; however, the

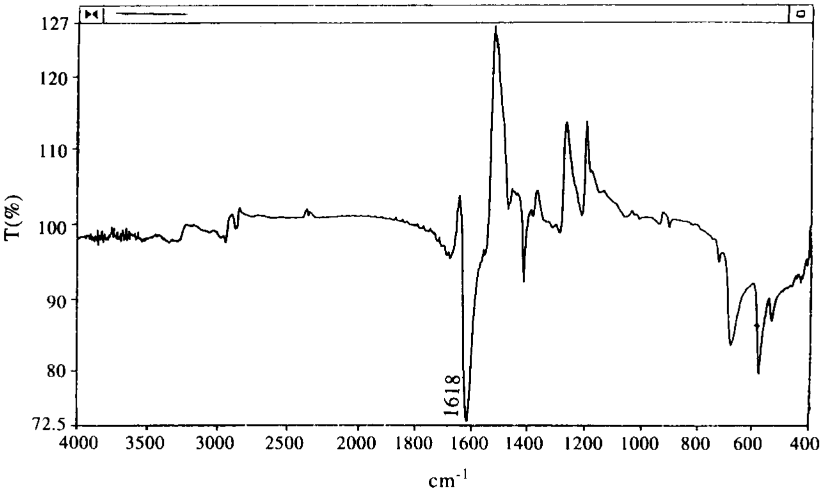


Fig. 2. FTIR spectrum obtained by subtracting the nylon IR spectrum from the FAP treated nylon IR spectrum. All treatments of nylon with FAP carried out at pH 8 for 60 min at 100°C.

industry favours substantive application processes rather than continuous processes and this option was therefore not pursued.

3.3 IR Study of treated and untreated nylon fabric

Figure 2 shows the FTIR-ATR spectrum of FAP (pH 8) treated nylon from which the spectrum of untreated nylon has been subtracted. The absorption at 1618 cm^{-1} is due to the presence of C=C bonds in the attached FAP residue. Figure 3 shows the corresponding spectrum of the substrate obtained by reaction of the FAP treated nylon with ammonia. The disappearance of the absorbance at 1618 cm^{-1} indicates that ammonia adds to the double bond. A new absorbance appears between 1580 and 1575 cm^{-1} due to the primary $—NH_2$ group which is introduced.

3.4 Analysis of the amino-ethyl anionic dye

Figure 4 shows the HPLC printouts from the analysis of CI Reactive Red 3 (dye B), the amino-ethyl anionic dye (dye A) and their mixture. The shorter retention time of the modified form (dye A) compared with the original form (dye B) indicates that the former is more basic than the latter.[7]

Figure 5 shows the CE results. In CE the migration time is proportional to the mass : charge ratio. Clearly there is a big difference in migration time; the unmodified dye reaches the detector at the negative

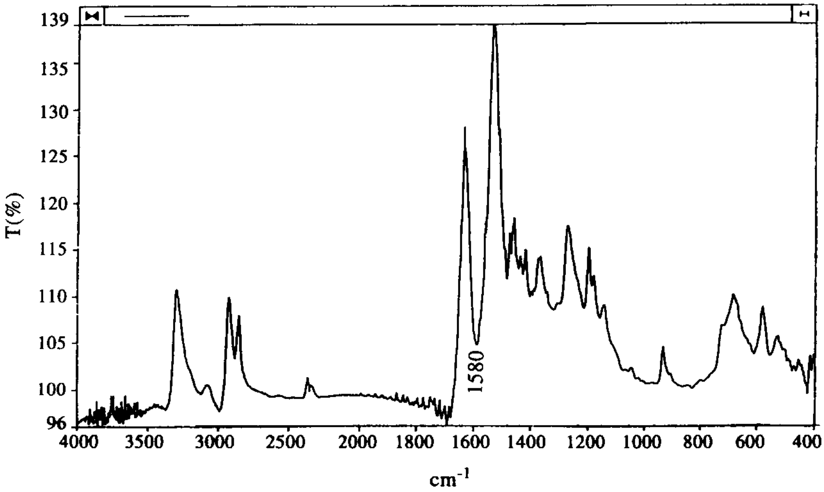


Fig. 3. FTIR spectrum obtained by subtracting the nylon IR spectrum from the FAP/NH_3 treated nylon IR spectrum. All treatments of nylon with FAP carried out at pH 8 for 60 min at 100°C.

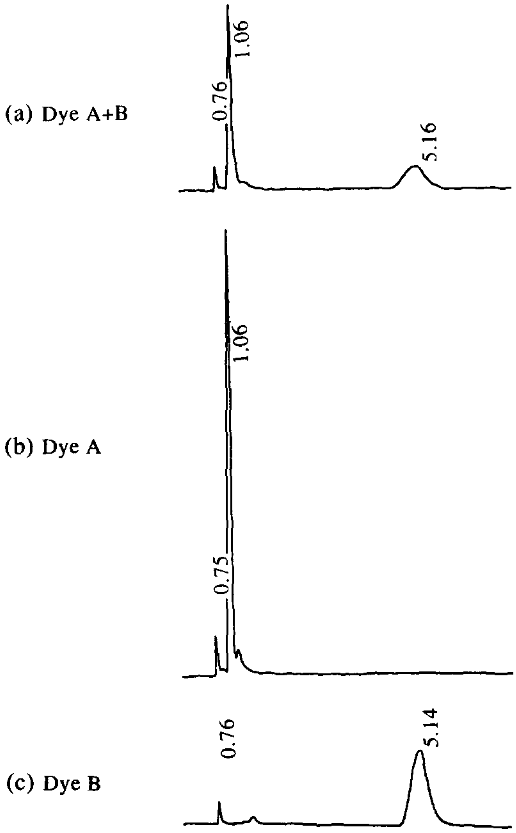


Fig. 4. HPLC printouts of CI Reactive Red 3 (dye B), amino-ethyl anionic dye (dye A) and their mixture. Retention time: dye A, 1·06 min; dye B, 5·14 min.

electrode in 13·33 min, whereas the amino-ethyl derivative migrates in 9·80 min. This is exactly the expected change in electrophoretic mobility in going from a dye molecule with three negatively charged groups to a dye molecule with three negative charges plus one positive charge from the alkyl–NH_3^+.

Figures 6 and 7 show the FTIR spectra of the amino-ethyl anionic dye and its orginal form. The disappearance of the absorbance at 799 cm^{-1} (C—Cl stretch) and the strong increase in the peak at 1600 cm^{-1} confirms the successful introduction of primary amino groups.

Elemental analysis of the purified amino-ethyl anionic dye gave the following result (assuming $3H_2O$). Found: C, 38·25%; N, 14·40%; S, 11·30%; H, 3·50%. Calculated: C, 38·10%; N, 14·80%; S, 11·33%; H, 3·33%.

The above analyses indicate that the reaction product is the pure trisodium salt of the amino-ethyl anionic dye derived from CI Reactive Red 3 as shown in Scheme 8.

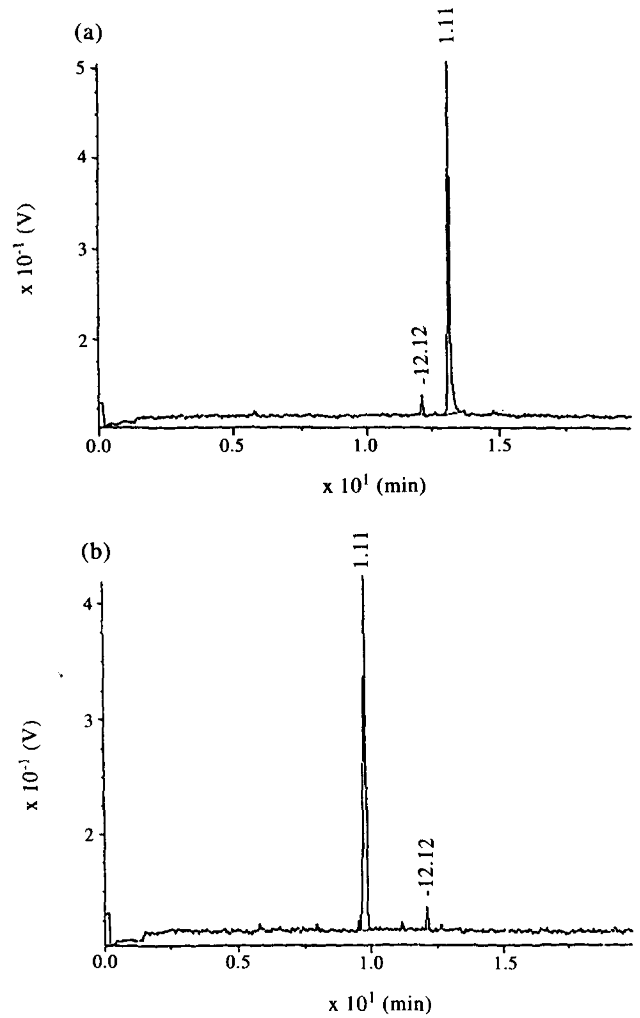
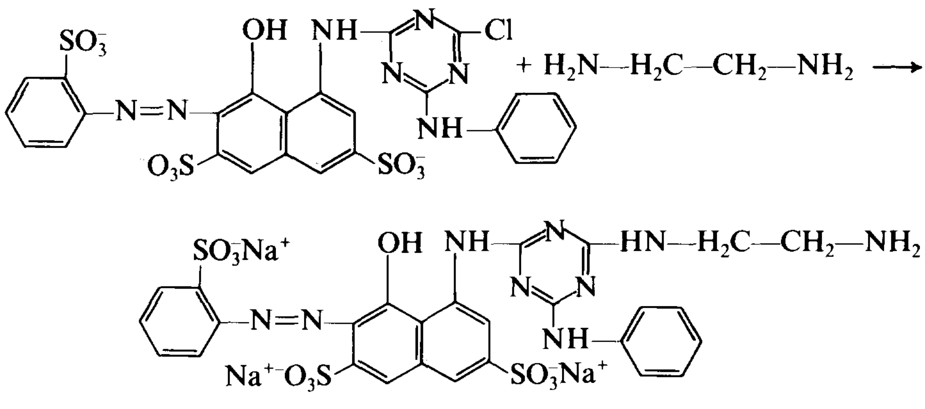


Fig. 5. CE analysis of (a) CI Reactive Red 3 and (b) amino-ethyl anionic dye (made from CI Reactive Red 3).

3.5 Exhaustion and fixation of CI Reactive Red 3 on treated and untreated nylon

Figure 8 shows the exhaustion and fixation values of CI Reactive Red 3 on treated and untreated nylon. The pH of the pretreatment of nylon fabric with FAP was 8. Dyeing (2% omf) was carried out at different pH values for 1 h at the boil using a 20 : 1 liquor to goods ratio. It can be seen clearly that no matter whether the substrate is untreated nylon or treated nylon fibre, the dye exhaustion values decrease with increasing



Scheme 8

pH and the dye fixation values increase with increasing pH. FAP/NH_3 treated nylon fibre gives the best exhaustion and fixation values in all three cases.

Due to covalent bond formation between the amino end groups of nylon and the double bonds in FAP, the number of available amino end groups in the nylon decreases; at the same time reactive C=C bonds are introduced into the nylon fibre. In this case, therefore, the exhaustion and fixation of CI Reactive Red 3 on FAP treated nylon fibre will not be as good as that on untreated nylon fibre because of the reduction in primary amino group concentration. This observation is born out in the results.

Compared with FAP treated nylon, FAP/NH_3 treated nylon show a better degree of exhaustion and fixation when dyed with CI Reactive

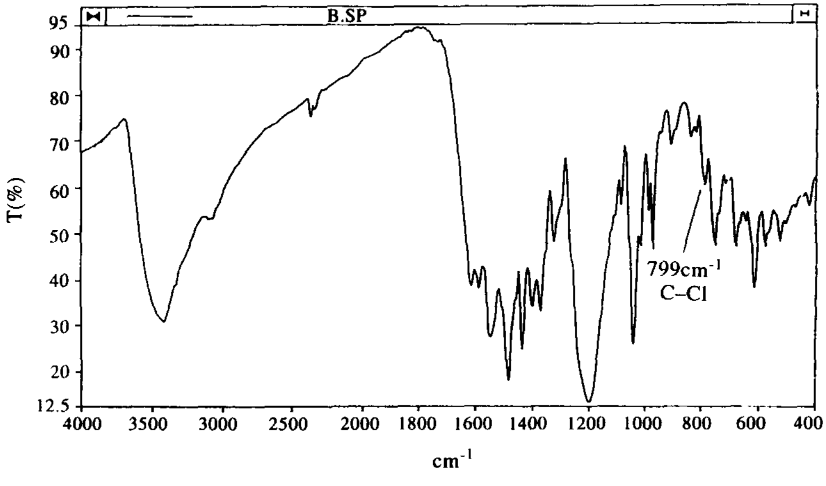


Fig. 6. FTIR spectrum of CI Reactive Red 3.

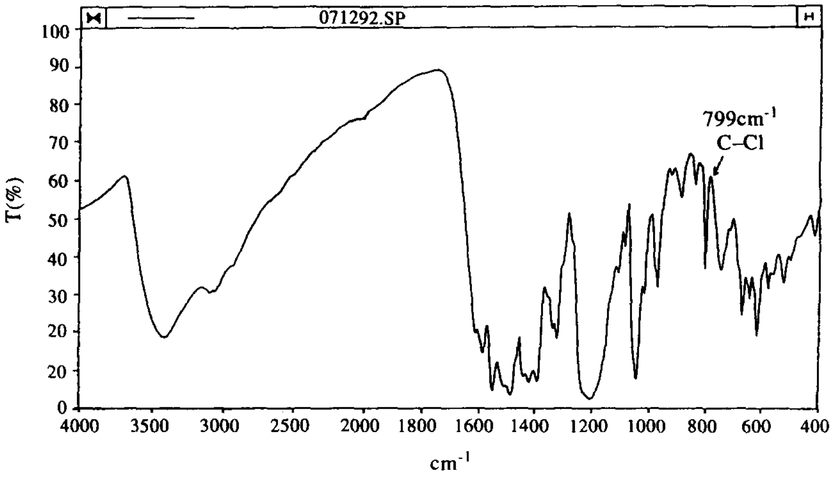


Fig. 7. FTIR spectrum of an amino-ethyl anionic dye prepared from CI Reactive Red 3.

Red 3. This is because extra amino groups are introduced by the reaction of the activated C=C bond in FAP treated nylon fibre with ammonia. It is the primary and secondary amino groups on the modified nylon fibre which are involved in covalent bonding with reactive dyes under ideal conditions. Under mildly acidic conditions these residues are also protonated, ensuring uptake of the anionic reactive dye. Schemes 9–11 summarise the

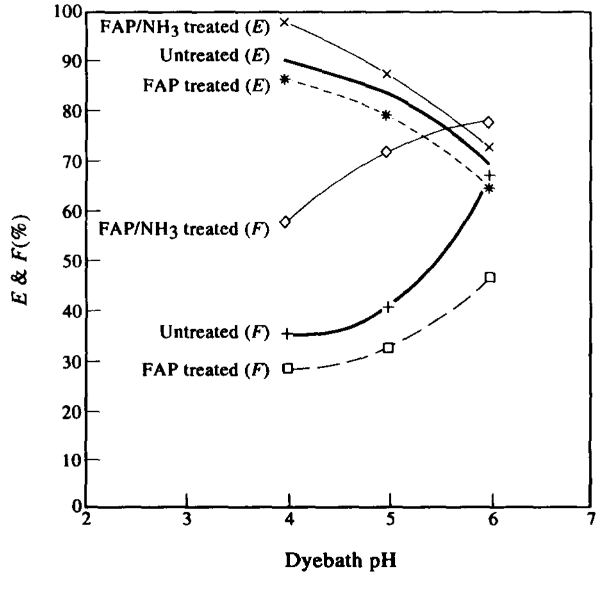
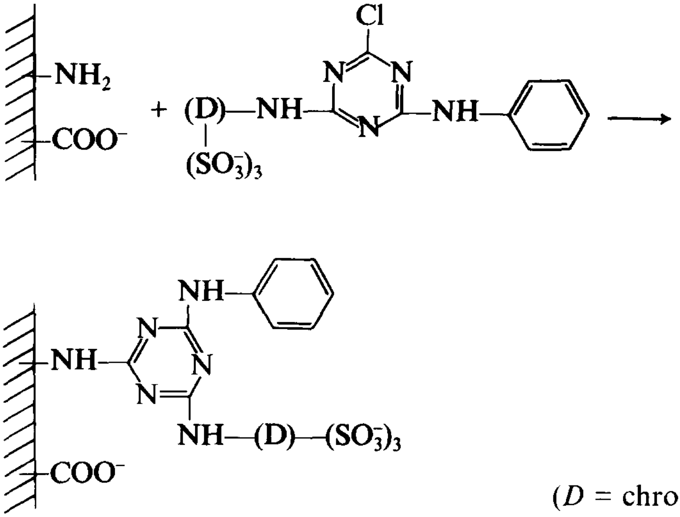


Fig. 8. Exhaustion (*E*) and fixation (*F*) of CI Reactive Red 3 (2% omf) on treated and untreated nylon.

Untreated nylon



(*D* = chromophore)

Good dye uptake (*E*) under acid conditions; moderate dye fixation.

Scheme 9

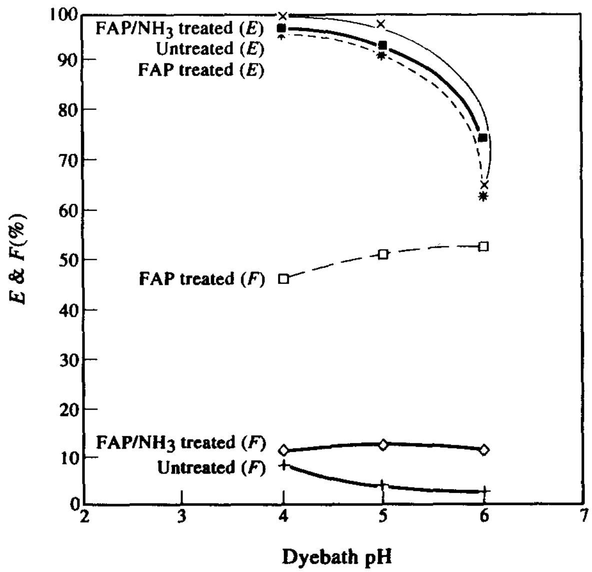
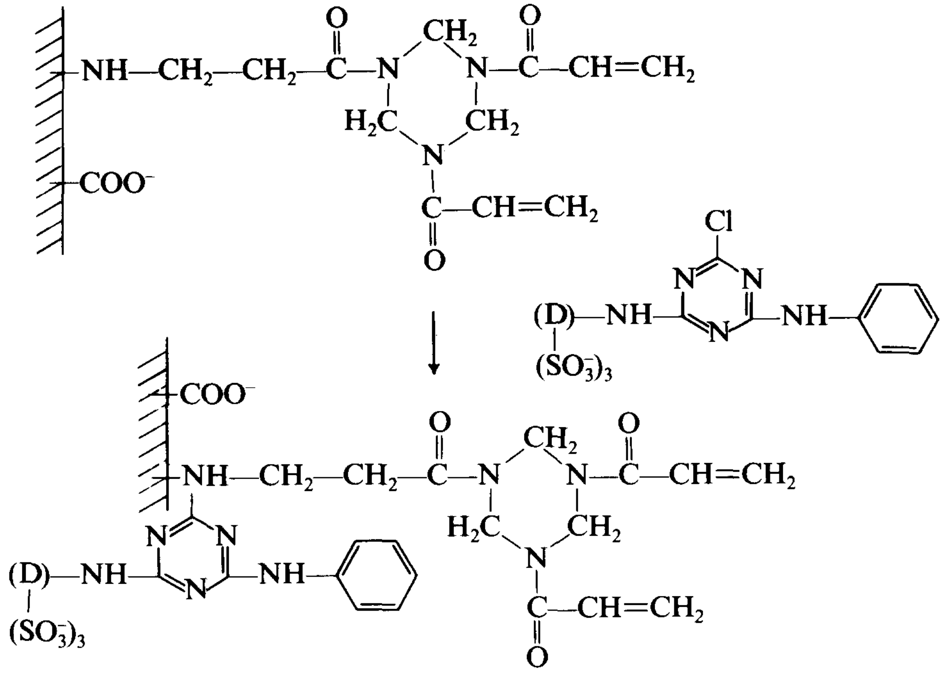


Fig. 9. Exhaustion (*E*) and fixation (*F*) of amino-ethyl anionic dye (2% omf) on treated and untreated nylon.

FAP treated nylon



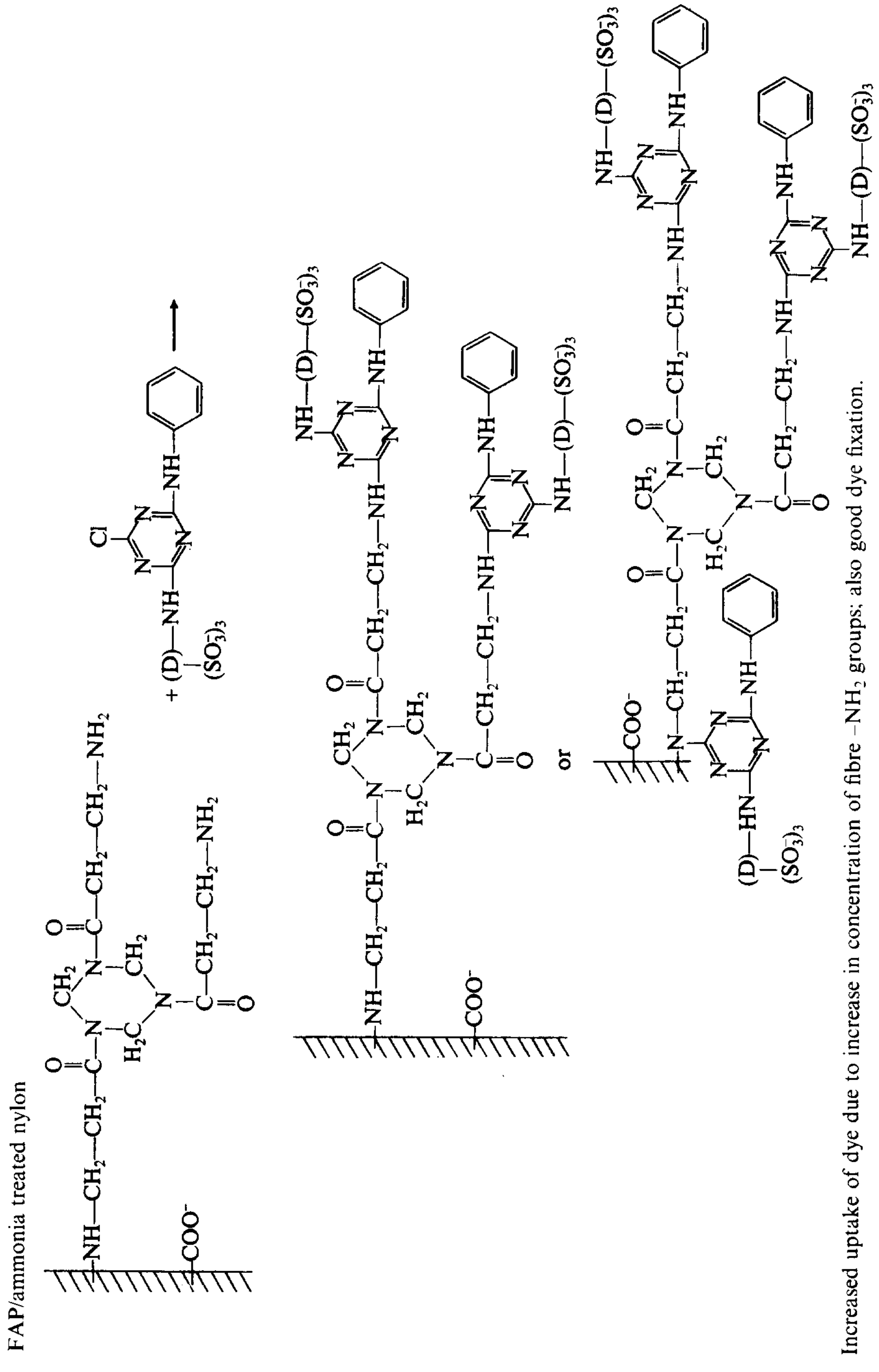
Reduced dye uptake possibly due to steric hindrance at blocked amine group; similarly reduced dye fixation.

Scheme 10

results for this monochloro-triazinyl reactive dye on the various nylon substrates.

3.6 Exhaustion and fixation of amino-ethyl anionic dye on treated and untreated nylon

The work was extended to study the dyeing of FAP treated nylon and FAP/NH_3 treated nylon with amino-ethyl anionic dyes. From Fig. 9 it can be seen that on untreated nylon the exhaustion of these dyes is good but, as expected, poor fixation is obtained. The reason is that no possibility of covalent bonding exists between the amino-ethyl anionic dye and the unmodified nylon fibre; the dye molecules were only absorbed as acid dyes and can thus be almost fully extracted in the aqueous pyridine stripping medium. The behaviour of FAP/NH_3 treated nylon with amino-ethyl dyes is very similar to that shown on untreated nylon, except the



Increased uptake of dye due to increase in concentration of fibre -NH$_2$ groups; also good dye fixation.

Scheme 11

former shows slightly better fixation than the latter. This small residual fixation may be caused by a residue of activated C=C bonds which did not react with ammonia and could thus subsequently react with the nucleophilic amino group in the amino-ethyl anionic dye. All the exhaustion values on FAP treated, FAP/NH_3 treated and untreated nylon were similar. The fixation of the amino-ethyl anionic dye on FAP treated nylon is, however, much better than the other two substrates and increases with increasing dyebath pH; the fixation values of this dye on untreated and FAP/NH_3 treated nylon were low and showed little dependence on the pH of the dyebath. These results confirm the presence of residual activated C=C bonds on FAP treated nylon; these are necessary for the covalent fixation of the amino-ethyl anionic dye.

4 CONCLUSIONS

The present study has explored a number of ways to modify nylon in order to improve its dyeability with reactive dyes, especially with the aim of achieving high fixation efficiency. The most important conclusions are given below.

(i) In order to improve the fixation efficiency of reactive dyes on nylon, chemical modification of the fibre should lead to an increase in both the substantivity of dyes for the substrate and the reactivity of the substrate towards the dyes. This has been demonstrated in the present study both theoretically and practically.

(ii) Modification of nylon fibres with FAP gives a reactive substrate which undergoes covalent fixation with an amino-ethyl anionic dye. The fixation values of the amino-ethyl anionic dye on FAP treated nylon increase with increasing dyebath pH. The presence of residual activated C=C bonds is necessary for the fixation of the nucleophilic amino-ethyl anionic dye.

(iii) FAP/NH_3 treatments produce a modified nylon fibre which shows good exhaustion and fixation values when dyed with chloro-triazine reactive dyes. This is because extra primary amino groups are introduced by the reaction of the activated C=C bond in FAP treated nylon with ammonia. It is the primary and secondary amino groups on the modified nylon fibre which are involved in covalent bonding with reactive dyes.

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