Advances in direct dyes

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Current trends in direct dyes research include: structural designs to minimize health risks from intermediates; improved sorbents and decolourising chemicals for dye residues; factors influencing dye sorption by cellulose; origins of dyeability variation in cellulosic materials; activation of cellulose to enhance dyeability; introduction of activated sites for nucleophilic dyes; and dyeability of cellulose crosslinked with N-methylol or polycarboxylic acid reactants.

Keywords: Amine intermediates, Cationised cellulose, Cellulose reactants, Direct dyes, Dyeing theory, Dye sorption

1 INTRODUCTION

The distinction between the classes of water-soluble dyes for cellulose is becoming less clear as a result of recent developments in dyeing and finishing. In the early 1980s, Sandoz\textsuperscript{1} introduced a range of reactant-fixable substantive dyes, the Indosol SF series. Initially, these were all copper-complex direct dyes selected from the existing Solar(S) range for good light fastness when aftertreated with the special Indosol(S) fixing agents used with them. Now, however, the Indosol range includes brighter unmetallized dyes that are unable to form co-ordinate linkages with the fixing agent and must become linked to the agent or to cellulose by other means\textsuperscript{2}.

Another trend in the 1980s was the interest of retailers of fashion garments in improving their response to consumer demand by deferring the decision on colour as late as possible. This was facilitated by dyeing as made-up garments or garment blanks, rather than fabric or yarn. Much research has been undertaken, mainly in the USA, into techniques for improving the dyeability of cotton that has already been given a crosslinking finish in fabric form. A successful outcome to these efforts will be highly dependent on integrating the requirements of dye and finish.

Increasing concern about residual colour and electrolyte in effluents from direct or reactive dyeing also led in the 1980s to numerous attempts to modify cellulose using reactive cationic agents with a view to enhancing uptake of anionic dyes and minimizing the need for added electrolyte. Many of these treatments brought their own disadvantages, none being entirely successful. More recently, a parallel development has been the concept of incorporating the reactive function into cellulose\textsuperscript{3}, either by pretreatment or in situ reaction, and selecting or designing dyes with nucleophilic amino substituents able to react covalently with the activated substrate.

2 DEVELOPMENTS IN ORGANIC CHEMISTRY

No dyer can afford to ignore the environmental consequences of his activities. A major study\textsuperscript{4} was undertaken by ETAD (Ecological and Toxicological Association of the Dyestuff Manufacturing Industry) to identify and assess the risks to health attributable to dyes and their intermediates. More than 90\% of over 4000 dyes tested in the survey had LD\(_{50}\) values greater than 2 \times 10\(^3\) mg/kg. The highest values for acute toxicity were found among the basic dyes and disazo direct dyes.

In July 1994, the German government banned the use of azo dyes that yield on reduction any of twenty named arylamines, including benzidine (I; R = H) and its disubstituted congeners (I; R = Cl, CH\(_3\), OCH\(_3\)). These amines are classified in Germany as carcinogenic\textsuperscript{5}. Most European dye makers no longer make dyes that break down to form these specific amines.

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Substances that have been proved unequivocally to be carcinogenic\textsuperscript{6}. The main potential risks to health from dyes and intermediates are acute toxicity, carcinogenicity and...
allergic sensitisation. Certain disazo structures derived from benzidine are known to be carcinogenic, including Congo Red (2), the first direct dye to be discovered. Early epidemiological studies revealed an increased incidence of bladder cancer in workers exposed to 2-naphthylamine. Later, benzidine was also identified as a causative agent but it was not until the 1970s that the major dye makers agreed to phase out the manufacture of benzidine dyes. An analytical study of over 40 direct dyes derived from benzidine revealed that all contained at least 2 mg/kg benzidine as impurity and three contained more than 50 mg/kg.

Thin-layer chromatography has been used to isolate and identify benzidine and other unsulphonated diamines (1). The dye is reduced with dithionite and the products separated on silica gel with a methanol-chloroform eluant. The diamine spots are rendered visible by uv irradiation or exposure to nitric oxide vapour. Strict safety procedures are essential in view of the toxic nature of the contaminated eluant. An alternative procedure is chloroform extraction followed by gas chromatography. Reduction of certain disazo and trisazo dyes for leather such as C.I. Direct Brown 2(3) and Black 38(4) yielded peaks with retention times characteristic of benzidine, whereas the benzidine-free tetrazo dye C.I. Direct Black 22 (5) did not.

A notable trend in research on novel direct dyes has been attempts to find satisfactory alternatives to these hazardous diamines as middle components. An example was the synthesis and use of 7-amino-3-(4'-aminophenyl)quinoline (6) to prepare disazo and trisazo dyes. The differential reactivity of the tetrazonium salt of 6 was helpful, the diazonium cation on the phenyl ring being more reactive, but unfortunately the derived dyes were only moderate in colour strength and light fastness.

Replacing benzene or naphthalene nuclei by heterocyclic analogues often enhances substantivity as well as avoiding the use of hazardous amines. Thus, in a series of azostilbenes and related dyes (7: Ar = phenyl or 2-thiophenyl, X = CO, CONH or CH = CH), the affinity values increased in the order of increasing electron mobility (vinylene > amide > keto) and were greater for the thiophenyls than the corresponding phenyl-substituted dyes.

The important contribution of hydrogen bonding to the substantivity of direct dyes was explored by the synthesis of red (8; X = CHO) and violet (8; X = PhNHCSNH₂) monoazo derivatives of R-acid. The existence of hydrogen bonding between the X group and hydroxy groups in cellulose was demonstrated. This research was followed up by a more comprehensive comparison of various disazo R-acid dyes derived from various alternatives to benzidine [9; Y = O, NH, CH₂, CO, SO₂, CH = CH, CONH, NHCONH, NHCSNH, CONHNHCO, NICOCONH, NICOCH₃, CONH, NH(= NH)NH, and CONHC (= NH)NHCO]. The significance of such central functional groups with scope for hydrogen bonding or dipolar interaction with the cellulose OH groups was clearly evident.
A more fundamental approach to non-hazardous azo dyes is to identify and utilize precursor intermediates that have been shown to be non-genotoxic. Increasing reliance on published data for the mutagenicity and carcinogenicity of azo dyes and their intermediates should ensure that the selected intermediates are non-mutagenic and will take account of the potential genotoxicity of any metabolites resulting from reductive cleavage of the azo groups. Incorporation of butyl or butoxy substituents ortho to the NH group of the parent amine eliminates mutagenicity, presumably by blocking N-hydroxylation. Although bulky alkoxy groups were useful in lowering the mutagenicity of certain analogues of C.I. Direct Black 17, the decrease observed was less than that seen in a series of monoazo disperse dyes.

Replacement of a C atom in the aryl rings of benzidine by an N atom leads to significant lowering of the mutagenicity exhibited by the parent amine in the standard Salmonella assay (Ames test). The above results highlighted the importance of the Prival modification of the standard Ames mutagenicity assay in evaluating azo dyes. A related project involved the design and synthesis of J-acid derivatives as potential magenta components for jet printing. The dyes had to be non-genotoxic in the Ames test and fast to light on paper. A disazo dye derived from J-acid and a suitable hydroxyminoquinoline exhibited the best all-round properties.

2.2 Dyes from Non-genotoxic Intermediates

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2.3 Dye Effluent Treatment and Recycling

Although direct dyes are particularly easy to apply, the need for electrolyte addition, the presence of chelated copper in many structures of high light fastness and the need to apply a cationic aftertreatment for high wet fastness means that careful attention must be given to final treatment of the exhaust liquors. Reviews of water supply and recovery for cellulose dyeing have specified the main contaminants and summarized methods of dealing with them.

The rising costs of water supply and effluent disposal are forcing dyers to re-examine the possibilities of repeated use of dyebaths. Equations have been derived to show how electrolytes build up during repeated use of dyebaths. The initial recycle of a direct cotton dyebath can give the same quality as a conventional fresh-bath dying, but metal ion build-up may modify the shade of dyeings after multiple recycles. A simple screening test has been devised using over 50 direct and acid dyes to assess whether they are precipitated by a typical hard water concentration of calcium salts. Ten of the dyes proved sensitive; solubility product constants were determined for some of them.

Residual salt levels in exhaust dyebaths must be lowered on environmental grounds. Several direct and reactive dyes were evaluated to determine the minimum salt required for an acceptable yield. Most direct dyes exhaust well at 2-5 g/L salt but reactive dyes need at least 20 g/L. Dyeing at the lowest practicable liquor ratio should be an integral aim of efforts to minimize the salt content of dyehouse effluent. Residual sodium chloride or sulphate can be harmful to fresh water organisms. Less toxic and
more readily precipitable alternatives have been evaluated. Direct dyes applied with a patented organic salt of magnesium have given results equal to those obtained in the presence of sodium chloride.22.

Methods of measuring the colour of waste dye liquors have been reviewed. A survey found that reactive reds and sulphur blacks caused most difficulty in this regard, but direct dyes can be readily removed by adsorption or precipitation. Detailed investigation by cyclic voltammetry of the mechanism of reductive stripping of C.I. Direct Red 1(11), Red 79(12), Violet 47(13) and Violet 51(14) has revealed that complete reduction of both azo groups in each dye, even the copper complex Violet 47, was achieved in sodium dithionite solution at pH 9.5 and 25°C.

Details have been given of dithionite reduction tests carried out on the azostilbene C.I. Direct Yellow 4(15) and eight other anionic dyes. Adsorption capacities and rates of adsorption of these dyes on activated carbon have been determined.25 Studies of the carbon sorption of direct dyes from dyehouse wastes have demonstrated that the saturation adsorption increased with: (i) the relative molecular mass (rmm) of the dye, (ii) the electrolyte concentration in the waste water, and (iii) the integral pore volume of the carbon.

Cheap and readily available sorbents for dyes are of great interest for this purpose. Fly ash is a finely powdered waste from thermal power plants and is a rich source of silica, alumina, ferric oxide and other inorganics. The chemical composition of fly ash from various sources has been tabulated. The application of this material to remove colour from direct dye effluents is reported. Cellulose prepared from sugar cane bagasse pulp was reacted with acrylamide at
alkaline pH and the effects of treatment conditions on contents of N and COOH groups were examined. The uptake of C.I. Direct Red 79(12) was evaluated spectrophotometrically. A pilot plant has been developed recently at the Denkendorf Institute for decolourisation and partial recycling of dyehouse effluents. Three flocculants for direct dyes were examined:

- an amide-amine condensation product,
- a dicyandiamide-HCHO condensate and ammonium salts, and
- a mixture of a polyelectrolyte and aluminium chloride.

Recent evaluation of the macrocyclic ligand cucurbituril in powder form as a precipitant for direct dyes varying in molecular size, including C.I. Direct Red 79 (12; disazo), Red 80 (16; tetrazo) and Blue 71 (17; trisazo), established the influence of pH and ligand concentration on adsorption. Near-quantitative removal of dye is only possible by passing the effluent through a column filled with the cucurbituril. The effects of nonionic and anionic surfactants, as well as inorganic electrolytes, on the formation of insoluble complexes of the ligand with these dyes were examined. Anionic surfactants compete with direct dyes for the available cucurbituril. Most of the copper in direct dyeing effluents is from copper-complex dyes. Selective removal of dye from the liquor by this ligand eliminates almost all of the heavy metal contamination.

The reductive biodegradation of Congo Red (2) and eight monoazo dyes by a cell-free extract from Pseudomonas stutzeri was evaluated. Six of the dyes were appreciably degraded. The extract was quite specific for three of them (all N-substituted orthoaniline acid→amine dyes) with the lowest redox potential.

Catalytic oxidation is probably the simplest approach to decolourisation of residual direct dyes. Poly-p-phenylene-1,3,4-oxadiazole may be used to induce oxidative decomposition under UV irradiation. The influence of substituents in aryloazo H-acid dyes on the rate of oxidation in hydrogen peroxide solution has been studied. The dissociated form of the 2-hydroxyazo group undergoes degradation by perhydroxyl radicals (·OOH) that are formed. The mechanism of oxidation of sulphonated mono- and hydroxy-aryloazo dyes in sodium percarbonate solution at pH 10.6 was also examined. The initial rate and apparent activation energy of the reaction were determined. The quinone hydrzone form of such dyes is more susceptible to attack than the hydroxyazo tautomer.

Ozone treatment has potential as a powerful means of decolourising exhaust dyebaths for recycling. Large-scale trials on dyehouse effluents have established a relationship between colour removal, pH and ozone consumption. Fundamental studies of the ozonolysis mechanism have demonstrated that the azostilbene C1. Direct Yellow 12(18) yields mainly 4-carboxy-4'-ethoxyazobenzene-3-sulphonate (19) and hydrogen peroxide. The stability to ozone of 2-aryloazo-1-naphthol-3,6-disulphonates was investigated. Electron-withdrawing nitro or bulky perfluorobutyl substituents in the 2-aryl nucleus gave improved stability.
3 Developments in Physical Chemistry

The transfer of a direct dye from an aqueous electrolyte solution to the interior of a cellulose fibre is an essentially simple process, yet it continues to stimulate research on the mechanism involved. A comprehensive treatment of the sorption equilibrium must take account of the ionic composition of the solution phase and the morphological and surface characteristics of the substrate.

3.1 Generalized Donnan Equilibrium and the Gouy-Chapman Theory

A generalized affinity equation was developed by elaboration of the classical Donnan theory. This was extended to take account of the influence of multivalent ions on the equilibrium as well as the effect of alkaline pH conditions on the ionisation of hydroxy and carboxy groups in the cellulose substrate. These refinements lead to some fairly complex equations for the computation of affinity. A practical limitation to their use for predictive purposes is the need to determine by analysis the concentrations of all the ionic species present in both phases of the system. The content of ionisable groups and the volume of the internal aqueous phase of the fibre must be established, as well as the mm, basicity and purity of each dye present, including the nature of the ionisable impurities. Moreover, it has been pointed out that advances in defining the characteristics of the electrical double layer at the fibre surface have shown the Donnan distribution of ions between the internal and external phases to be incorrect.

According to the Gouy-Chapman theory, dyeing equilibria with direct dyes can be characterized with regard to three constants that are readily obtainable experimentally. These are the standard affinity ($A_0$) and two terms that define the electrostatic interaction between the dye and the dyed substrate. The term $A_1$ is related to the charge density on the substrate and $A_2$ is related to the specific surface accessible to dye anions. The ratio $A_1/A_2$ represents the state of charge at the inner surface, i.e. the charge concentration of the surface accessible to dye. Dyeings of various combinations of C.I. Direct Yellow 50(20), Red 81(21), Blue 15(22) or Blue 106(23) demonstrated that the interactions between component dyes can be quantified in a simple manner using this approach.

More recently, the merits of the Donnan theory and the Gouy-Chapman model have been compared. Both methods offer useful advantages and have some features in common, such as the representation of adsorption behaviour in terms of three parameters: affinity, fixed charge and internal volume in the Donnan treatment, or affinity, charge density and accessible surface in the Gouy-Chapman equations. Data for the copper-complex disazo C.I.
Direct Red 83(24) at various concentrations of Glauber's salt were used to illustrate the Gouy-Chapman approach.

### 3.2 Sorption and Accessibility of Cellulose Structure

Two direct dyes of markedly different molecular sizes are widely used in the red-green test to reveal different degrees of maturity in raw cotton: C.I. Direct Red 81(21; rmm 675) and Green 26(25; rmm 1350). Adsorption isotherms for both dyes on unmercerized cotton and viscose yarns were measured. Reciprocal plots suggested Langmuir-type sorption onto a limited number of sites and saturation values that were higher on viscose. Both dyes showed evidence of sorption as a monomolecular layer. The cotton yarn was subjected to controlled acid hydrolysis to leave a crystalline residue and dye sorption was again determined. As the time of hydrolysis increased, the sorption of Red 81 decreased, ultimately to approximately half that of the intact fibre. With Green 26, on the other hand, accessibility initially increased but later fell slowly to a level about double that of the control. Presumably, this internal increase is attributable to improved access of the bulky Green 26 molecules to previously inaccessible internal surfaces.

### 3.3 Influence of Electrolytes on Dye Sorption

In a study of the kinetics of direct dye uptake, cotton yarns were dyed continuously by a column chromatographic technique. The influence of control parameters on the initial rate of strike was examined. Relevant variables included dye type and concentration, electrolyte concentration and temperature. The trisazo C.I. Direct-Blue 71(17) was one of the dyes tested. The role of electrolytes in promoting exhaustion was examined in relation to dye structural features. Cotton was dyed with two direct dyes differing in rmm and degree of sulphonation in the presence of various electrolytes and a phosphate buffer. Under these conditions, the uni-divalent electrolytes, e.g. calcium chloride, were the most effective in boosting exhaustion, presumably by forming calcium dye sulphonate aggregates.

The effects of sodium chloride in direct dyeing have been interpreted using 5% ethanol as a disaggregating agent. The Nernst equation was used to describe adsorption equilibria for two disazo dyes derived from 4,4'-diaminodiphenylmethane and 4,4'-diaminostilbene-2,2'-disulphonic acid. A related study of the symmetrical disazo C.I. Direct Blue 1(26) demonstrated that ethanol exerted a disaggregating effect at low salt concentration, decreasing the saturation uptake of dye, but at high salt level the solvent favoured the electrostatic association of dye molecules via protonated amino and sulphonate groups with enhanced adsorption of the aggregated dye. The Langmuir equation was appropriate to describe the adsorption equilibrium.
the adsorption of the copper-complex disazo C.I. Direct Violet 66(27) by viscose have been investigated. The size of the cation is much more important than its valency. A linear relationship was found between dye saturation values in the presence of various ions and their ionic radii. The rate of sorption also increased with the size of the cation, particularly at lower temperatures.

Equilibrium isotherms and rates of uptake of the symmetrical disazo C.I. Direct Blue 1(26) on viscose were determined in the presence of electrolytes with predictably different capabilities to modify water structural characteristics. Saturation values at 45°C increased in the order: tetraethylammonium Cl < tetramethylammonium Cl < propylamine HCl < ethylamine HCl < NaCl < KCl < guanidinium Cl. These results clearly demonstrated that variations in water molecules clustering around the hydrophobic groups in dye molecules influence the dye-binding mechanism in cellulose. In the presence of alkali-metal chlorides the absorption of Blue 1 by viscose and dyeing rate at constant salt concentration both increased in the order: LiCl < NaCl < KCl. In binary mixtures of these electrolytes, the (larger) cation with the greater ability to disrupt clustering in water considerably enhanced the ability of the smaller cation to influence dye uptake. When another symmetrical disazo Congo Red(2), a dye that readily aggregates by electrostatic attraction between protonated amino and sulphonate groups, is applied to viscose in the presence of electrolytes capable of modifying the clustering of water molecules in a predictable manner, the adsorption and rate of dyeing are similar to those for much less aggregated anionic dyes. Thus, although Congo Red readily forms aggregates, the influence of electrolyte cations on water clustering around the dye ions is unaffected.

3.4 Influence of Organic Additives on Dye Sorption

Most inorganic salts enhance the uptake of direct dyes but the effects of organic additives are more difficult to predict. The influence of pH and various concentrations of auxiliaries on the dyeing of cotton with the disazo C.I. Direct Blue 67(28) and the tetrazo C.I. Direct Black 19(29) was examined by spectrophotometry of the dyebaths. Urea, pyridine and amyl acetate markedly increased exhaustion by
disaggregating the dyes, whereas gelatin and carboxymethylcellulose had a restraining effect by forming dye-agent aggregates. Strongly acidic liquors decreased uptake of dye, as did alkali above pH 8.5.

In aqueous media the phosphonic acid groups in the sequestering agent ethylenediaminetetramethylphosphonic acid (EDTMP; 30) are ionised and the N atoms exert a weakly basic effect. The presence of small amounts of EDTMP in the dyeing of cotton with the copper-complex disazo C.I. Direct Red 79(13) accelerated the rate of uptake and improved the fastness to washing. Similar effects were observed when the cotton was pretreated overnight with small amounts (~0.03 g/L) of the aminoacids alanine (31), valine (32), phenylalanine (33) and histidine (34). This was attributed to protonation of the amino group of the aminoacid which is hydrogen bonded to cellulose, facilitating uptake of the copper-complex anionic dye.

3.5 Pore Size and Diffusion Kinetics

A variable porosity model was adopted to describe the diffusion of the symmetrical disazo dyes C.I. Direct Yellow 12(18), Red 2(35), Blue 1(26) and Blue 15(22) in water-swollen cellophane at various ionic strengths. The validity of this model was tested by adsorption experiments. The discrepancies observed between apparent diffusivities obtained by sorption rate and steady-state methods were attributed to the concentration dependence of the diffusion process. The influence of the crosslinking of cellulose film using bis(hydroxyethyl)sulphone and dimethylethyleneurea on the diffusion behaviour of Yellow 12(18) was examined. Crosslinking reduced the steady-state diffusivity by almost twice the decrease in equilibrium adsorption. The diffusivities were calculated by the time-lag technique and from permeability measurements. The results were interpreted in terms of the pore model and the gel model for water-swollen cellulose. Diffusion rates of four direct dyes were measured in cellophane at various concentrations of dye and electrolyte. The apparent diffusion coefficient and another coefficient expressing diffusion of the free form of the dye, unrestricted by immobilisation effects, were derived. The free diffusion values were two or three orders of magnitude larger than the overall values.

The pore structure of cellulosic fibres is decisive for direct dyeing. It can be defined using probe molecules of specific graduated sizes, measurement being by either the stationary non-solute water method or by chromatographic elution on a cellulose column. The distribution of pores can be determined from chromatographic measurements, revealing the accessibility of the inner voids to dye molecules of different sizes. Pore structure data have been related to the adsorption and kinetics of the disazo dyes C.I. Direct Red 81(21) and Blue 1(26). The specific pore surface can be decisive for equilibrium uptake, whereas the porosity or the amount of free water can be important when interpreting differences in diffusion rate.

In a recent detailed study of the kinetics of direct dyeing from finite baths, curves of adsorption against
time formed the basis for determining sorption equilibria, specific rate constants, diffusion coefficients, resistance to diffusion, steady-state equilibria, adsorbent capacities, finite bath exhaustions, activation energies and interaction enthalpies. The kinetic constants were correlated with the number of aryl rings and ionisable sulphonyl groups in the direct dye molecules.

3.6 Influence of Energy Fields on Direct Dyeing

An interesting trend in recent years has been the application of certain novel energy systems to the dyeing process. Direct dyeing is particularly convenient for this because of its essential simplicity. By selecting dyeing conditions that give a slow rate of dyeing or only moderate exhaustion in the absence of the specific energy input, the positive influence of the treatment can be sensitively assessed.

The diffusion behaviour and affinity values of the symmetrical disazo dyes C.I. Direct Yellow 12(18), Red 2(35) and Blue 1(26) on cellophane under hydrostatic pressures up to 600 MPa have been measured and at 55°C. The uptake of Yellow 12 increased slightly but those of the other two dyes decreased considerably with increasing hydrostatic pressure. The central sulphonyl groups in the Yellow 12 molecule tend to inhibit aggregation, whereas Red 2 and Blue 1 aggregate much more readily. The small increase in affinity observed with Yellow 12 may indicate that cis-trans isomerisation is favoured as the pressure increases.

The effects of ultrasonic cavitation (the formation and violent collapse of microbubbles) on the dyeing of cotton fabrics with Yellow 12(18) and Blue 1(26) have been studied in detail. Ultrasonic waves heat the medium of propagation appreciably. The dyeing rate and equilibrium adsorption are both increased to an extent dependent on the cavitation intensity. Determination of the combined effects of ultrasound-induced heat and cavitation has shown that external heat requirements are much lower. Both cavitation and induced heat accelerate the dyeing rate but the effect of cavitation is dominant. In a recent study of three direct blue dyes on cotton, the influence of dye type, electrolyte concentration, temperature and ultrasonic intensity on dyeing kinetics was examined.

A direct dye solution was passed through a magnetic field and immediately used to dye cotton fabrics. The degree of exhaustion varied with the strength of the magnetic field, the temperature and the rate of flow of the dye solution. The relation between exhaustion and field strength was complex, which explained inconsistencies in previous work. The treatment was more effective at lower temperatures and higher flow rates, providing the flow was not turbulent. The effect of the magnetic pretreatment was lost after storage for about 6 h at ambient temperature.

Electrochemical activation of the aqueous medium allows the direct dyeing process to be accelerated and the equilibrium exhaustion increased. The effect of such activation on the state of aggregation of the dyes in solution has only recently been clarified. The electrochemical loading of the dyebaths required for optimum solubility characteristics of the dyes has been determined.

Applications of radio-frequency energy, γ-rays, ultrasonic waves, plasma and laser treatments in dying and finishing have been reviewed. Six disazo direct dyes were applied to cotton fabrics that had been irradiated for 4-8 h with γ-rays. Some dyeings were aftertreated with a cationic fixing agent. The irradiation resulted in enhanced uptake of dye, better fastness to washing and partial resistance to extraction with 50% aqueous dimethylformamide, perhaps as a result of covalent reaction of the dye with activated sites in the irradiated substrate. After treatment with the fixing agent, however, was a more effective method of improving wash fastness.

4 Effect of Preparation on Dyeing Behaviour

Cellulosic fibres require thorough preparation before dyeing and direct dyes are quite sensitive to differences in degree of penetration. There is a need for more selective and specific dyeing tests to be developed to reveal the effects of inadequately controlled preparation processes on these fibres.

4.1 Mercerisation and Liquid Ammonia Treatment

The relationship between fibre porosity and direct dye uptake was examined by pretreatment with NaOH solution or zinc chloride and measurement of pore size distribution and porosity. Substantial dye savings were demonstrated by treatment of cotton fabrics with 20% NaOH solution for 1 min at ambient temperature, followed by washing, neutralisation and dyeing with C.I. Direct Yellow 28, Red 81(21; disazo) or Blue 78(37; trisazo). The improved colour yield was attributed to increased dye uptake, the selective effect of fibre swelling and internal light scattering influenced by the change in total pore volume. Dyeings of the disazo dyes Red 81(21) and Blue 1(26) on bleached cotton fabrics that had been mercerised in various ways provided further evidence that the dye saving is related to the reduction in diffuse light scattering and depends on the pretreatment given. The reduced light scattering...
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(36)

(37)

(38)

occurs at the interface between the fibre secondary wall and the cell lumen.

Grey and mercerised samples of cotton were compared with viscose staple for steam sorption and water retention. Sorption measurements with sugars and dextrans of graduated sizes were used to determine changes in pore structure caused by mercerising. By correlating these results with the uptake of the symmetrical disazo C.I. Direct Blue 1(26) it was deduced that transition pores in the cellulosic fibres with a diameter of about 20-60 nm are responsible for dye sorption. Characteristics of the pore structure of cotton and viscose in the water-swollen state enabled new volume terms to be estimated for calculation of thermodynamic affinity. Substantivity parameters for Blue 1(26) on cotton under various conditions after hot mercerising at 60 and 90°C have been determined. The effects of alkali concentration and temperature, addition of surfactants, vacuum impregnation and the Thermox saturation process on the mercerising at 60° and 90°C have been determined. symmetrical disazo C.I. Direct Red 2(35) at 10:1 liquor ratio were investigated.

Warm mercerisation of grey cotton fabrics below 50°C resulted in little difference in absorption of the symmetrical disazo C.I. Direct Blue 1(22), although treatment at higher temperatures did produce a measurable increase. The relative effectiveness of hot and cold methods of mercerisation was assessed by tests of water retention, iodine absorption and dyeing trials using C.I. Direct Green 26(25) and C.I. Reactive Red 2.

Pretreatment with liquid ammonia is a highly effective and well controlled alternative to caustic soda mercerisation, but the high capital cost of the equipment necessary for recovery of the ammonia as well as the application step limits the adoption of this sophisticated process more widely. Bleached cotton fabrics treated in these two ways were examined for changes in morphology by X-ray analysis, fibre cross-section and measurements of the sorption of iodine, steam and C.I. Direct Blue 1(26). Marked differences between the two treatments were found and liquid ammonia swelling does not always yield a stable fibre structure. In later work, treatment with liquid ammonia and then caustic soda was compared to treatment with ammonia alone. The changes in fibre structure were again examined by X-ray analysis and sorption of the disazo dyes C.I. Direct Red 110(38) and Blue 1(26).

More recently, untreated and mercerised cotton were treated with liquid ammonia and then tested for absorbency, moisture regain and dyeability with the symmetrical disazo dyes C.I. Direct Red 2(35) and Blue 1(26). The dyeing properties of the mercerised cotton were adversely affected by subsequent liquid ammonia treatment. The more open structure achieved by mercerisation is evidently converted back to a more compact arrangement by ammonia, which apparently induces changes of fine structure, especially in the amorphous regions of the mercerised cotton.
An important area for liquid ammonia treatment is prior to crosslinking with cellulose reactant finishes. High-quality cotton shirting subjected to this pretreatment and then given a durable press finish shows good easy-care properties with only modest strength loss. Changes in morphology during this sequence have been evaluated with the direct dyes of markedly different molecular sizes (21 and 25) used in the red-green test for immature cotton (see Section 3.2).

4.2 Coverage of Immature Neps in Cotton Fabrics

Pale flecks in dyed cotton fabrics can be caused by immature or dead cotton. Clumps of immature fibres tend to exhibit poor dyeability and the flattening of such clumps may form small, highly reflective surfaces. Poor dye penetration may leave undyed spots if the clumps of loosely attached immature fibres change position after dyeing.

The dyeability of immature cotton can be improved by mercerisation but the lack of secondary cell wall development in dead cotton makes such treatment ineffective. Cotton fabrics containing both immature fibre neps and process neps composed of damaged mature fibres were given various mercerising treatments. After dyeing with ten direct dyes, fully mercerised fabrics showed 95% increase in visual coverage of neps, but coarsened fabrics showed only 85% increase. After liquid ammonia treatment, a significant improvement in nep coverage occurred with only five of the ten dyes. The differences between dyes in their behaviour towards nep coverage are most evident with those neps composed of immature fibres with some secondary wall development. Aggregation and migration properties of direct dyes appear to be related to nep coverage.

Careful dye selection is the best way to deal with the problem of dead cotton. Direct dyes containing more than one amino or amido group in their structure tend to achieve relatively good coverage of neps. The content of primary amino groups is not the only criterion, since carbonamido, sulphonamido and ureido are also powerful hydrogen bonding sites. More than 100 dyes of known structures were evaluated for coverage properties. The most effective dyes in each hue category were identified and correlations between structure and coverage ability were analyzed.

A test has been developed to distinguish between immature fibre neps and neps composed of thin mature fibres. Wets made from lint processed to form mechanical neps were dyed with C.I. Direct Red 81 (21), selected as yielding particularly poor coverage of immature cotton. Neps that showed contrast against the web background were identified as immature rather than thin mature fibres. This test was compared with other fibre-level evaluation procedures to identify cloth problems. Excellent correlation was found between undyable neps seen in dyed webs and in dyed cloth made from the same fibres. The web-nep test gave better prediction of cloth neps than direct instrumental measurements of average fibre quality, including micronaire, maturity and linear density.

It has been claimed that a pretreatment with chitosan (partially deacetylated poly-N-acetyl-D-glucosamine) on cotton containing immature fibre neps improves the coverage in subsequent dyeing with Indosol SF(S) dyes, as well as other direct and reactive dyes. More recently, the polyelethyleneimine auxiliary Polyamin P (BASF) was applied in a similar way. Both of these weakly cationic polymers can be used in conjunction with cellulose reactant finishes but the treatment may adversely affect the subsequent penetration and light fastness of direct or reactive dyes.

4.3 Diagnostic Dyeing Tests for Undyed Cellulose

Many latent faults in textile materials only become apparent during dyeing. The sensitivity of dyes to inherent variations in properties of an undyed substrate can be exploited in developing diagnostic dyeing or staining tests to define the nature and extent of such differences. A long established stain test is based on the violet colour formed by spotting iodine on cotton containing residual starch size. Durable violet scales produced with direct dyes, vat dyes or pigments can be used to quantify the degree of staining in the iodine test, which fades rather quickly on storage.

Two methods have been compared to assess the degree of wettability of enzyme-desinged cotton fabrics: The Tegewa Drop Test and a dyeing test using 10 g/L C.I. Direct Red 23 (39). Various singeing and steaming treatments have been applied to cotton
yarns, which were then dyed with selected dyes. The influence of these thermal treatments on the problem of streaky dyeings has been distinguished from other possible causes such as the presence of immature fibres.

Consistent dyeability in cotton fibres may be estimated using a specific concentration of the sensitive tetrazo dye C.I. Direct Green 27(40). After spectrophotometric measurements the results are expressed as % variation; shade variations less than 5% are too slight for visual perception. Critical mixtures of reactive dyes were applied to test yarns containing known dyeability variations. Typical direct dyes covering all chemical types were evaluated on the same yarns. Certain dyes, including the symmetrical disazo C.I. Direct Red 79(12), showed good correlation with the reactive mixture recipes.

Several dyeing tests are available to assess the degree of maturity within cotton samples and their response to alkaline treatments. A comprehensive series of tests for maturity has been reviewed in relation to dyeability response. The potential exploitation of maturity test data to control bulk dyeing has been assessed. The red-green test at the boil with two dyes differing widely in mm has already been mentioned (see Section 3.2). Ripe cotton is stained violet red and immature or dead cotton fibres show up as green.

Another sensitive test of this kind is based on a mixture of the monosulphonated C.I. Acid Red 151(41) and the tetrasulphonated C.I. Direct Blue 10(42). Untreated cotton is stained red but an increase in alkali concentration during mercerising or causticising results in progressively bluer staining. Fully mature cotton is stained dull violet but immature or dead cotton fibres appear as navy blue. In a recent study of the treatment of cotton with cellulase enzymes, the mixture of dyes 41 and 42 was used to follow the kinetics of swelling. Mercerised cotton is hydrolysed much more readily by cellulase enzymes than an unmercerised control. These changes were followed by monitoring the uptake of the trisazo tetrasulphonate C.I. Direct Blue 71(17) as well as tests of various physical properties.

5 Exhaust Dyeing with Direct Dyes

A comprehensive account of the mechanisms of dye exhaustion and levelling in batchwise conditions included valuable insight into the significance of electrolytes in direct dyeing. Direct dye adsorption isotherms were measured on cotton fabric forming the stationary phase in a liquid chromatography column. Frontal analysis gave similar results to standard equilibrium sorption techniques and yielded a reliable quantitative measure of dye compatibility. Experience of the controlled dosage of
salt in solid form in the dyeing of cotton yarn packages has been reported. The effects on levelness of the dosing technique, machine design and type of salt were elucidated. Electrical resistance measurements were used to estimate salt concentrations in the dyebath.

5.1 Influence of Surfactants on Direct Dyeing

Studies of the interaction between dyes and auxiliaries have stimulated much research but one of the attractions of direct dyes is that they can be dyed level simply by control of dyebath temperature and electrolyte addition. Complexes of direct dyes and polyvinylpyrrolidone are thermally stable and can be used for the fugitive tinting of wool or cellulosics but casein-dye complexes become unstable after a few days of storage.

The interaction between three direct dyes and a series of dodecylpolyoxyethylenes (penta to octa) was investigated by filter paper capillary analysis. The effects were dependent on dye structure, oxyethylene chain length and loss of water structure associated with the hydrophobic groups in dye and agent. The interaction between C.I. Direct Red 111 and several anionic, cationic and nonionic surfactants was examined by spectrophotometry. Anionic agents do not interact with fully solubilised dye molecules but a specific equilibrium is established with nonionic types. Cationic products interact strongly, resulting in neutralisation and further solubilisation. Spectrophotometry was also applied to the stoichiometry of interaction between two stearylamine polyoxyethylenes (11 and 22 EO units/mol) and the disazo dyes C.I. Direct Red 23(39) and Blue 2(43). Maximum dye uptake was observed at the highest molar ratio of dye to surfactant.

5.2 Interaction between Direct Dyes in Mixtures

An important practical objective of theories of dyeing has always been the reliable prediction of behaviour in mixtures from data assembled for individual members of a range of dyes. Sorption data for individual dyeings and binary mixtures of the disazo disulphonates C.I. Direct Yellow 12(18), Red 2(35), Red 81(21) and Blue 1(26) were analysed. A modified Langmuir equation accounted for positive and negative dye interactions on the fibre. Factors influencing selectivity in mixture recipes include:

- competition of dye anions for the available adsorbing surfaces,
- decrease in sorption of either dye anion because of increase in total concentration of sodium ions on the fibre,
- electrical repulsion of incoming dye anions by those of like charge already adsorbed,
- attraction of dye anions for one another on the adsorbing surface, and
- interaction between different dye anions in the dyebath.

Equilibrium sorption isotherms of three direct dyes and their binary and ternary mixtures were determined on cotton. Sorption of an individual dye from any mixture was invariably lower than sorption alone at any given dye and salt concentration. A recent detailed study involved the trichromatic combination of C.I. Direct Orange 46, Red 79(12) and Blue 71(17) on mercerised cotton yarn in the presence of a nonionic surfactant or a mixture of linear and cyclic dextrans. The initial strike and ultimate exhaustion values depended on the individual dyes, auxiliaries and the interactions between them. Six direct dyes of various types were applied in self shades and mixtures on cotton fabric. The effects of nonylphenolethoxylate and tridecylethoxylate surfactants on the kinetics of dyeing were also investigated.

5.3 Dyeing of Bast Fibres

Direct dyes are particularly useful for the dyeing of jute. The effects of dye and electrolyte concentrations, time and temperature on the uptake of such dyes by jute were studied. Selected products to achieve optimum fastness to light, washing and chemical treatments were recommended. The ability of various aftertreatments to improve these fastness properties and the resistance to photodegradation of jute dyed with direct dyes has been evaluated. The photostability was enhanced by aftertreatment with copper sulphate and potassium permanganate and the washing fastness by subsequent application of a cationic fixing agent. Dyes with peak wavelengths in the range 590-670 nm showed low light fastness on jute. So, the hues that
depend on dyes that absorb mainly below 560 nm are preferred.

The surface morphology of raw sisal fibres, as well as after alkaline or acid treatment and grafting with styrene and ethyl acrylate, was investigated by electron microscopy\textsuperscript{123}. Dyeability tests with C.I. Direct Green 1(44) and with blue disperse and basic dyes on the grafted fibres are reported. The common milkweed plant yields cellulosic fibres with interesting thermal insulation and absorption properties\textsuperscript{124}. Direct, disperse and basic dyes were evaluated to achieve satisfactory fastness ratings on milkweed fibres.

5.4 Dyeing of Regenerated Cellulosic Fibres

Comparisons of the structural characteristics of regenerated cellulosic fibres with the fine structure of cotton yield valuable insight into dyeability differences between them. Four high wet modulus modal fibres were compared with cotton and viscose for dyeability with typical direct dyes\textsuperscript{125}. The fibres varied in cross-section and in skin-core ratio. Cotton contains more ordered material inaccessible to direct dyes than do the regenerated fibres. Prima modal fibres showed higher exhaustion than viscose, but exhaustion values on the hollow fibre Viloft were intermediate between those on cotton and viscose.

Substantivity values for several Solar(S) direct dyes, including the symmetrical dyes C.I. Direct Yellow 28(36; monoazo disulphonate) and Red 80(16; tetrazo hexasulphonate), were determined on cotton, viscose and modal fibres. The sulphonated phthalocyanine Blue 199 was anomalous in showing much lower substantivity on the regenerated fibres, despite their larger accessible surface area\textsuperscript{126}. Increasing the electrolyte content of the dyebath brought the substrates closer in dye uptake. Analysis of these results in terms of the Gouy-Chapman theory (see Section 3.1) yielded an exceptionally high $A_2$ value (specific surface accessible to dye) for Blue 199, typical of an unusually large dye anion.

In another recent investigation\textsuperscript{127}, C.I. Direct Blue 1(26; disazo), Blue 86 (phthalocyanine) and Blue 106(23; triphenodioxazine) were applied to cotton, viscose, modal and carbamate-spun fibres. Initial strike and final exhaustion values were related to ultimate levelness. Factors with a bearing on dyeability were evaluated by scanning electron microscopy, porosity and crystallinity. Exhaustion values decreased in the order: viscose and carbamate-spun > high tenacity > modal and cotton. The structural characteristics, moisture sorption and swelling behaviour of viscose fibres have been discussed\textsuperscript{128} in the context of the dyeing and finishing of outerwear fabrics woven from filament yarns.

6 Continuous Dyeing with Direct Dyes

Direct dyes are much less suitable for continuous dyeing than for exhaust methods. Tailing and migration problems are encountered and prolonged diffusion is necessary in pad-batch methods. The pad-roll process is probably the most appropriate semi-continuous method for direct dyes at 80-100°C. Recommendations have been given\textsuperscript{129} for control of fabric moisture and pad liquor temperature, dye selection for optimum compatibility and the use of suitable auxiliaries. The pad-roll system is more versatile than steaming methods with direct dyes but the development of compact pad-steam ranges has enabled more valid cost comparisons to be reached against the semi-continuous alternatives\textsuperscript{130}.

Many water-soluble dyes show undesirable migration in continuous dyeing. In a recent work on this problem\textsuperscript{131}, mercerised cotton was pretreated with wetting agent and then padded with various direct dyes, including Red 81(21) and Blue 78(37). Factors identified as influential in this context include:

\begin{itemize}
  \item liquor retention and swelling of the substrate,
  \item dye substantivity and solubility during padding and drying,
  \item presence of electrolytes and migration inhibitors, and
  \item design of dryer and conditions of drying.
\end{itemize}

There is a tendency for migration of direct dyes to increase as substantivity decreases, but reactive dyes migrate less than this trend because of the immobilising effect of reaction with the substrate\textsuperscript{132}.\[\text{图}(44)\]
7 Activation of Cellulose to Enhance Dyeability

The status of cotton cellulose as a naturally occurring biodegradable polymer is in tune with the times but that does not mean that cellulose dyeing is free from environmental problems. Direct dyes have high inherent substantivity but they still need electrolyte addition to ensure high exhaustion in full depths. Reactive dyes are less substantive and thus need more salt. There has been a surge of interest recently\textsuperscript{133} in techniques to introduce cationic groups into cellulose, neutralising the negative charge on the fibre surface and boosting the substantivity of anionic dyes.

7.1 Cationic Epoxy or Azetidinium Reactants

There has been much activity in this area, many of the attempts to incorporate quaternary N sites in cellulose being dependent on epoxy derivatives. The first product of this type on the market\textsuperscript{134,135} was Glytac A (Protex; 45). This is readily available\textsuperscript{136} from epichlorohydrin and trimethylamine (Eq. 1).

Glytac reacts with cellulose via the glycidyl group at alkaline pH. Cellulose modified in this way can be dyed with acid dyes and shows enhanced uptake of direct or reactive dyes, although some early claims of improved wet fastness were exaggerated\textsuperscript{137,138}.

Reactive dyes can be applied at neutral pH without salt, conditions that are environmentally attractive. This behaviour has been attributed to predomination of the zwitterionic form of the Glytac side chain after alkaline fixation (Eq.2).

\[
\text{CH}_2\text{-CH}_2\text{Cl} + \text{N(CH}_3)_3 \rightarrow \text{CH}_2\text{-CH}_2\text{N}^+\text{CH}_3 \text{Cl}^- \quad \text{(45)}
\]

Thus, the anionic dye is absorbed on the quaternary N site and, if reactive, it is attacked by the nucleophilic ionised alcoholic group nearby\textsuperscript{139}.

A reagent exhibiting some features in common with Glytac is 1,1-dimethyl-3-hydroxyazetidinium chloride (DMAC)\textsuperscript{133,140}. It reacts with cellulose by a similar alkali-catalysed ring-opening etherification. The modified substrate contains mainly the zwitterionic form of a secondary amine analogue of Glytac (Eq.3).

The results from the two quaternised cellulose ethers are similar, but there is marginally better reactive dye fixation to the DMAC grouping.

An alternative approach\textsuperscript{141} to aminisation of cotton fabric involves padding with caustic soda solution, then immersion overnight in an acetone solution of epichlorohydrin and triethanolamine (mole ratio, 3:1). The etherifying agent is assumed to be mainly the reactive tertiary amine (46) formed by condensation between the starting materials (Eq.4).

7.2 Cationic N-Methylole Reactants

The N-methyloleation reaction that has been so important in traditional chemical finishing can be exploited as a first step to the aminisation of cellulose using N-methyloleacrylamide (NMA; 47) (Eq.5).

This acrylamidomethylated cellulose reacts readily with ammonia or alkylamines to yield cellulose derivatives\textsuperscript{3} containing amine or quaternary N groups (Eq.6).

\[
\begin{align*}
\text{CH}_2\text{-CH}_2\text{Cl} + \text{N(CH}_3)_3 & \rightarrow \text{CH}_2\text{-CH}_2\text{N}^+\text{CH}_3 \text{Cl}^- & \text{(45)} \\
\text{Cellulose-OH} + \text{NCH}_2\text{CHOH} & \rightarrow \text{Cellulose-OCH}_2\text{NHCOCH} = \text{CH}_2 & \text{(47)}
\end{align*}
\]

This acrylamidomethylated cellulose reacts readily with ammonia or alkylamines to yield cellulose derivatives\textsuperscript{3} containing amine or quaternary N groups (Eq.6).
Dyeing tests on these derivatives showed generally good colour yields and high fixation, but reactive dyes on those aminised with di- or trimethylamine gave poor fixation. The dye-fibre linkage is labile owing to the strongly electron-withdrawing quaternary group (eqs 7 & 8).

7.3 Cationic Active Halogen Reactants

Groups of the haloheterocyclic type found in traditional reactive dyes, such as aminochlorotriazine or difluoropyrimidine, have been exploited in aminising agents that also contain mono- or bis-quaternary N groups to boost the uptake of anionic dyes by the aminised substrate. Such agents react more readily with cellulose and show higher thermal stability than the ring-opening types such as Glytac or DMAC. Both classes of monofunctional reactive system, however, share the disadvantages of low substantivity for cellulose and must be applied by padding. More complex multifunctional structures were designed for exhaust application and these gave impressive colour yields. There are practical drawbacks to all these agents, however, including lower light fastness, hue changes and poor penetration into the fibre.

An alternative approach to the aminisation of cellulose involves esterification using chloropropionyl chloride (48) (eq. 9).

Chloropropionylated cellulose condenses readily at 50°C with ammonia or alkylamines to yield aminised cellulose derivatives (eq. 10).

If aminisation is carried out at the boil, however, chloroproplionic acid is eliminated and the cellulose derivatives do not contain ester groups. The ester bond is still intact after reactive dyeing but it is hydrolysed during alkaline soaping at the boil (eqs 11 & 12).

7.4 Polymeric Cationic Reactants

Many cationic polymers have been applied to cellulose with a view to enhancing uptake of anionic dyes. It is considerably more difficult in those instances to interpret the precise mechanisms involved, apart from the obvious participation of electrostatic interaction between dye anions and basic groups in the polymer. Recent studies have included the application to cotton of the polyamide-epichlorhydrin resin Hercosett 125 (Hercules), originally marketed as a shrink-resist treatment for wool. The essential objective was the absorption and fixation of reactive dyes at neutral pH.
in the absence of salt. Improved dyeability and good wet fastness were obtained, but dullness of hue and impaired light fastness were disadvantages.

Incorporation of thiourea into the Hercosett polymer during application was intended to overcome deficiencies when using low-reactivity dyes on Hercosett alone. Thiourea reacts with azetidinium groups in the resin to form isothiouronium groups (Eq. 13).

These are more strongly nucleophilic and improve the fixation of low-reactivity dyes. Some of the isothiouronium groups decompose during dyeing to yield thiol groups, which form further sites for dye fixation and may also react with remaining azetidinium groups to form thioether crosslinks in the resin (Eqs 14 & 15).

Differences in colour yield were still observed between dyes of high and low reactivity and therefore ethylenediamine was evaluated as an additive to the Hercosett resin. This reacts readily with azetidinium groups to form primary, secondary and tertiary amino sites for fixation of reactive dyes (Eq. 16).

Enhanced substantivity for direct and reactive dyes, good brightness and excellent fastness to washing were achieved but the light fastness was still impaired in most cases.

Epichlorohydrin can be polymerised using the ring-opening catalyst boron trifluoride etherate (BF₃·OEt₂) in carbon tetrachloride. Quaternised derivatives of polyepichlorohydrin (PECH) were prepared by reaction with dimethylamine (Eq. 17).

Cotton was treated with polymers of this kind and dyed with C.I. Direct Orange 39 (azostilbene), Blue 78 (trisazo tetrasulphonate) and Blue 86 (sulphonated phthalocyanine). Residual chloromethyl groups in the PECH derivative are capable of reacting with cellulose under alkaline conditions. The higher the rmm of the polymer, the higher the direct dye exhaustion as a result of complex formation. Colour yield on the treated cotton in 2 g/L NaCl solution is higher than on an untreated control at 25 g/L NaCl concentration. Perspiration fastness is excellent but fastness to washing is not improved. Reactive dyes show high fixation on the treated cotton even when dyed without salt or alkali.

7.5 Simultaneous Application of Reactants and Nucleophilic Dyes

A relatively uncontrolled attempt to enhance the colour yield and wash fastness of selected direct dyes involved addition to the dye bath of a colourless reactant that would react with nucleophilic groups in
the dyes and hydroxy groups in cellulose. Most of the dyes selected\textsuperscript{13-15} contained at least two primary amino groups in aminonaphthol residues, as in C.I. Direct Red 2(35), Red 28(2) and Blue 2(43). The reactants evaluated were cyanuric chloride (49), 1,1-diethyl-3-hydroxyazetidinium chloride (DEAC; 50), and 2,4-dichloro-6-(4'-sulphoanilino)-s-triazine (51), which will indeed react readily with primary arylamines. Some of the dyes selected, however, contained only salicylic acid residues, as in C.I. Direct Brown 2(3), or diphenylurea components, as in Yellow 50(20), and these are most unlikely to react efficiently under dyeing conditions.

In a later development\textsuperscript{140,150}, cyanuric chloride was proposed as an aftertreatment of cotton already dyed with amino-containing direct dyes. This approach appears even less likely to succeed than in situ addition to the dyebath. Serious hazards are associated with the handling of cyanuric chloride under these conditions. Dye-agent reaction will be inefficient because of hydrolytic deactivation of these reactants and uptake of cyanuric chloride (or its hydrolysis products) will be poor on the pre-dyed substrate.

7.6 Introduction of Activated Sites for Nucleophilic Dyes

This is a much more controlled approach to the concept of incorporating the reactive function into the substrate and carrying out a reactive dyeing with a 'non-reactive' dye containing nucleophilic groups\textsuperscript{11}. A model dye of this kind was prepared by reacting the aminochlorotriazine dye C.I. Reactive Red 58 with ethylenediamine to form a 2-aminoethylamino-triazine derivative (Eq. 18).

Acrylamidomethylated cellulose prepared by condensation of N-methylolacrylamide with cotton cellulose (see Section 7.2) reacts readily with nucleophilic dyes of this kind which show no hydrolysis during dyeing. High fixation is achieved either by exhaustion at pH 10.5 in 80 g.L salt solution or by pad-batch at the same pH for 24 h (ref.139). These aminoalkyl dyes show zwitterionic characteristics below pH 8 and this lowers the nucleophilicity of the primary amino group (Eq. 19).

Nucleophilic dyes containing thiol groups would be more reactive than aminoalkyl analogues but there would be problems of toxicity, odour and a tendency to oxidise to disulphide. Aminoaryl and hydroxyalkyl analogues would be less reactive than these aminoalkyl derivatives.

The novel reactant 2,4-dichloro-6-(2'-pyridinoethylamino)-s-triazine (DCPEAT; 52) was evaluated\textsuperscript{151} as a means of activating cellulose by pad-batch application at pH 8.5 for 24 h. After a cold water wash, the modified substrate was dyed with aminoalkyl dyes prepared by reacting C.I. Reactive Red 58 (monofunctional) and the bistaminochlorotriazine) Red 120 with ethylenediamine. Both dyes.
especially the latter, gave high fixation by exhaust dyeing at pH 9 without salt.

Nucleophilic aminoalkyl dyes can also be fixed on either cotton or nylon that have been pretreated with the trifunctional reactant 2-chloro-4,6-bis(4'-sulphatoethylsulphonylanilino)-1,3,5-triazine (53).

Developments in this area seem to be leading to daunting complexity rather than elegant simplicity. Certain aspects of this concept inspire unease rather than confidence:
• the risk of premature hydrolysis leading to impaired fixation has been transferred from the dye to the substrate,
• the pretreatment with a colourless reactant necessary to activate the substrate must be exceptionally uniform if dye fixation is to be consistent,
• if penetration of the reactant is poor (more likely the higher the room), ring dyeing will follow and the fastness properties will be adversely affected,
• only the aminoalkyl dyes will react with the activated substrate and other classes of dyes for unmodified cellulose may be inapplicable, and
• cost implications give concern because both dye and substrate must be specially modified before the desired reaction can occur.

8 Cationic Aftertreatment of Direct Dyeings
The aftertreatment of direct dyeings to improve their fastness performance has been a perennial objective of research in this field.

8.1 Conventional Aftertreatments
Recent developments in this area have not been spectacular. Five direct dyes on cotton were aftertreated with a cationic fixing agent. Addition of formic or acetic acid surprisingly impaired the effectiveness of the agent. Efficiency indices have been devised to assist users of fixing agents to evaluate their cost-effectiveness in improving wet fastness, as well as adverse effects on shade and light fastness. Fastness to wet rubbing can be a serious problem in full depths of direct dyes aftertreated, with a cationic agent. Mechanical destruction of the dyed fibres produces microscopically small fragments that stain the adjacent white fabric. Six proprietary aftertreatments marketed for cotton dyed under domestic conditions have been evaluated with C.I. Direct Red 81(21). None of the agents was satisfactory and colour loss was increased in some instances. Chitosan (see Section 4.2) has been applied to dyed viscose, cupro and polyacrylic fabrics by a pad-rinse technique. There was a marked increase in fabric stiffness and lower moisture absorbency. Effects on fastness of reactives were negligible but fastness of direct dyes to wet treatments was impaired.

8.2 Reactant-fixable Direct Dyes
Probably the most significant development in direct dyes during the 1980s was the introduction of the Indosol SF(S) dyes and fixing agents. The original range of twelve dyes, C.I. Direct Violet 66(27) being a typical member, were all copper-complex types selected for good light fastness when aftertreated. The patent literature revealed that Indosol CR was a mixture of three components designed for simultaneous crosslinking and dye fixation. The components were:
• a polybasic condensate of diethylenetriamine and an amide, e.g. cyanamide, dicyandiamide, guanidine or biguanide,
• an N-methylol precondensate of the dicyandiamide-formaldehyde type, and
• an acid catalyst, e.g. lactic acid.

The polybasic condensate was later marketed alone as Indosol E-50 for the exhaust aftertreatment of Indosol dyeings. This agent does not confer any improvement in crease recovery.

Compared with reactive dyes, Indosols offered savings in dyes, chemicals, water and process time. Treatment with Indosol CR eliminated the need for any subsequent resin finishing. Partial replacement of Indosol CR by dimethyldihydroxyethyleneurea (DMDHEU) offered a further saving, but this was accompanied by higher formaldehyde release.
Trends in washing and laundering practice were shown to be favourable for the Indosol system\textsuperscript{162}. The original Indosol SF range was strong in blues and greys but somewhat deficient in the yellow to violet sector. Novel reactive yellow and red dyes were later added, blurring the distinction between the reactive and reactant-fixable classes. A third type of aftertreatment agent was introduced to give even better fastness to washing. Indosol E-F forms a similar dye-agent complex to that produced by Indosol E-50, but it is held more securely by virtue of covalent bonds between agent and fibre\textsuperscript{163} that resemble those formed in conventional reactive dyeing.

9 Interaction between Crosslinking Finishes and Direct Dyes

The influence of DMDHEU on cotton dyed with several classes of dyes, including direct dyes, has been studied\textsuperscript{164}. Dye structure, inorganic catalyst type and curing conditions were taken into account. Differences in colour yield, fixation, light fastness and crosslinking were interpreted in terms of the extent of interaction between fibre, dye and finish. The formaldehyde-induced discolouration of twice-coupled H-acid dyes, i.e. those containing a 1-amino-2,7-bis(phenylazo)-8-naphthol grouping, by N-methylol reactants was investigated recently\textsuperscript{165}. Electrophilic attack at the amino group by the +CH\_2\_OH cation initiates the hue change. Bulky and/or electron-withdrawing groups close to the 1-amino position have a retarding effect.

9.1 Simultaneous Dyeing and Finishing

An obvious way to minimize processing costs in dyeing and finishing is to operate two stages simultaneously rather than in sequence. Unfortunately, the moist/wet alkaline fixation that is necessary for most cellulose dye classes (reactive, sulphur, vat, azoic coupling) is highly incompatible with dry curing of a cellulose reactant finish in the presence of a latent acid catalyst. Direct dyes, on the other hand, do not need alkali addition and they benefit greatly from the improved wet fastness conferred by a crosslinked finish.

Cotton fabrics were padded with acid, direct or disperse dyes, resin and ammonium chloride, dried and cured at 160°C. In general, increasing the number of nucleophilic groups in the dye molecule gave higher colour yield within each dye class, but resin was also significant. Fastness to rubbing and perspiration was good but light fastness varied widely, depending on dye structure and resin type\textsuperscript{166}. C.I. Direct Orange 61 (azostilbene), Red 80 (16; tetracosulphonate) or Red 81 (21; disazo disulphonate) was applied to cotton simultaneously with DMDHEU and a catalyst. Colour yield increased with curing temperature and the deepest dyeings were achieved using ammonium persulphate as catalyst\textsuperscript{167}.

The phthalocyanine C.I. Direct Blue 86 was applied with DMDHEU and magnesium chloride on untreated, alkali-treated and diethylaminoethylated cotton fabrics. The substrate containing cationic dyeing sites invariably showed the highest colour yield and crease recovery, irrespective of the DMDHEU concentration and curing conditions\textsuperscript{168}. Bleached viscose fabrics were padded with various direct dyes, including C.I. Direct Red 79(12; disazo tetrasulphonate) and Red 81(21; disazo disulphonate), N-methylol reactant and inorganic catalyst, dried and cured under various conditions\textsuperscript{169}. The extent of crosslinking and interaction with the dyes depended on the reactant and catalyst combination, as well as curing conditions.

9.2 Dyeing after N-Methylol Crosslinking

The reorganization by retailers of fashion garments in recent years to bring their garment orders closer in line with customer demands in terms of colour and style has resulted in a revival of interest in dyeing after making-up as garments. If a resin finish is required to provide easy-care performance, however, this is normally only feasible as a continuous treatment of the fabric before garment manufacture. Accordingly, there has been a great deal of interest in the garment dyeing of cotton that has already been crosslinked and is therefore difficult to dye conventionally. Nevertheless, it is possible to achieve a neat durable press look after garment dyeing of cotton twill or corduroy, for example, by soaking the dyed garments in a resin formulation, vacuum extraction, tumble drying, pressing and oven curing\textsuperscript{170}.

If trimethylolmelamine (54) is used to crosslink cotton, remarkably enhanced affinity for direct dyes without salt is observed\textsuperscript{171}. There is much less wastage of dye in the effluent than from salt-assisted dyings on conventionally finished fabrics. Diformaldeydr reactants varying in chain length between the aldehyde groups were used to crosslink cotton. Sorption curves for direct dyes demonstrated how the type and extent of crosslinking reduced the rate constants, diffusion coefficients and equilibrium adsorption of all the dyes tested\textsuperscript{172}.

A compromise approach to the problem of lower dyeability is to partially hydrolyse the resin finish. Thus, aftertreatment of a urea-formaldehyde finish with 5% acetic acid solution at 60°C improves dye uptake with sacrifice of some crease recovery.
Bleached cotton crosslinked with dimethylethyleneurea (DMEU), DMDHEU, methylated DMDHEU or dimethyloisopropyl carbamate (55) was subjected to partial hydrolysis in various ways (liquid ammonia, NaOH mercerisation, acetic acid, urea-phosphate). All gave some improvement in dyeability with the disazo disulphonate C.I. Direct Red 81 (21).

Cotton fabrics crosslinked with formaldehyde, DMEU or DMDHEU were dyed with C.I. Direct Red 81 (21; disazo disulphonate) or Blue 78 (37; trisazo tetrasulphonate). Dye uptake depended on whether the cotton had been mercerised, the type of crosslinking agent and the dye structure, as well as curing and dyeing conditions. In general, sorption of the larger Blue 78 was favoured by formaldehyde-treated cellulose, whereas sorption by the fibres crosslinked with DMEU or DMDHEU was greater for the smaller Red 81. The pore structure of cotton crosslinked with DMDHEU or 4,5-dihydroxy-1,3-dimethylimidazolidone (DHDMI; 56) was investigated using reverse gel permeation chromatography. The results were interpreted in terms of the reactivity of these substrates towards Red 81 (21). Although crosslinking reduced accessibility, samples reacted with DHDMI retained substantially more accessible internal volume across the entire range of pore sizes. Post-mercerisation of DHDMI-treated cotton before dyeing confers a further improvement. Direct dyes of high RmM that normally give poor yields are strongly absorbed. Such dyeings on the post-mercerised finish are substantially deeper than on an untreated but mercerised control. Yields are best at pH 8 because acidic dyebaths cause partial stripping of the DHDMI finish.

Much more progress has been made by incorporating a cationic modifier into the resin finish formulation. Thus, trimethylolacetyleneurein (TACD; 57), choline chloride (58) and a catalyst were applied to mercerised cotton and cured in the usual way. Tests with the symmetrical disazo C.I. Direct Blue 1 (26) and a reactive dye demonstrated that this route provided an easy-care finish that could be readily dyed in full depths after crosslinking.

Mono-, di- and tri-ethanolamines were compared as additives for a DMDHEU finish on cotton. Triethanolamine was the most effective in enhancing dyeability, giving results approximately equivalent to direct and reactive dyes on the untreated fibre. The DMDHEU reacts with the OH groups in the alkanolamine and the N atoms in the latter provide sites for dye sorption. Various salts of triethanolamine with organic and inorganic acids were compared as additives to the DMDHEU finish. The dyeing characteristics of cotton crosslinked with DMDHEU in the presence and absence of triethanolamine were compared with those of mercerised and unmercerised controls. Crosslinking decreased all the dyeing kinetic constants but incorporation of the alkanolamine reversed these effects and enhanced dyeability.

The inclusion of an alkylene glycol or polyethylene glycol in a DMDHEU formulation that already contains a cationic modifier such as choline chloride or triethanolamine greatly improves the dyeability, even with direct dyes of high RmM in full depths. Cotton fabrics were given durable press finishes formulated in this way and then dyed with C.I. Direct Red 79 (12; disazo tetrasulphonate), Red 80 (16; tetaazo hexasulphonate) and other direct and acid dyes. Cross-sectional microscopy confirmed good penetration and distribution of all the dyes applied. Two carbamoylethylamine adducts,
prepared by reaction of acrylamide with diethylamino or diethanolamine, were evaluated\textsuperscript{176} as cationic modifiers with DMDHEU. In this case, the DMDHEU reacts with the amide grouping and the alkylamino centre becomes the site for dye adsorption.

9.3 Dyeing after Polycarboxylic Acid Crosslinking

The N-methylolated cyclic amines, notably DMDHEU, have dominated chemical finishing since the 1950s but the hazards associated with release of loosely bound formaldehyde from the finished fabric stimulated a search in the 1980s for crosslinking reagents that are incapable of yielding formaldehyde as a product of decomposition. One of these is the cyclic urea derivative DHDMI (56), which condenses with cellulose via the 4,5-dihydroxy groups. This was followed by an entirely new class of formaldehyde-free crosslinking reagents, the polycarboxylic acids\textsuperscript{182,183}. Cellulose is readily esterified with polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA; 59), 1,2,3-propanetricarboxylic acid (PTA; 60), citric acid (61) and succinic acid (62). Acidic salts of phosphorus oxoacids are the preferred catalysts\textsuperscript{184,185}, their effectiveness decreasing in the order: \( \text{NaH}_{2}\text{PO}_{4} > \text{Na}_{2}\text{HPO}_{4} > \text{Na}_{3}\text{PO}_{4} \). The catalyst has a buffering effect that minimizes the acidic hydrolysis of cellulose. Polycarboxylic acids are of considerable interest as crosslinking reagents for formaldehyde-free durable press finishing, giving excellent appearance and high strength retention. Dyeing trials were carried out using C.I. Direct Red 79 (12; symmetrical disazo tetrapsulphonate), Red 80 (16; symmetrical tetra hexapsulphonate) and Red 81 (21; asymmetrical disazo disulphonate) to assess the degree of crosslinking\textsuperscript{186}.

Thermally analytical techniques have revealed\textsuperscript{182,187} that the esterification proceeds by initial formation of cyclic anhydrides (e.g. 63) as the actual esterifying agents (Eq.20).

The hypophosphite catalyst is believed to promote the rate of anhydride formation, as well as accelerating the esterification of cellulose OH groups by the anhydride. In the case of citric acid, there is a risk of yellowing as the dehydrating conditions\textsuperscript{188} may result in the formation of aconitic acid (64) and its anhydride (Eq.21).

As in the case of DMDHEU, incorporation of a cationic modifier considerably enhances dyeability. Mercerised cotton fabrics were crosslinked by padding with BTCA (59), sodium hypophosphite and various additives\textsuperscript{189}: mono-, di- and tri-ethanolamines, tris(hydroxymethyl)aminomethane (65), their hydrochlorides, and the quaternary compound 2-hydroxethyltrimethylammonium chloride (66). Acid, basic, reactive and several direct dyes, including C.I. Direct Red 80(16) and Red 81(21), were applied at pH 3 to evaluate the relative effectiveness of the cationic modifiers. Triethanolamine proved particularly suitable for this purpose because it contains three hydroxyethyl groups per molecule. In a similar evaluation\textsuperscript{190}, triethanolamine compared favoura-
bly with N-methyldiethanolamine (MDEA; 67). The BTCA anhydride reacts with the OH group(s) in the N-hydroxyethyl compound, hence incorporating N atoms to provide dyeable sites in the finished fabric. The use of these additives also gives improved durable press performance, allowing a decrease in the amounts of BTCA and hypophosphite catalyst required.

The dyeing properties of cotton finished with citric acid (61) and a series of N-hydroxyethyl additives were investigated using acid, reactive and direct dyes. The most effective cationic modifiers were triethanolamine hydrochloride and tetrakis(2-hydroxyethyl)ammonium chloride (THEAC; 68). The presence of these additives has an inhibiting effect on the dehydration of citric acid to aconitic acid (64), thus giving improved brightness of pastel shades.

The inclusion of an alkylene glycol or polyethylene glycol in a BTCA or citric acid formulation containing an N-hydroxyethyl modifier markedly enhances the dyeability, even with direct dyes of high rmn.

Recent research has revealed that unsaturated dicarboxylic acids, such as maleic (69; cis), fumaric (69; trans) and itaconic (70), can be used as crosslinking reactants instead of the saturated acids, provided a free radical initiator (e.g. sodium persulphate) is included as well as the esterification catalyst (e.g. sodium hypophosphite). Alternatively, mono- or di-sodium salts of these unsaturated acids are themselves effective catalysts for the BTCA (59) esterification of cellulose. FTIR and FT-Raman analyses revealed that these salts do not form part of the esterification complex. Likewise, the sodium salts of certain hydroxyacids were found to be useful catalysts of the BTCA reaction. Sodium salts of citric acid (61) gave BTCA-finished fabrics with the best durable press ratings.

Certain N-containing heterocyclic compounds have been shown to accelerate the crosslinking of cellulose with BTCA. Imidazole and its 2-alkyl derivatives were evaluated in BTCA formulations for their effects on hue changes of direct dyes. It was concluded that these compounds can be used as catalysts instead of sodium hypophosphite in durable press finishes based on BTCA. Another interesting possibility is to use sodium bromide as a co-catalyst for BTCA esterification. As much as 75% of the sodium hypophosphite can be replaced by the bromide without significant loss of effectiveness.

A recent comprehensive comparison of BTCA and citric acid finishes, incorporating several types of cationic modifier, hypophosphite catalyst and polyethylene glycol to boost the effect of the modifier, demonstrated the importance of pH control in the subsequent dyeing stage. The cationic modifiers were: triethanolamine hydrochloride, MDEA (67) hydrochloride, choline chloride (58), THEAC (68) and bis(2-hydroxyethyl)dimethylammonium chloride (BHEDMAC). Acid, reactive and several direct dyes, including C.I. Direct Red 80 (16; symmetrical tetrazo hexasulphonate) and Red 81 (21; asymmetrical disazo disulphonate), were applied at various pH. Finishes based on DMDHEU, magnesium chloride catalyst and the same series of cationic modifiers were included as controls.

The citric acid finishes were inferior to those based on BTCA or DMDHEU for durable press rating and dyeability. With the alkanolamine hydrochloride additives, BTCA gave higher N content and dyeability than the corresponding citric acid finish, presumably because BTCA anhydride (63) reacts more readily with OH group(s) in the N-hydroxyethyl compound and in cellulose. With either polycarboxylic acid, triethanolamine (three HOEt groups) boosted the dyeability and N content more...
effectively than MDEA (only two). Agents with quaternary N atoms, viz. choline chloride, THEAC and BHEDMAC, conferred higher fastness to washing than the tertiary amine hydrochloride. Satisfactory washing fastness of BTCA-treated cotton is attainable for a wider range of dyes than on cotton treated with citric acid. DMDHEU finishes, however, yield better wash fastness ratings than those based on either of the polycarboxylic acids.

Control of dyebath pH is particularly important when dyeing on fabrics finished with a polycarboxylic acid and an N-hydroxyethyl additive. For example, dyeings of C.I. Direct Red 81(21) on BTCA with BHEDMAC, choline chloride (58) or triethanolamine hydrochloride gave Kubelka-Munk K/S values of 15-20 at pH 3 but only 5-7 at pH 4.7. Finishes based on DMDHEU and choline chloride show optimum uptake when dyed at pH 4-5. With a polycarboxylic acid and an alkanolamine hydrochloride, however, the carboxy groups should be undissociated to minimize repulsion of direct dye anions and the tertiary amine N atoms should be protonated to attract them, thus, optimum dyeability is found below pH 3.5.

10 Direct Dyes on Non-Cellulosic Substrates

Direct dyes are designed for efficient absorption by any of the cellulosic fibres. Their anionic character, however, also imparts good affinity for wool, silk, nylon and leather. Reviews of the bleaching and colouration of silk usually include recommendations for exhaust dyeing with direct dyes. Natural silk warp yarns can be dyed continuously by incorporating direct or reactive dyes in the size bath. Redox systems (peroxide/glucose or persulphate-glucose) have been incorporated in dyebaths of the disazo-disulphonates C.I. Direct Yellow 12(18) and Red 23(39) for dyeing silk at various temperatures. Colour yields depended on the substrate, dye and redox system. Fastness to washing was good and strength losses insignificant in a recent work on the dyeability of silk fabrics given a BTCA-crosslinked durable press finish. C.I. Direct Red 81(21) as well as acid and basic dyes were used to evaluate the effects of the polycarboxylic acid and N-hydroxyethyl modifier on dyeing behaviour.

Acid, direct and reactive dyes showed good exhaustion at 30°C on silk and at 50°C on nylon when dyed from a glyoxal/peroxide redox system. In similar studies, nylon and wool were dyed with direct dyes, including C.I. Direct Red 79(12), Red 81(21) and Blue 67(28), in the presence of ammonium persulphate alone and together with various reducing agents. The influence of the reducing agent on the enhancement of colour yield increased in the order: sodium thiosulphate < potassium pyrosulphate < thiourea < glucose. The initial strike on nylon was extremely rapid, 80°C being the optimum dyeing temperature on this fibre, but colour yield on wool increased progressively from 50°C to 90°C. The exhaustion of selected direct dyes on nylon at 70-90°C could be accelerated markedly by addition of benzyl chloride to the dyebaths. Radiation grafting of nylon with acrylonitrile and styrene was assessed using C.I. Direct Orange 115 and other dyes at various levels of polymer add-on.

Direct dyes are widely used on chrome-tanned leathers but they give generally poor yields on vegetable-tanned material. Penetration is normally low but C.I. Direct Blue 2(43) and certain copper-complex dyes will give dyed-through effects. When combined with toning dyes of more penetrating character, the conventional low-penetration direct dyes impart good surface colour yield at moderate cost. The effects of fatliquoring on direct dyeings were reviewed recently. The type, colour and concentration of dyes present are all relevant. Direct dyes of high mmr and extensive hydrogen-bonding potential tend to produce a firmer leather than does a simple monosulphonated acid dye. Raising the dye concentration for through-dyed leathers demands a higher salt concentration with adverse effects on emulsion stability, depending on whether the fatliquor is sulphated, sulphited, cationic or nonionic.

Typical leather dyes, such as the trisazo-tetrasulphonate C.I. Direct Blue 78(37), possess good water solubility and satisfactory fastness to migration. Poor migration is often attributed to coloured impurities. Metal-complex dyes have good wet fastness but only moderate fastness to migration. The latter is usually adequate if two or more sulpho groups are present but the fastness to perspiration may be lower. Cationic aftertreatment usually provides a marked and lasting improvement in perspiration fastness. The need for careful dye selection to minimize metamerism in shade matching and to achieve adequate fastness to light, perspiration, migration and dry cleaning has been highlighted in relation to demands for improved performance on car upholstery leathers.

11 Definitions Required

Traditionally, direct dyes (as the name implies) are absorbed and retained within the cellulosic substrate by operation of the forces of substantivity alone, without the formation of covalent dye-fibre bonds. Reactive dyes (again implicit in the name) are fundamentally dependent on covalent dye-fibre
bond formation. But what of the reactant-fixable dyes (Section 8.2)? Originally, these were renamed direct dyes that had to be linked to the fibre by means of an agent designed for the purpose. Moreover, the initial range has been supplemented with selected reactive dyes in order to attain a full gamut of brighter hues. Are reactant-fixable dyes direct or reactive?

Conventional reactive dyeing processes on cellulose involve a nucleophilic attack by ionised OH groups of cellulose on an active centre in the reactive dye molecule, such as a polarised carbon-halogen bond or a vinyl group. Recent research on the incorporation of such active centres in cellulose and the use on these modified fibres of substantive dyes containing nucleophile primary amino groups is reported (Section 7.6). Many conventional direct dyes contain groups of this kind. Are the new nucleophile dyes direct or reactive?

In the last few years, much research effort has been devoted to the problem of overcoming the poor dyeability of garments made from cotton fabric that has already been given a durable press treatment. The best solution so far is to incorporate in the latter a tertiary amine or quaternary salt containing N-hydroxyethyl groups that enable it to react with the crosslinking agent (Sections 9.2 and 9.3). What should we call this combination of cellulose reactant and cationic modifier? The term 'pretreating finish' or 'finishing pretreatment' is an oxymoron. We need a better description of a process that achieves effective crosslinking and durable press performance while avoiding the serious loss of accessibility to dyes that normally accompanies resin finishing. Perhaps 'substantive crosslinking' would serve to distinguish the new process from traditional chemical finishing and signal that it is intended to precede substantive dyeing.

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