DYES, REACTIVE

1. Introduction

The concept of producing a dye-fiber covalent bond to achieve dyeings of very high wet-fastness has been around since the pioneering work of Cross and Bevan (1). Most of the earlier studies were directed at producing a covalently bonded color on cellulosic fiber substrates; the impetus clearly came from the only modest wet-fastness performance of dyeings produced with direct dyes on cotton and viscose. However, significant early developments also took place in the field of covalently attaching dye chromophores to wool but there was always much less urgency since wool fibers could be dyed to reasonably high fastness standards using chrome mordant dyes.

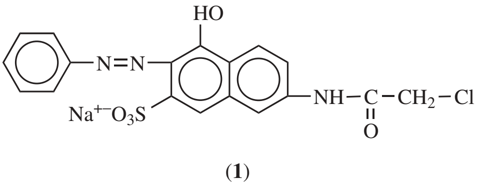
Cross and Bevan (1) had a clear idea of the above requirement to improve the wet-fastness properties of cellulosic fibers by covalently bonding chromophores; they pretreated cotton with benzoyl chloride, nitrated the benzoyl ester, reduced the nitro group to an amine and diazotized and coupled to 2-naphthol, producing an orange coloration that was resistant to the very severe washing conditions. The above is conveniently summarized in Fig. 1.

Clearly, the above six-step process is highly impractical but it did set down the marker as to the excellence of the wet-fastness achievable from such covalently bonded colorations.

2. The History of Reactive Dye Development

2.1. Early Dyes Containing Pendant Reactive Groups.

It is interesting that in 1938 IG Farben Industries patented and marketed an acid dye with a pendant ω-chloroacetylamino side chain—Supramino Orange R—this dye had the following structure (**1**).



(**1**)

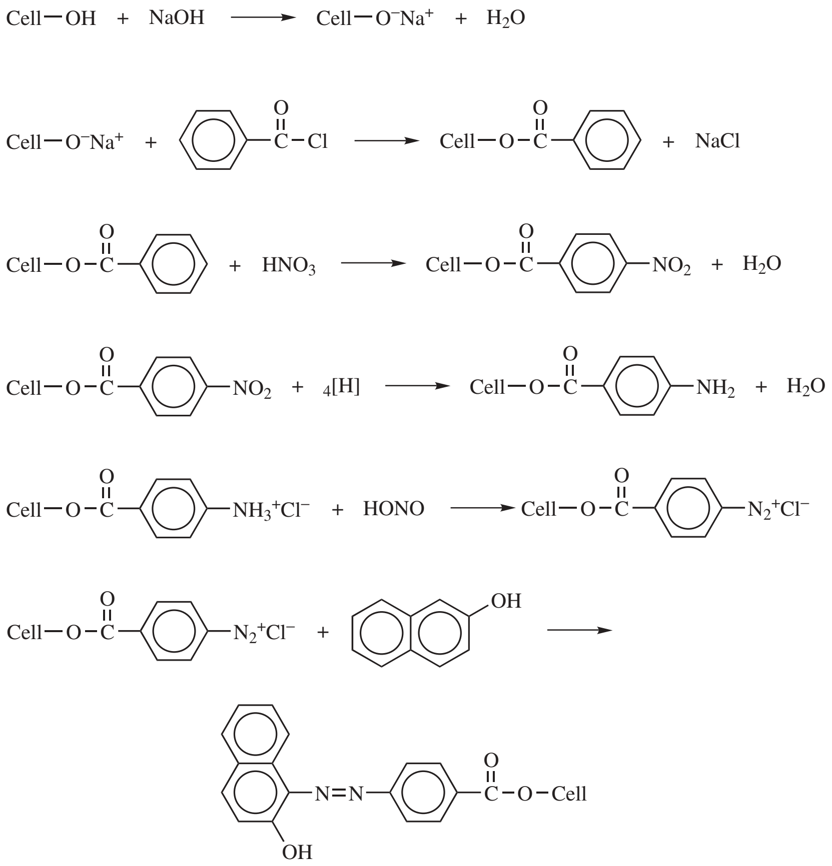
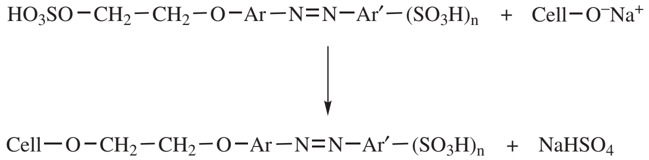


Fig. 1. The Cross and Bevan procedure for covalent bonding a colorant to cotton cellulose.

Supramino Orange R was sold for dyeing wool under mildly acidic conditions; at the time the very good wet-fastness properties of the dyeings were not put down to dye-fibre covalent bonding; it was believed that increased molecular mass through incorporating a chlorine atom in the side chain was the reason for the enhanced fastness properties observed for such dyeings compared with dyeings produced from the acetate analogue of the above dye.

In 1948, Heyna and Schuhmacher (2) and the Hoechst Company patented dyes that gave wool dyeings of excellent wet-fastness—the Remalan Fast dyes. These dyes contained a β-sulfatoethylsulfone side chain. It is difficult in hindsight to believe that the patentees did not realize that these were in fact reactive dyes and perhaps one may conclude that the sales division of the company did not wish such an idea to be common currency. This ground-breaking work was recognized in 2000 by the posthumous award of the Perkin Medal of the Society of Dyers and Colourists to both Heyna and Schumacher (2).

Guthrie published an important paper in 1952 (3) in which it was shown that a sulfatoethyloxyphenylazo dye could be applied and fixed on cotton by an



$$HO_3SO{-}CH_2{-}CH_2{-}O{-}Ar{-}N{=}N{-}Ar'{-}(SO_3H)_n + Cell{-}O^{-}Na^{+}$$

$$\downarrow$$

$$Cell{-}O{-}CH_2{-}CH_2{-}O{-}Ar{-}N{=}N{-}Ar'{-}(SO_3H)_n + NaHSO_4$$

(where Ar and Ar′ represent different substituted aromatic moieties)

Fig. 2. The covalent fixation of a sulfatoethyloxyphenylazo dye on cotton (where Ar and Ar′ represent different substituted aromatic moieties).

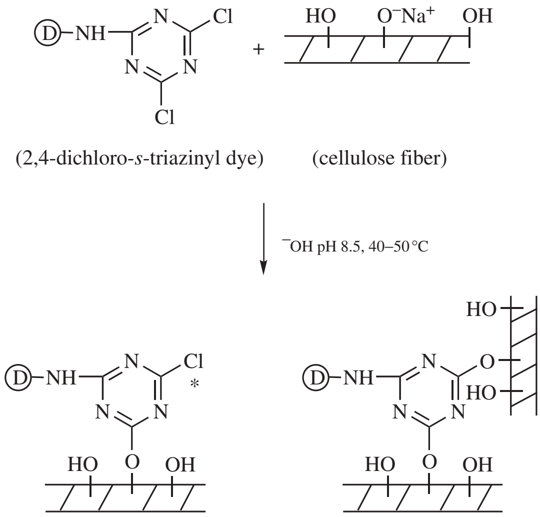
alkaline pad-dry-thermofixation process to give dyeings of good wash-fastness. Some of these dyes were only made water soluble by the pendant sulfato group; thus the fixation process produced a mixture of covalently bonded dye and water-insoluble pigment; the latter was not readily removed by a soaping procedure and was the source of poor rub-fastness properties of the dyeings especially in deep shades; however, some of the dyes did contain sulfonate groups directly attached to the chromophore (eg, the bluish-red dye prepared by diazotizing 2-(*p*-aminophenoxy)ethylsulfuric acid and coupling to 1,8-dihydroxynaphthalene-3,6-disulfonic acid). In some respects this work deserves greater acclaim than it has received since it was the first time that good wash-fast dyeings had been achieved on cotton fabric using a preformed chromophore containing a pendant reactive group. The reactions carried out may be summarized as in Fig. 2.

The above workers also found that the pendant sulfato group could be replaced with chlorine to give dyes that would covalently bind to cotton under alkaline pad-bake application conditions.

2.2. The First Commercial Ranges of Reactive Dyes for Cellulosic Fibers.

In 1956, the first range of fully water soluble reactive dyes for cellulosic fibers was launched by ICI and named Procion MX. Work by Rattee and Stephen (4), who were subsequently awarded the Perkin medal of the Society of Dyers and Colorists, had established that dichloro-*s*-triazine dyes could be applied to cellulosic substrates by long-liquor (exhaust) dyeing procedures and by a variety of pad-fixation processes. These dyes following absorption underwent efficient covalent bonding or *fixation* with cellulose hydroxyl groups under surprisingly mild conditions (pH 8–9, 40°C). At first it looked as though this development might remain a laboratory curiosity, since the storage stability of these new dyes was poor due to moisture sorption and subsequent acid catalyzed hydrolysis to the inactive dihydroxy-triazine derivative; the tenacity and ingenuity of the scientists at ICI overcame this problem by dry mixing the dye powder with solid sodium dihydrogen phosphate and sodium hydrogen phosphate buffer. Horrobin has very adequately described the hydrolysis chemistry of these dyes (5). Figure 3 summarizes the basic chemical principles of this particular dye-fiber reaction.

In the above scheme, Type I and Type II dye-fiber bonds have good stability but Type III bonds show poor acid stability; hence, dyed goods that originally show excellent wet-fastness properties may show a deterioration of these properties on storage due to uptake of acid fumes.



* A Type III dye-fiber bond is formed by the alkaline hydrolysis of the Type I system (thus replacing chlorine with hydroxyl)

Ⓓ represents a sulfonated chromophore

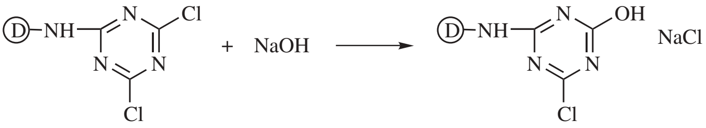
Fig. 3. The dye-fiber fixation process for a dichloro-*s*-triazine dye on cellulosic fibers.

The reactions of dichloro-*s*-triazine dyes with cellulose are classical S_N2 bimolecular substitution reactions resulting from nucleophilic attack of the electron-rich oxygen in the cellulosate anion on electron-deficient carbon atoms in the heterocycle. Chloride anion is the leaving group in these reactions.

One of the major problems defining the efficiency of reaction with the cellulose fiber was the nucleophilicity of the hydroxyl anions present in alkaline solution—these would react with the dichloro-*s*-triazine dye to give the monochloro-monohydroxy-*s*-triazine dye (Fig. 4):

Under alkaline conditions, the reaction stops at the monochloro-monohydroxy-*s*-triazine stage since the triazinyl hydroxy group is deprotonated (phenolate character) and the electron-rich cyanurate oxygen essentially feeds electrons back into the heterocyclic ring and deactivates the carbon atom (attached to chlorine) toward further nucleophilic substitution.

As might be expected, it was quickly realized that the stability of the dichloro-*s*-triazines in water-based printing pastes would be too low—printers



where Ⓓ represents a sulfonated chromophore

Fig. 4. The competing hydrolysis reaction.

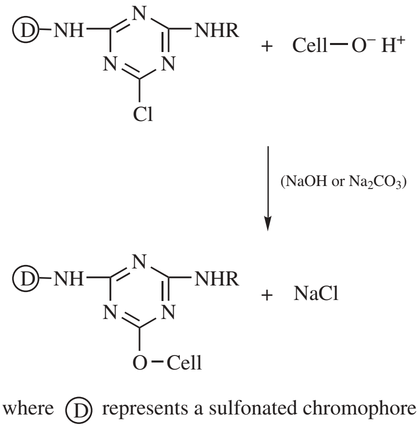


Fig. 5. The reaction of monochloro-monoamino-triazine dyes with cotton cellulose.

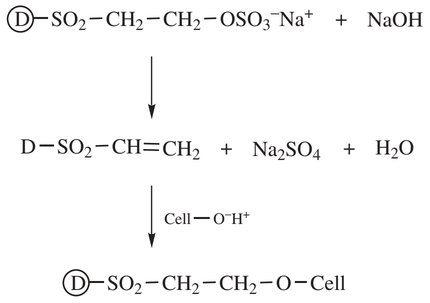
need to store such pastes at least 24 h; an alternative system was thus quickly devised—the deactivated monochloro-monoamino-*s*-triazine dyes were developed (Procion H—now Procion P dyes). Such reactive dyes required more severe conditions to achieve dye-fiber covalent bonding, such as increased alkalinity and higher temperature. Figure 5 summarizes the reaction of these dyes with cellulosic fibers.

Dyes containing monochloro-*s*-triazine residues had already been produced as direct dyes for cellulose fibers by Ciba although their potential to react covalently with cotton had not been appreciated; it is thus not surprising that ICI and Ciba came to agreement in 1957 to respectively market Procion H and Cibacron dyes.

Patenting new reactive dye systems then became intensive as other major dye manufacturing companies rushed to get into this promising area. Hoechst revisited their Remalan Fast wool dyes mentioned earlier and quickly devised application conditions making the vinylsulfone dyes suitable for cellulose fiber coloration, thus launching the very successful Remazol range of dyes in 1957. Most of the Remazol dyes were based on the β-sulfatoethylsulfone residue; the blocking sulfato group is removed by a 1,2-trans elimination reaction, during the dyeing process, to form the free vinylsulfone group that then reacts with fiber nucleophiles by the Michael addition reaction. Figure 6 describes these reactions:

Geigy and Sandoz developed the less activated pyrimidine ring system and launched 2,4,5-trichloropyrimidine dyes in 1959. Bayer devised the 2,3-dichloroquinoxaline Levafix E dyes and marketed them in 1961.

In all the above, the major drive was to develop molecules to dye cellulose to the widest possible shade gamut giving dyeings of good wash-fastness; thus wool where much of the reactive dye innovation started was temporarily side lined. There is no doubt that reactive dyes have been a major success for cellulose fibers; in 2000 130,000 tonnes of reactive dye were sold for cotton and regenerated cellulosic fiber dyeing and printing, which represented 38.3% of the cellulose fiber dye market of 339,000 tonnes (6).



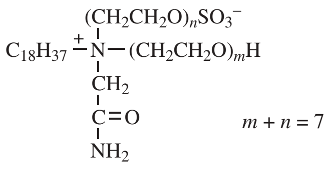
where Ⓓ represents a sulfonated chromophore

Fig. 6. The reactions involved when dyeing cotton cellulose with Remazol reactive dyes.

2.3. The First Commercial Ranges of Reactive Dyes for Polyamide Fibers.

Early Reactive Dyes for Wool. As discussed previously, wool featured highly in early developments of reactive dyes; in particular the chloroacetylamino reactive group appeared as early as 1938 in the IG dye, Supramino Orange R, and Ciba put together a small range of bright wool dyes containing this grouping in 1954 (Cibalan Brilliant); in 1952 Hoechst marketed Remalan and Remalan Fast, 2:1 premetallized reactive dyes (7) for wool that contained pendant sulfatoethylsulfone residues capable of elimination to vinylsulfone reactive groups when applied from boiling dyebaths >pH 5. Hoechst even sold chrome dyes with the sulfatoethylsulfone residue being incorporated in the dye molecule, these being Metachrome Orange H3R, Metachrome Gey RL, Salicinchrome Orange H-3R, and Salicinchrome Grey RL. However, it seemed that the marketing push for selling these dyes as fiber reactive systems was somehow lacking, probably because wool had only a small share of the textile fiber market; only when developments took place that allowed covalent fixation of dyes on the major textile fiber, cotton, did a major marketing effort commence to sell the reactive dye concept.

Also, note that the above early reactive dyes for wool gave considerable problems of unlevel dyeing, especially in piece dyeing and yarn hank dyeing, thus their useage was mainly for loose stock and top dyeing. The major advance in reactive dyes for wool occurred in 1966 with the launch of the Lanasol dyes (Ciba-Geigy); these dyes were based on the α-bromoacrylamido group (8) and were sold with the very important level dyeing auxiliary, Albegal B. Albegal B is an amphoteric product that possibly has the following general structure (**3**) (9):



$$C_{18}H_{37}\overset{+}{-}N(CH_2CH_2O)_nSO_3^-\,(CH_2CH_2O)_mH\,CH_2C(=O)NH_2 \qquad m + n = 7$$

(**3**)

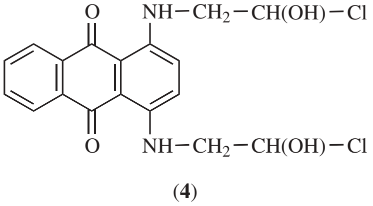
Many of the unlevelness problems associated with reactive dyeing of wool were alleviated by dyeing with this novel product. By happy coincidence the launch of the Lanasol dyes coincided with the marketing of truly machine washable wool, produced by the continuous chlorine–Hercosett treatment of wool tops, a process developed by scientists at CSIRO and IWS (10). Other companies followed suit, Bayer and Sandoz launching difluoro-monochloro-pyrimidine dyes (Verofix/Drimalan F) (11) and Hoechst launching a reassembled range of blocked vinylsulfone dyes (Hostalan) (12). Dyeings produced on the chlorine–Hercosett treated substrate with acid dyes, acid milling dyes and premetallized dyes did not show adequate wash-fastness properties but dyeings produced with reactive dyes gave outstanding washing performance (13).

Dyeing Synthetic Polyamide Fibers with Reactive Dyes. Attempts to dye nylon fibers with reactive dyes have been frustrated by the paucity of nucleophilic sites available for reaction; typically nylon 6,6 from Du Pont contains only 0.036 mol of amine per kilogram of fiber that contrasts greatly with wool (0.820-mol amine/kg) and silk (0.150 mol amine/kg). This factor alone has meant that achieving build-up of sulfonated dyes even in moderate depths of shade is impossible, since every dye molecule covalently fixed means that, depending on the chromophoric component, one, two, or even three strongly anionic sulfonate groups become fixed at the same time, resulting in a build-up of negative charge on the fiber that acts as a resist to further anionic dye uptake.

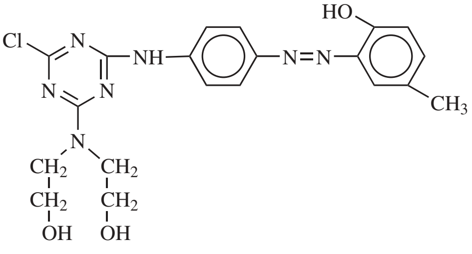
In light of the above, it is not surprising that the first range of reactive dyes for nylon was based on disperse dyes containing a pendant reactive group; these dyes were marketed as Procinyl dyes by ICI in 1959 and contained a variety of reactive groups, all but the yellow requiring alkali activation to form a more reactive residue:

Procinyl Yellow GS (**5**)	monochloro-*s*-triazine
Procinyl Scarlet GS (**6**)	chloroethylaminosulfonyl
Procinyl Orange G	chloroethylaminosulfonyl
Procinyl Red GS	chloroethylaminosulfonyl
Procinyl Blue RS (**4**)	bis(chlorohydrin)

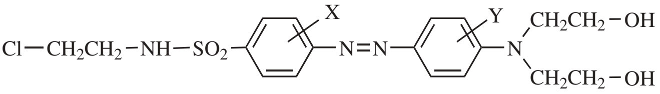
Structures **4**–**6** are typical for this dye class.



(**4**)



(**5**)



(**6**)

The dyes were all applied at the boil firstly under neutral conditions for 30 min, the pH was then raised to 10.5 by the addition of sodium carbonate and boiling continued a further 30 min. The alkaline processing step achieved two objectives; first the amino end groups in nylon would not be significantly protonated giving maximum nucleophilicity, and second chlorohydrin groups in Procinyl Blue RS were converted to the highly reactive epoxide form or the chloroethylaminosulfonyl groups in Procinyl Scarlet GS, Procinyl Orange G, and Procinyl Red GS were converted to the highly reactive aziridinylsulfone form. Scott and Vickerstaff (14) described the interesting chemistry behind these dyes and the application process, and demonstrated that in full shades of Blue RS or Scarlet GS more than the theoretical amount of dye, based on an amino end-group content of 0.0426 mol/kg. of fiber, could be covalently bonded to the substrate. In particular, results with Scarlet GS were very surprising; if 20% dye (on mass of fiber) was applied, then 0.1280 mol of dye/kg. of fiber was covalently bonded. Double addition of the dye at each amino residue is clearly possible as is reaction with ionized hydroxyl nucleophiles in the dye itself (15).

3. Modern Reactive Dyes

The early reactive dyes described above were applied to cellulosic fibers by a variety of processes including long liquor (so-called “exhaustion” dyeing), pad-batch, pad-steam, pad-bake, print-steam, and print-bake. Currently, padding and printing processes account for ~30% of the market, the residual, most popular application method being “exhaustion” dyeing; the reason for the popularity of this method lies in the short-run, high fashion nature of the textile industry that also requires that coloration should be delayed to the piece goods or even garment stage. Dye is lost to dye-house effluent for a number of reasons, but reactive dye hydrolysis during application is one of the most important. An analysis of this situation was carried out by workers at Sumitomo (16) who published the following table comparing dye-fiber covalent bonding efficiencies versus type of reactive group; “fixation” or covalent bonding efficiency was determined by X-ray fluorescence of bound sulfur associated with the sulfonated chromophore.

Table 1 indicates that in medium shades up to 30% of the dye applied ends up in the effluent, whereas in full depths up to 50% of the dye may be wasted. Given that reactive dyes are highly water soluble and thus difficult to remove from dye-house effluent at the water treatment works, color in rivers is a problem associated with the practice of cellulose fiber dyeing using reactive dyes.

As mentioned above the major use of reactive dyes is in long-liquor dyeing processes and for this process to operate well three factors apply, but only in the case of cellulosic fibers:

- Dye substantivity must be as high as possible during the so-called neutral exhaustion phase (typically 30 min at the required dyeing temperature)—

Table 1. **The Fixation Yield of Various Reactive Red Dyes**[a]

Dye[b]	3% o.m.f.	6% o.m.f.
MCT/VS	76	68
MFT	64	56
MFT/VS	61	50
DMFMCP	74	67
VS	68	58
MCT/MCT	57	49

[a] From (16).

[b] Where MFT = monofluoro-*s*-triazine, VS = vinylsulfone, DFMCP = difluoro-monochloro-pyrimidine.

dye uptake by the fiber under these conditions involves minimal covalent bonding and most of the sorbed dye can usually be removed by cold water rinsing (with the exception of quaternized triazinyl dyes discussed later); the amount of dye sorbed at this stage is usually termed %S (*substantivity factor*). The substantivity of the dye for the fiber during this phase of dyeing is almost wholly related to the salt concentration in the dye-bath—with most reactive dyes concentrations of sodium sulfate of 80 g/dm^3 are normal.

- Following addition of alkali (usually sodium carbonate) dyeing is continued for a further 30 min to bring about covalent bonding with the fiber—dye-bath exhaustion at this stage is referred to as % E (*exhaustion factor*).
- At the end of dyeing, repeated rinsing in cold water and then in boiling water, until no more color is removed, is carried out to remove all noncovalently bound dye. The amount of dye desorbed in these processes can be measured spectrophotometrically, and hence the total efficiency of dye-fiber covalent bonding can be calculated as % T (*total fixation factor*). In some cases, it may be useful to know the degree of fixation of the sorbed dye and this is referred to as %F; this factor is related to E and T by the simple relationship: $\%\text{T} = \%\text{F} \times \%\text{E}/100$

A typical exhaustion–fixation curve for a sulphatoethylsulfonyl dye, C.I. Reactive Blue 19 (Remazol Brilliant Blue R), is reproduced in Figure 7 (17) and the schematic of the dyeing process used to obtain these results is shown in Figure 8.

Figure 1 shows that there is rapid uptake of this dye molecule in the salt-only phase of dyeing and extremely rapid fixation of the sorbed dye on addition of alkali. These kinetics indicate that unlevelness during reactive dyeing can be a problem; therefore machines should be selected that give good mechanical interchange between the dye-liquor and the goods being dyed. A further important feature, emerging from this study, is the T value of 72%; this value indicates that 28% of the dye originally applied is lost to the dye-house effluent; if deeper shades than the 2% applied in this case are used the dye discharge problem increases greatly; Table 1 reinforces this observation.

3.1. Polyfunctional Reactive Dyes for Cellulosic Fibers.

The concept of polyfunctionality in reactive dyes was around from the start, in-so-far

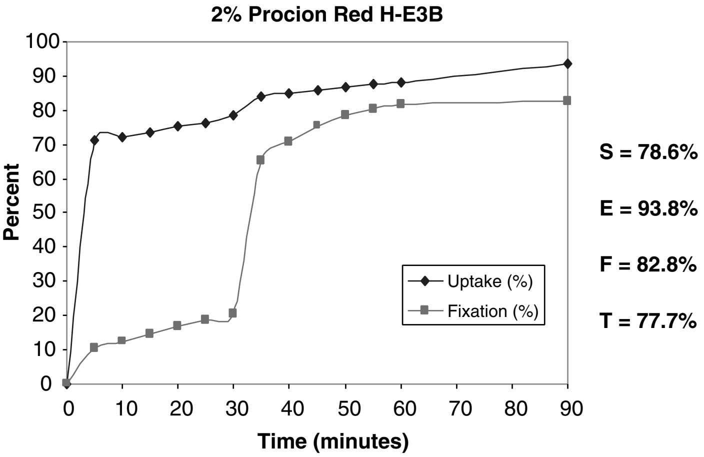
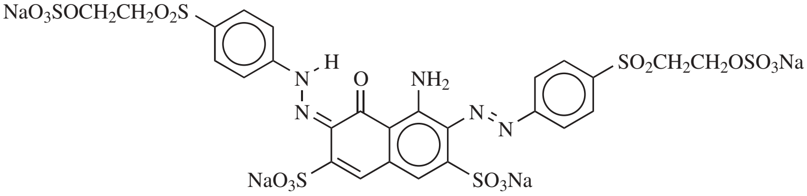


Fig. 7. Substantivity, exhaustion and fixation values versus time (C I Reactive Blue 19).

as the dichloro-*s*-triazinyl dyes contained two reactive sites but the likelihood of actually achieving two dye-fiber bonds was low due to their ease of hydrolysis. The first efficient bifunctional dye was Remazol Black B (C I Reactive Black 5), which was marketed in 1957 as part of the original Remazol range; this dye is now by far the biggest selling dye in the world for producing navy blue and black shades. (See structure **7**).



(**7**)

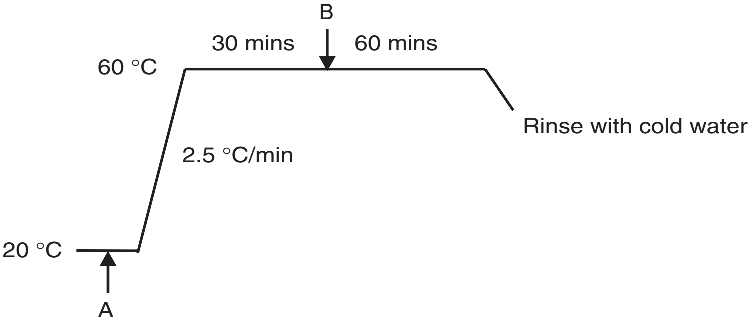


Fig. 8. Schematic of a typical long-liquor reactive dyeing procedure for cotton. (A) 2% owf dye, 80 g/dm^3 sodium sulfate, pH 7, liquor ratio 10:1. (B) 20 g/dm^3 Trisodium phosphate; Soap-off – 2 g/dm^3 Sandozin NIE, 100°C, 15 min.

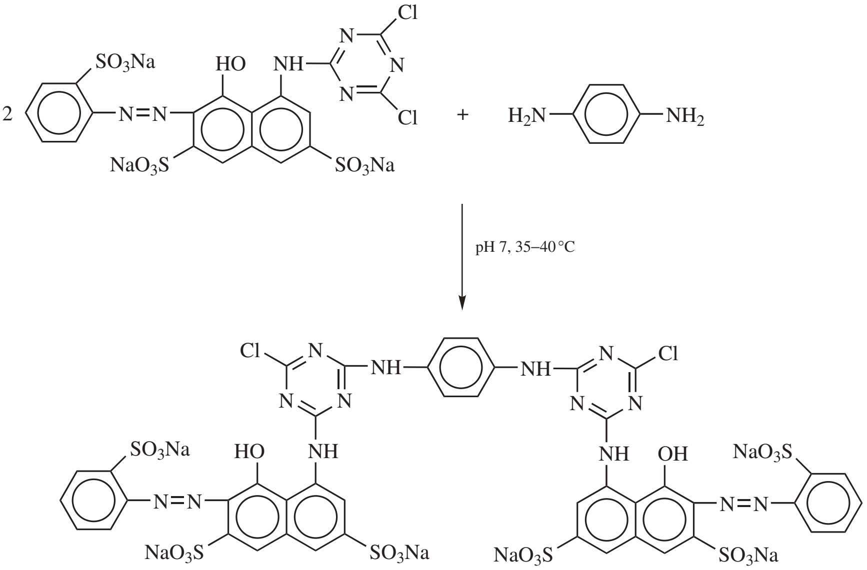


Fig. 9. Preparation of a typical bis(monochloro)-*s*-triazine dye.

In cold pad-batch applications this dye is capable of giving total fixation values >90% in moderate depths of shade but in long-liquor applications total fixation is of the order of 70% because of its relatively moderate substantivity. An elegant, cheap, highly practical method to develop homo-bifunctional dyes was developed by ICI in the early 1970s; simply by adding 2 mol of dichloro-*s*-triazine dye to 1 mol of a diamine such as *p*-phenylenediamine, high yields of a bis(monochloro)-*s*-triazine dye could be obtained; in this way the technically important Procion HE range of reactive dyes was developed. A typical synthetic route to the manufacture of Procion Red HE-3B (C I Reactive Red 120) is shown in Fig. 9.

Typical long liquor dyeing properties for a 2% depth dyeing of this dye on cotton (dyed in the presence of 80 g/dm^3 sodium sulfate, 30 min 80°C, then add 20 g/dm^3 sodium carbonate and fix a further 30 min at 80°C) using this dye are shown in Figure 10 (17).

In the mid-1990s Ciba launched Cibacron LS bifunctional dyes based on bis(monofluoro)-triazines; these dyes were prepared from the condensation of 2 mol of difluoro-triazine dye with a suitable diamine (eg, α,ω-diaminopropane). These dyes were of such a molecular size as to be highly substantive to cellulose and thus could be dyed in the presence of reduced salt, eg, 40 g/dm^3 sodium sulfate—hence the suffix LS (Low-Salt). The monofluoro-triazines are significantly more reactive than the monochloro-triazine dyes and are thus fixed at pH 10.5–11 at 60°C rather than 80°C.

In 1980, Sumitomo launched the first complete range of hetero-bifunctional reactive dyes that contained both a monochloro-triazine and a sulfatoethylsulfone group in the same dye molecule; these were named Sumifix Supra. This

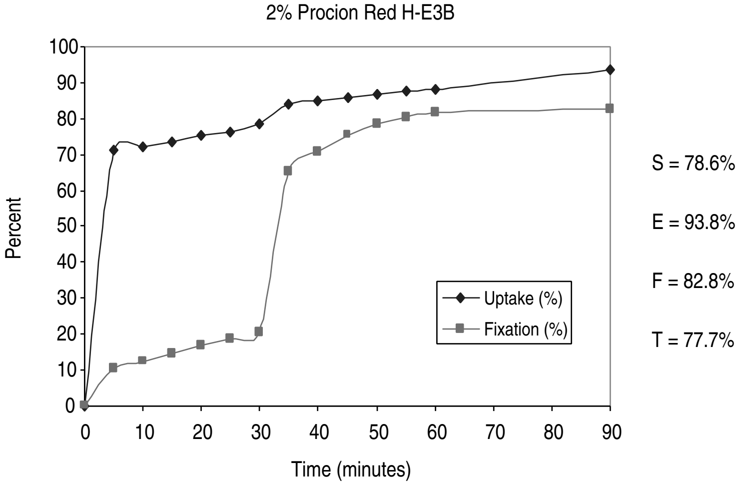
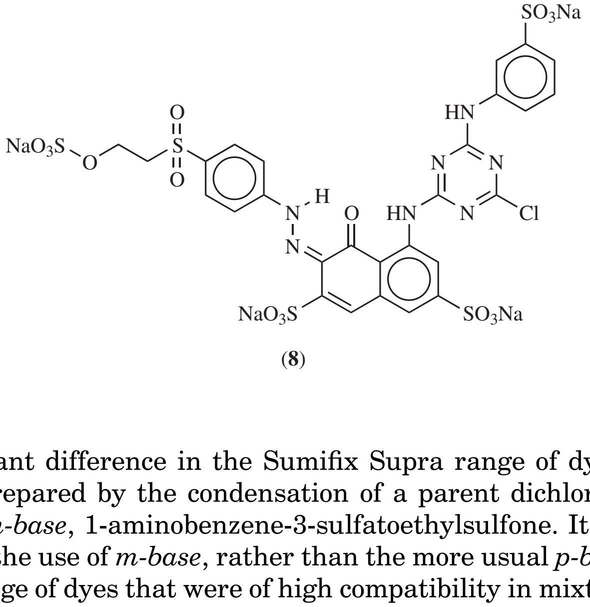


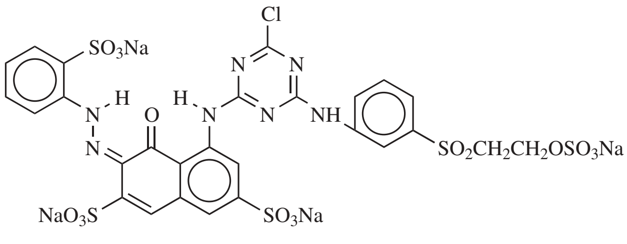
Fig. 10. Substantivity, exhaustion and fixation values versus dyeing time for C I Reactive Red 120.

concept was not entirely novel, Hoechst already had one or two similar dyes in their Remazol range; eg, Remazol Red RB has the structure shown below (**8**).



(**8**)

An important difference in the Sumifix Supra range of dyes was the fact that all were prepared by the condensation of a parent dichloro-*s*-triazine dye with so-called *m-base*, 1-aminobenzene-3-sulfatoethylsulfone. It was claimed by Sumitomo that the use of *m-base*, rather than the more usual *p-base*, allowed the creation of a range of dyes that were of high compatibility in mixture shades (18); corresponding *p-base* dyes showing wider variations in individual dye reactivity. As well as being of high combinability these dyes showed repeatable fixation in the temperature range 60–80°C; thus if there was temperature variation front to back of a dyeing machine, shade reproducibility would not be compromised. A typical structure of a Sumifix Supra dye is shown below (**9**).

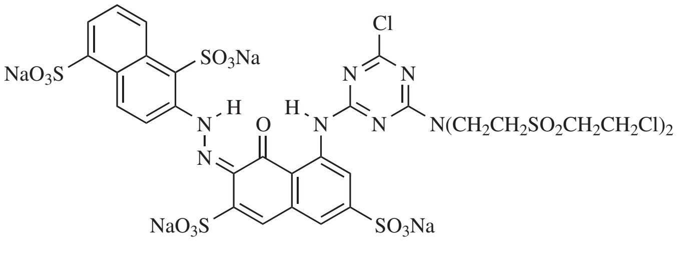


(**9**)

The concept of hetero-bifunctionality has been further developed commercially by Ciba with their Cibacron C dyes designed particularly for pad-batch application; many of these dyes were based on the reactive 2-vinylsulfonylethylamino-4-fluoro-*s*-triazine residue. In this case, the reactive electrophilic groups in the dyes were designed to be of similar reactivity; having the reactive vinylsulfone residue attached through an aliphatic amine attached to triazine, imparted flexibility to the reactive group that increased the likelihood of reaction with the cellulosate anions; in addition aliphatic vinylsulfone-alkylamine-triazine residues affected the aqueous solubility of the dye less than if aromatic vinylsulfone-arylamine-triazine residues were to be used.

The halo-pyrimidine-based dyes may be viewed as being hetero-bifunctional as they contain halogen leaving groups that are selectively activated since the pyrimidine ring is asymmetric; thus in the case of 2,4-difluoro-5-chloropyrimidine dyes the 4-fluorocarbon site is most reactive, reacting with cellulose in the presence of sodium carbonate at 60°C; it is likely that the 2-fluorocarbon electrophile will require a temperature increase of some 10–15°C for efficient reaction with cellulose.

Trifunctional dyes capable of fixation efficiencies from long-liquor dyeing processes approaching 90% in medium depths of shade have been developed. Thus Everlight have a trifunctional range (Everzol ED) and it is believed that some of the Procion HE-XL+ dyes are tris(monochloro)-triazines; the latter may be prepared by the reaction of 3 mol of a dichloro-triazine dye with 1 mol of a trifunctional amine. As early as 1975 Hoechst launched the trifunctional dye, Remazol Red SBB (CI Reactive Red 181) (**10**); Hoechst also patented dyes of this type (19):



(**10**)

The preparation of this dye is interesting and involves the steps shown in Figure 11.

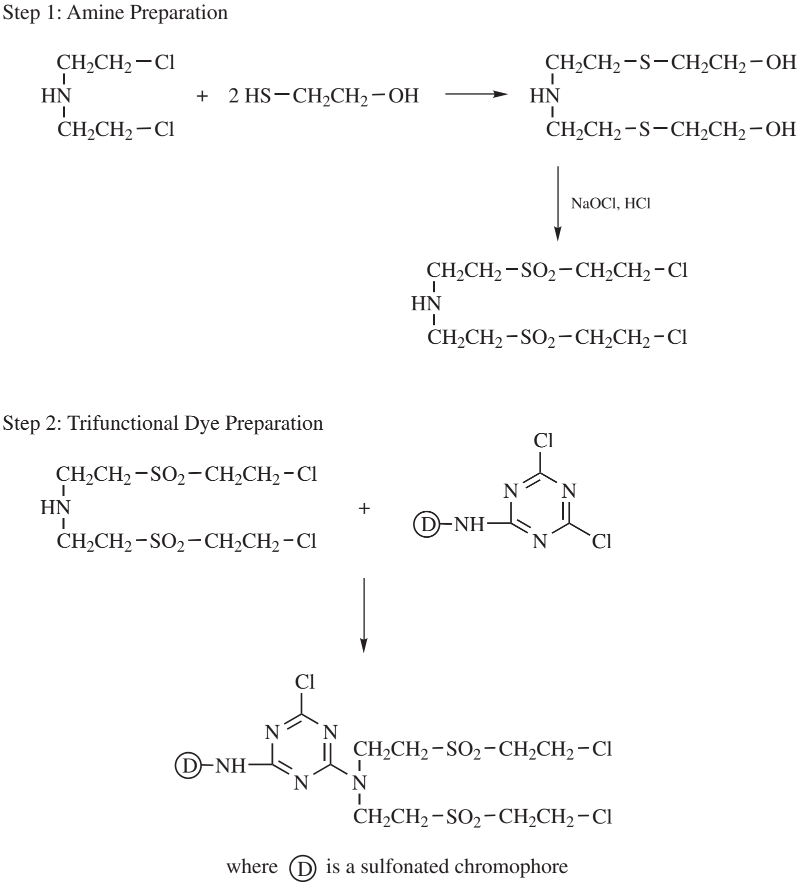
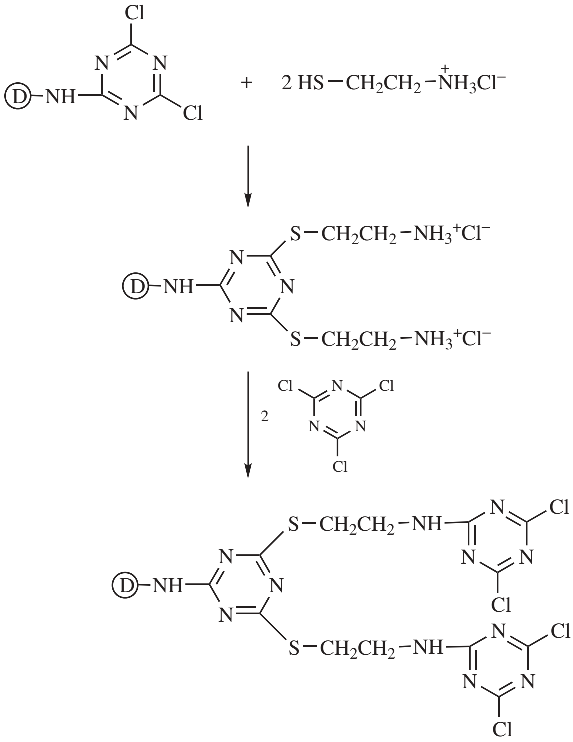


Fig. 11. Preparation of a trifunctional reactive dye.

It is interesting that tetrafunctional reactive dyes have not, as yet, been prepared by replacement of the residual monochloro-triazine in the above scheme with a further mole of bis(chloroethylsulfone)-ethylamine; the problem lies in the conditions required (pH 8–9, 80–90°C), which lead to vinylsulfone formation and then self-reaction of the amine. Less reactive vinylsulfone blocking groups may lead to a resolution of this problem.

Tetrafunctional reactive dyes have been claimed in the patent literature; eg, Ciba have covered chromogens containing two vinylsulfone/monohalo-triazine residues (20). A Proctor and Gamble patent (21) describes tetrafunctional reactive dyes prepared from the reaction of dichloro-triazine dyes (or difluoro-monochloro-pyrimidine dyes) with cysteamine and their subsequent reaction with cyanuric chloride; the preparation route is summarized in Fig. 12.

When applied, in medium shade depths, by long-liquor processes at 50°C in the presence of 40 g/dm^3 sodium sulfate and then fixed with sodium carbonate additions, these dyes were claimed to give total fixation efficiencies >95%; in

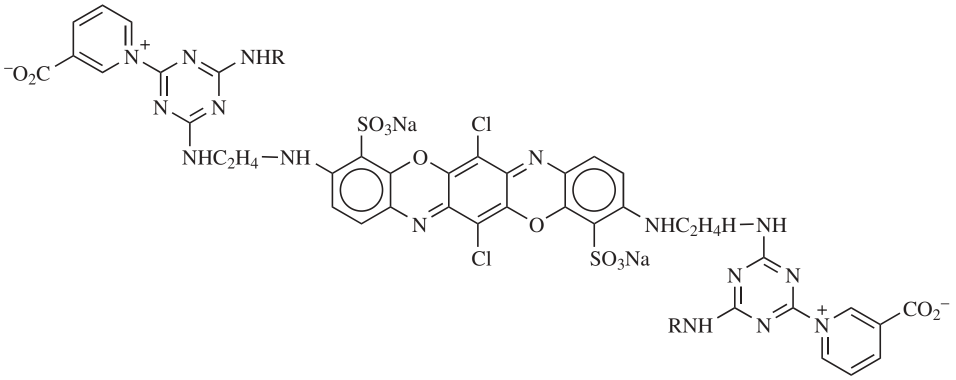


where (D) is a sulfonated chromophore

Fig. 12. Preparation of tetrafunctional halo-triazine dyes.

addition the large hydrophobic side chain gave the dyes very good combinability properties in tertiary shades. The dyes were also applicable by pad-batch processes but in this case it was preferable to replace the cysteamine bridging group with cysteine in order to enhance water solubility of the dyes.

3.2. Neutral Fixing Reactive Dyes for Cellulosic Fibers. Nippon Kayaku introduced the first range of "neutral-fixable" reactive dyes for cellulosic fibers in 1983; these dyes were bifunctional bis(nicotinoyl)-triazines (22). The chemistry behind this range of dyes was based on an early observation that the reactivity of monochloro-*s*-triazine dyes could be greatly enhanced by dyeing in the presence of tertiary amines (23); thus alkaline fixation at 50°C rather than 80°C was possible in long-liquor dyeing processes. Subsequently, catalytic quantities of tertiary amines such as diazabicyclo-octane (DABCO) were promoted as dyebath additives to convert hot dyeing systems to warm dyeing systems; a good example was Cibacron Catalyst CC1 from Ciba (24). The procedure did not develop as rapidly as expected probably because of the odour and toxicity problems of certain tertiary amines. In 1979, ICI launched Procion Blue HE-G (CI Reactive Blue 187), which was a bis(monochloro)-triazine dye modified by reaction with nicotinic acid; the structure of this dye is shown below (**11**).



(**11**)

The use of nicotinic acid as a low toxicity, nonodorous tertiary amine attracted the interest of Nippon Kayaku researchers who made the novel observation that simply applying these dyes in boiling baths containing usual amounts of electrolyte along with a pH 7.5 buffer, achieved dye uptake and fixation; for deep shades it was recommended that fixation temperature should be increased to 130°C. Croft and co-workers (25) investigated this concept in depth, deriving various quaternized dyes from the reaction of the bis(monochloro)-triazine dye, Procion Red HE-3B, with nicotinic acid, DABCO, iso-nicotinic acid, nicotinamide, trimethylamine, and pyridine; the reactions were carried out at pH 6.5 for 2–3 h at 80–90°C. All of these dyes showed good exhaustion and fixation values after dyeing at pH 7 at the boil for 1 h (eg, for 2% shades 80–85% exhaustion and relative fixation of 70%). The concept of neutral fixation is of great interest since it simplifies the dyeing process—there is no separate fixation stage thus eliminating the need to make additions of alkali 30 min into the dyeing cycle. Hydroxyl groups in cellulose behave as very weak acids having estimated pK_a values of ~ 13 at room temperature; as the temperature increases so does the dissociation, and hence the nucleophilicity of the substrate. Even at the boil at pH 7.5 the number of dissociated hydroxyl groups will be very small and other reasons must be sought to explain the vastly improved fixation efficiency of quaternised triazines versus halo-triazines. Chlorine or fluorine heterocycle-based reactive dyes produce hydrochloric or hydrofluoric acids following reaction with dissociated cellulose hydroxyl groups, but in the case of quaternized dyes the neutral haloacid salt of the tertiary amine is the leaving group. Additionally, the quaternized dyes carry a positive charge adjacent to the electrophilic site that may orientate the reactive system to promote ready reaction with the negatively charged nucleophile, the cellulosate anion; Figure 13 shows this effect.

3.3. Acid Fixing Reactive Dyes for Cellulosic Fibers. In order to improve the efficiency of cotton–polyester blend coloration, with mixtures of reactive and disperse dyes, mildly acidic fixation conditions would be desirable as many disperse dyes are alkali sensitive.

Early attempts to produce an acid-fixable system resulted in *N*-methylol-amino-triazine dyes from American Cyanamide (Calcobond dyes) but these were subsequently withdrawn from the market (26). The above dyes were fixed

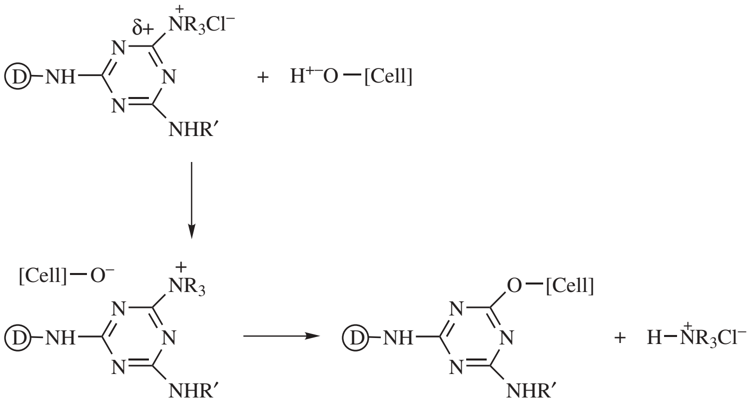
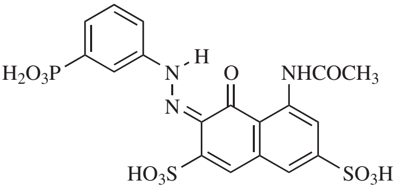


Fig. 13. Fixation of a quaternary-amino-triazine dye.

with a Lewis acid catalyst such as magnesium chloride by a pad-dry-bake procedure.

The ICI Procion Resin process (27) is reminiscent of the above. In this case, dichloro-*s*-triazine dyes were mixed with a cotton durable press cross-linking agent such as *N,N′*-dimethylol-dihydroxy-ethylene urea (DMDHEU), and magnesium chloride; the mix was padded on to cotton fabric, dried and cured at 170–180°C for 30 s; excellent fixation values were obtained. The procedure still finds practical use in the printing of cotton–polyester sheeting materials. The main problem on 100% cotton fabrics is loss of strength due to the acidic conditions employed. The mechanism for dye-fiber covalent bonding is presumably as shown in Fig. 14 (28).

Much effort has been directed at the covalent fixation of phosphonic acid containing dyes to cellulosic fiber substrates using a high temperature dry fixation procedure (thermofix) under mildly acidic conditions. In 1977, ICI introduced acid-fixable phosphonic acid dyes for the pad- or print-thermofix coloration of cellulosic fibers (29). The research that formed the basis of this system was actually carried out at Stamford Research Institute and Burlington Industries (30,31) and resulted in a range of dyes derived from the intermediate *m*-aminobenzene-phosphonic acid supplied by Stauffer. The range was sold as Procion T dyes and, in admixture with alkali dischargeable disperse dyes, as Procilene PC dyes for coloration of cotton polyester blends. The structure of Procion Red T2B prepared from simple diazotization of *m*-amino-benzene phosphonic acid and coupling it to *N*-acetyl H acid is shown below (**12**).



(**12**)

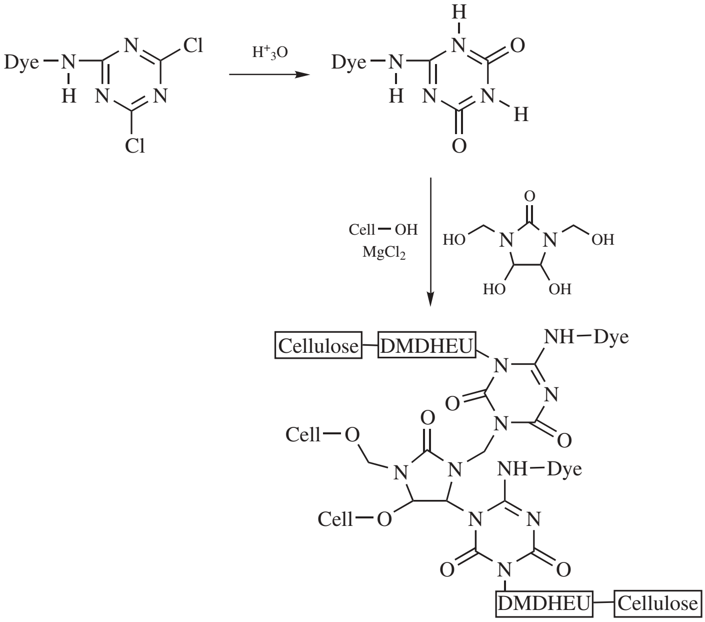


Fig. 14. Cross-linking hydrolyzed triazines to cotton cellulose using DMDHEU; after Clark (28).

Despite the fact that phosphonate dyes could not hydrolyze during application to form the phosphonate ester bond with cellulose, only modest fixation efficiencies were recorded. It was important to include a dehydrating catalyst such as cyanamide or preferably dicyandiamide with the dye in order to promote the above esterification reaction. The above catalysts can form carbodiimide tautomers that are the dehydrating agents. Figure 15 shows the proposed reaction schemes.

Aliphatic polyphosphonate dyes have been prepared by the simple expedient of condensing aminoethyl-phosphonic acid with existing bis(monochloro)-*s*-triazine reactive dyes (32) according to Figure 16.

In the above study, cotton fabric was padded with a pad-liquor containing 120 g/dm^3 cyanamide, 10 g/dm^3 ammonium dihydrogen phosphate, and 20 g/dm^3 pure phosphonate dye (it is important to prepare the dye as the ammonium salt); after drying and thermo-fixing at 200°C for 90 s the alkyl-phosphonate dyes gave 95% fixation, whereas the mono-functional Procion T aryl-phosphonate dye gave only 46% fixation. Thus the fixation values of the alkyl phosphonate dyes in thermofixation processes are outstanding; this result was for 2% o.m.f. pure dye (o.m.f. is the abbreviation for on mass of fiber), which corresponds to a 3–4% shade of commercial dyes since the latter contain salt, buffers, and dedusting agents. The dye-fiber phosphonic acid ester bond is remarkably resistant to treatments in acidic or alkaline media (33).

In a similar vein polycarboxylic acid containing dyes have been synthesized as their ammonium salts and applied to cotton by thermofixation procedures (34)

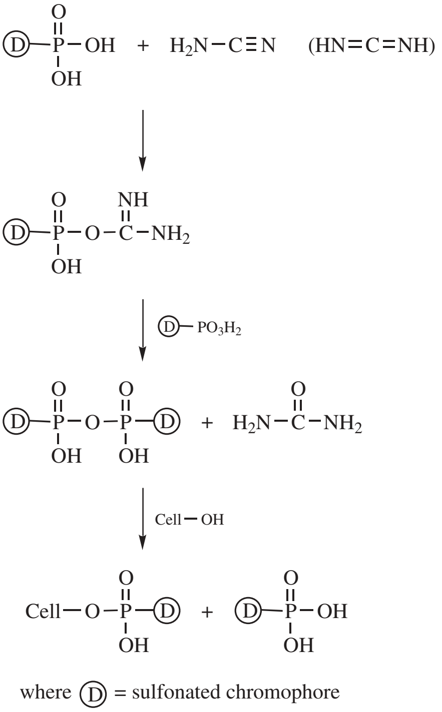


Fig. 15. Fixation of phosphonate dyes on cotton cellulose.

in the presence of cyanamide as a catalyst. In this case, aspartic acid was used to make 2,4-diaspartyl-*s*-triazine dyes according to Fig. 17.

The fixation values achieved when the above dye was applied by a pad-batch-thermofix (200°C, 90 s) procedure, from a pad-liquor containing 10 g/dm^3 pure carboxylate dye, 150 g/dm^3 of cyanamide and 10 g/dm^3 ammonium dihydrogen phosphate, were of the order of 75%. These results indicate that the system is not as effective as the phosphonate system perhaps due to the instability of the carboxylate ester dye-fiber bond under the alkaline (pH 10.5) boiling soaping-off conditions used. The fixation mechanism is shown in Fig. 18.

3.4. Improved Dyeing of Cotton Cellulose by Fiber Pretreatment.

The fixation of reactive dyes on substrates containing amino groups is much higher than on cellulosic substrates. Thus wool, which contains amino terminal groups on individual amino acid side chains, can be dyed with reactive dyes from baths set at pH 5–7, to give very high fixation efficiencies. In some cases, total overall color yields (fixation *T*) of 95–100% are recorded, even in moderate depths of shades. These excellent results on wool are achieved without the need to add electrolyte. It is therefore not surprising that a large amount of work has been done to prepare modified cellulosic substrates containing amino residues in order to improve dyeability.

At one time, it was thought that a cheap convenient way of modifying cotton to make it readily reactive dyeable was to pretreat it, from a long liquor, with a

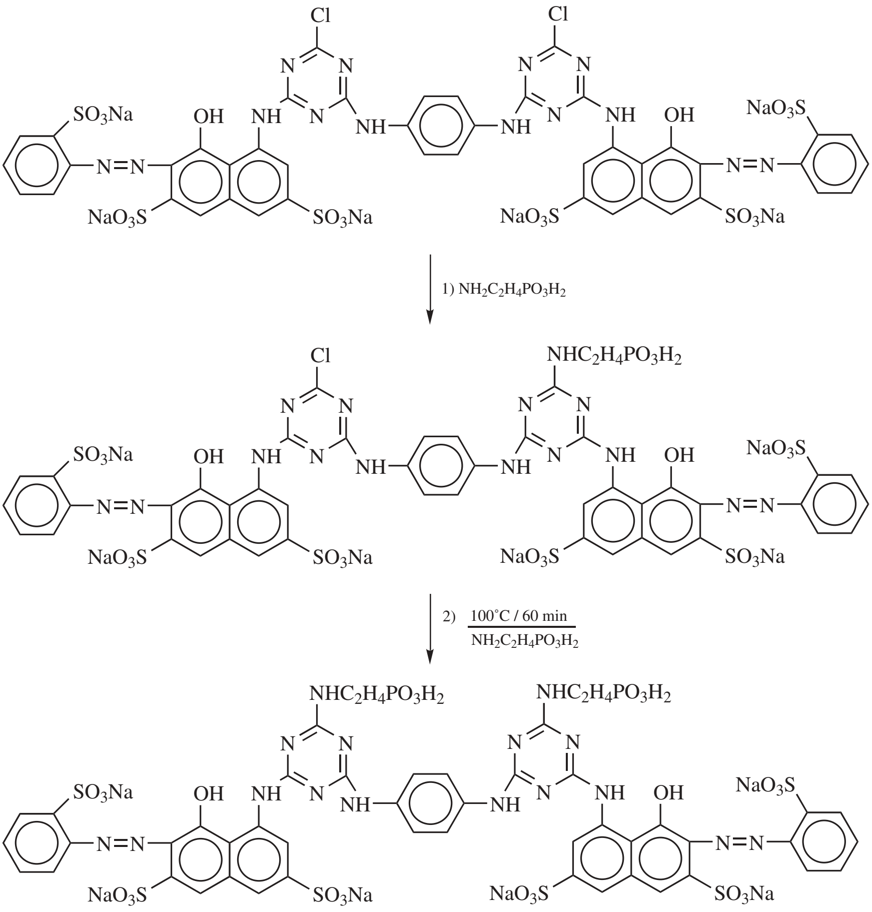


Fig. 16. The reaction of C.I. Reactive Red 120 with aminoethylphosphonic acid.

reactive cationic polymer under alkaline conditions (35). Such treatments imparted a very high neutral substantivity for reactive dyes, in the absence of electrolyte, and gave dyeings of good wet-fastness. However, such approaches have not met with commercial success, as the treated fabric dyed to duller shades than those produced by the conventional salt–alkali process and a significant drop in light-fastness of 1–2 points was noted (36).

Bright, light-fast dyeings could, however, be obtained by using a variety of methods to incorporate amino residues on cellulosic substrates and some of the most promising techniques will be discussed.

Rupin and co-workers (37), Dvorsky and Cerovsky (38) and Rippon (39), studied the dyeability of cellulose substrates modified with glycidyl-trimethyl-ammonium chloride (Glytac A from Protex) or its precursor 1-chloro-2-hydroxy-3-trimethyl-ammonium-propane chloride. This modification may be carried out by an alkaline pad-bake (200°C) (36) or by an alkaline pad-batch procedure. Unfortunately, the product has insufficient substantivity to allow its application by long-liquor methods. The modified substrate may be considered

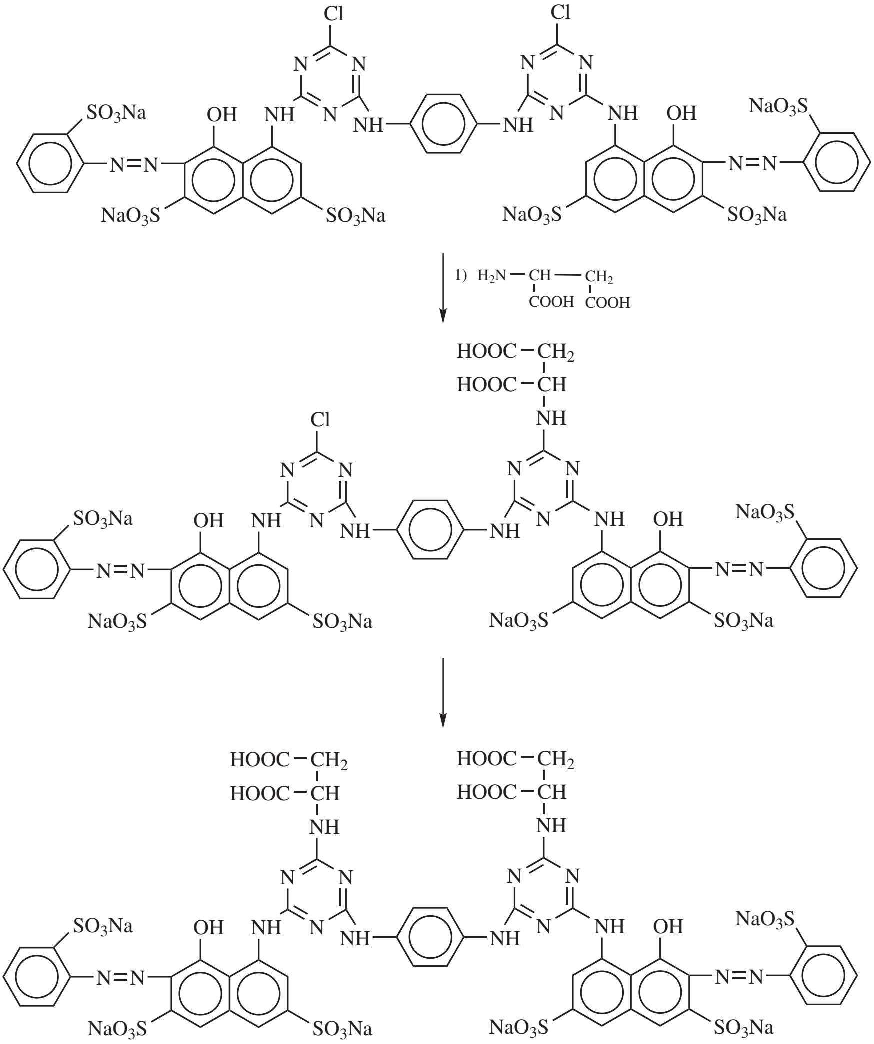
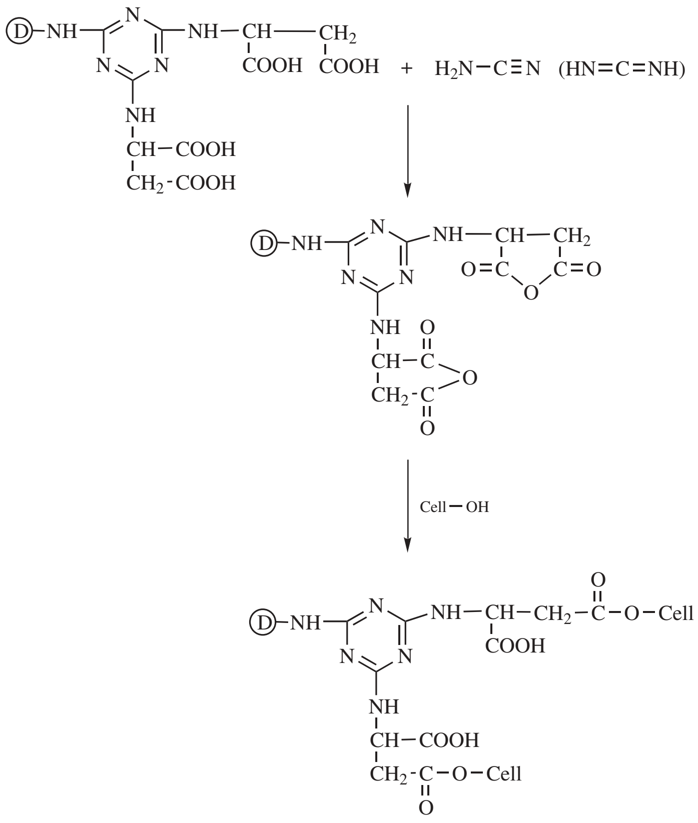


Fig. 17. The reaction of C.I. Reactive Red 120 with aspartic acid.

to have the structure shown in Fig. 19, although the possibility such treatments leading to the introduction of oligomeric polyether chains, bearing cationic functionality, has not been established;

The ease of neutral dyeing of this substrate with reactive dyes led Lewis and Lei (40) to speculate that the deprotonated form II predominates even when dyeing at pH 7. Thus, the anionic sulfonated reactive dye is initially absorbed on to the fiber by a powerful ionic attraction to the quaternary ammonium residue and fixes to the adjacent ionized (nucleophilic) hydroxyl group. Typical dyeing conditions that could be employed were pH 7, with no salt, the bath being raised to the boil over 30 min and dyeing continued at the boil for a further 60 min. Dyeing, eg, with a 2% o.m.f. shade of C1 Reactive Red 5 (dichloro-



where Ⓓ is a sulfonated chromophore

Fig. 18. Fixation of polycarboxylate aspartyl-triazine dyes on cotton cellulose.

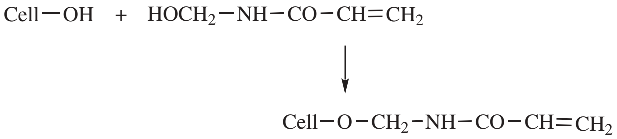
s-triazine dye) gave exhaustion values of 85% and even more interestingly, 99% of the absorbed dye was apparently covalently fixed; thus soaping-off the dyeing gave rise to hardly any color removal. Color yields compared to the conventional salt–alkali method on untreated cotton were doubled.

Due to perceived health and safety problems in handling the epoxide form, recent efforts to modify cotton in this manner have concentrated on a pad-batch procedure using a mixture of the chlorohydrin analogue, 3-chloro-2-hydroxy-*N*,*N*,*N*-trimethyl propanaminium chloride and sodium hydroxide. This product converts the above agent, during the batching procedure, to the corresponding epoxide that then fixes covalently to the fiber. In the United States, the

$$\text{Cell}{-}\text{O}{-}\text{CH}_2{-}\underset{\text{OH}}{\text{CH}}{-}\underset{{}^{+}\text{N(CH}_3)_3\text{Cl}^-}{\text{CH}_2} \;\xrightleftharpoons{-\text{HCl}}\; \text{Cell}{-}\text{O}{-}\text{CH}_2{-}\underset{\text{O}^-}{\text{CH}}{-}\underset{{}^{+}\text{N(CH}_3)_3}{\text{CH}_2}$$

I II

Fig. 19. Different forms of cotton modified with Glytac A.



$$\mathrm{Cell{-}OH} + \mathrm{HOCH_2{-}NH{-}CO{-}CH{=}CH_2} \longrightarrow \mathrm{Cell{-}O{-}CH_2{-}NH{-}CO{-}CH{=}CH_2}$$

Fig. 20. Reaction of NMA with cotton.

commercial development of the Virkatone ECO system (Virkler) is worth noting and there is undoubtedly mill production of cotton modified by this method. This treated cotton can be dyed with selected reactive dyes in the absence of salt; dyebath exhaustion is 99–100%, even in full depths of shade, and fixation values also equal or approach 100%.

Lewis and Lei (36) also prepared the water-soluble cationic agents from the reaction of dimethylamine and epichlorohydrin and found that they would fix to cotton by an alkali catalysed pad-dry-bake procedure. The constitution of such products was not established, however, generation of an ionene-type cationic polyelectolyte could be a possibility. As with the glycidyl-trimethylammoniumchloride (Glytac A) pretreatment with the above agents gave a substrate that was readily neutral dyeable with reactive dyes, in the absence of electrolyte. Such dyeings exhibited wet and light-fastness properties that mirrored the performance of the selected reactive dye applied to untreated cotton by the normal salt–alkali process.

An alternative method of introducing different aliphatic amino groups into cotton involved a pad-bake pretreatment of the fabric with *N*-methylol acrylamide (NMA), which reacted covalently with cellulose by a Lewis acid catalyzed baking reaction (40) (Fig. 20).

Reaction of the above substrate with appropriate amines gave a series of amino-substituted cellulosic substrates (Fig. 21). Substrates II–V inclusive were dyed at pH 5 in the absence of electrolyte, with 2% o.w.f. C1 Reactive Red 5, raising the bath to the boil and boiling 1 h. The results, in terms of color yield (K/S) before and after soaping-off, are illustrated in Figure 22. A study of this figure reveals that optimum exhaustion/fixation are achieved on substrate II and III; substrate IV containing the tertiary amine gives surprisingly poor fixation results.

Undoubtedly, the highly reactive dichloro-*s*-triazine dye is likely to form a quaternary derivative with the tertiary amine residues in substrate IV and, failing reaction with a nearby fiber bonded nucleophile, this highly reactive species will rapidly hydrolyze. The work on substrate IV only involved highly reactive

$\mathrm{Cell{-}O{-}CH_2{-}NH{-}CO{-}CH_2{-}CH_2{-}NH_2}$ II

$\mathrm{Cell{-}O{-}CH_2{-}NH{-}CO{-}CH_2CH_2{-}NHCH_3}$ III

$\mathrm{Cell{-}O{-}CH_2{-}NH{-}CO{-}CH_2CH_2{-}N(CH_3)_2}$ IV

$\mathrm{Cell{-}O{-}CH_2{-}NH{-}CO{-}CH_2CH_2{-}N(CH_3)_3}$ V

Fig. 21. Amino derivatives of NMA—treated cotton.

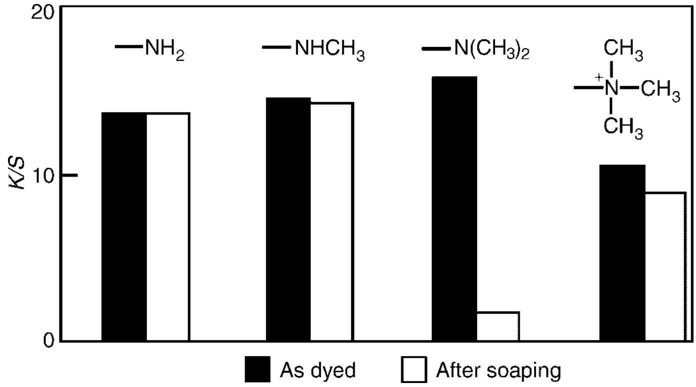


Fig. 22. Comparison of color yields obtained for dyeings of Cl Reactive Red 5 (2% o.w.f.) on various aminopropionamido-methylene-oxycelluloses (Cell-O-CH_2NH-CO-CH_2CH_2 $NR_1R_2R_3$).

dichloro-*s*-triazine dyes; with hindsight it is likely that more useful results could have been obtained on dyeing the substrates with monochloro-*s*-triazine dyes, since in this case any quaternary triazine derivatives formed would be stable under acidic to neutral conditions.

3.5. Reactive Fibers. Existing reactive dye systems depend on two basic elements: an electron deficient “reactive” carbon centre in the dye and an electron rich “nucleophilic” centre in the fiber.

The above concept may be reversed by producing dyes containing pendant nucleophiles. Aminoalkyl dyes are conveniently prepared from the reaction of aliphatic diamines with existing reactive dyes.

Reactive cellulosic fibres may be prepared by the following two methods:

1. Reaction of cotton with *N*-methylol-acrylamide.

   It was shown (40) that the aminoethylamino-*s*-triazinyl dye, prepared from the reaction of C1 Reactive Red 58 (Procion Red H8BN-ICI) with ethylene diamine, gave excellent colour yields when applied to NMA activated cotton at pH 10.5 in the presence of 80 g/dm^3 salt (Dye AA). Typical results are reproduced in Figure 23; this figure also shows color yield (K/S) versus dye applied, before and after soaping, for the unchanged parent monochlorotriazine dye applied to untreated cotton by the recommended reactive dyeing procedure (Dye P).

   This figure demonstrates that practically no dye is removed from the activated cotton, even when soaping at the boil (15 min) in an aqueous solution of nonionic detergent (5 g/dm^3) and sodium carbonate (2 g/dm^3). The comparative result, achieved with unmodified CI Reactive Red 58 on untreated cotton, indicated that up to 30% of nonreacted dye is removable during the soaping procedure. Thus dyeing activated cotton with aminoalkyl dyes offers significant potential savings, since on the basis of these results the soaping process could be omitted.

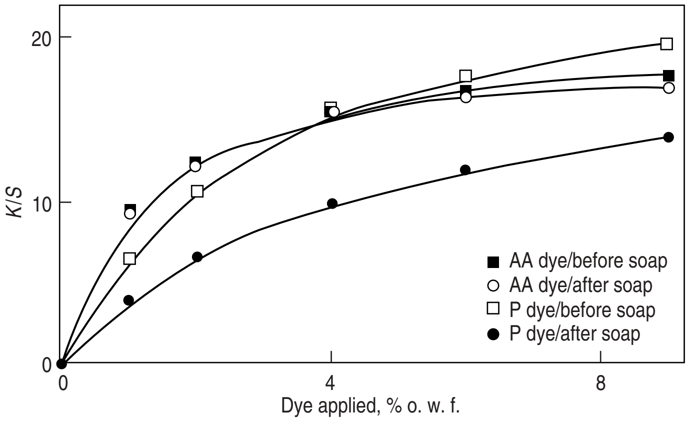


Fig. 23. Build-up curves for Cl Reactive Red 58 (P dye) on untreated cotton and its aminoethyltriazine derivative (AA dye) on NMA cotton.

2. Reaction of 2,4-dichloro-6-(2-pyridino-ethylamino)-*s*-triazine (DCPEAT) with cotton.

   In an attempt to improve substantivity in the no-salt dyeing system, a novel compound, 2,4-dichloro-6-(2-pyridino-ethyl-amino)-*s*-triazine (DCPEAT) has been studied by Lewis and Lei (41). If this compound were to be applied and fixed on cellulosic substrates under well-defined conditions the following modified substrate would be produced (Fig. 24).

This reactive substrate shows excellent dye-fiber fixation when it is dyed with amino-alkyl dyes (**13**). DCPEAT contains two reactive chlorine atoms—when applied to cellulosic substrates under weakly alkaline conditions one of the chloro substituents is displaced, leading to covalent fixation. The cellulosate substituent deactivates the triazinyl ring, ensuring that the product of the pretreatment reaction contains significant numbers of mono-chloro-triazine

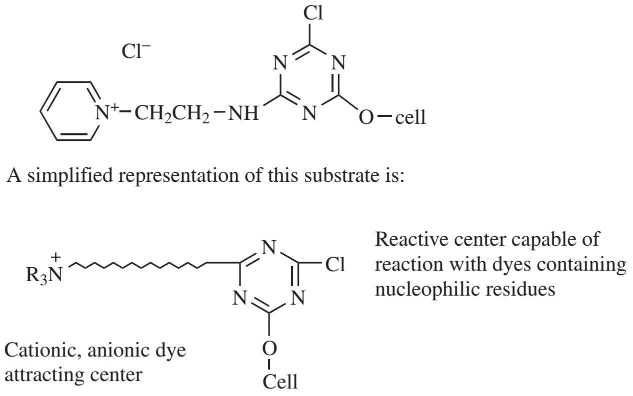
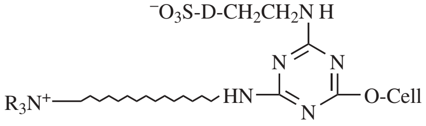


Fig. 24. DCPEAT activated cotton.

residues. Since aliphatic amino is a more powerful nucleophile than cellulose hydroxyl, very efficient reaction of the dye at the monochlorotriazine residue should be possible during subsequent dyeing with aminoalkyl dyes.



(**13**)

It was found that the DCPEAT modified substrate was best prepared by a pad-batch cold (24 h) technique at pH 8.5, followed by a thorough cold water wash-off. Although long-liquor applications of DCPEAT were studied, inadequate substantivity of this compound for the fiber gave poorer subsequent dyeings than those obtained on pad-batch prepared substrates.

Two aminoalkyl dyes were employed to dye this modified substrate in the absence of salt, namely,

> Procion Red H8BN—monoaminoethyl-aminotriazine derivative and Procion Red HE3B (C1 Reactive Red 120)—bis(aminoethyl-aminotriazine) derivative.

The results obtained when dyeing these two nucleophilic dyes on the above substrate are shown in Figure 25 (dyeing conditions: no salt, pH 9, dye—2%

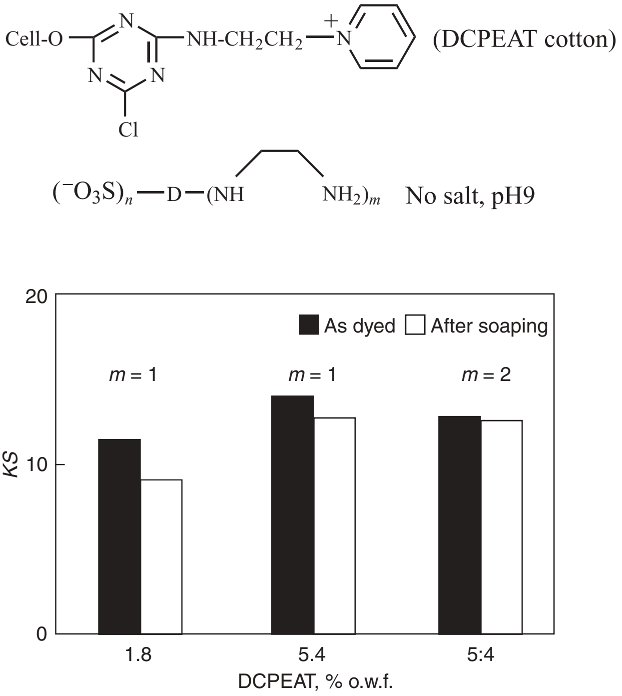


Fig. 25. Application of various aminoethyl dyes to DCPEAT cotton.

o.m.f., raise to the boil, boil 1 h). This figure demonstrates that good substantivity and fixation are achieved at the higher levels of DCPEAT application (5.4% o.m.f.); slightly better results were achieved using the bifunctional aminoethyl dye derived from C1 Reactive Red 120.

3.6. Covalent Fixation of Dyes on Fibers Using Cross-Linking Systems. The earliest commercial success in this area was achieved by BASF with the Basazol system (42,43). In this case, dyes containing pendant nucleophilic groups were fixed to cellulose hydroxyl residues using a trifunctional cross-linking agent 1,3,5-triacroylaminohexahydro-*s*-triazine (Fixing Agent P). The dyes employed contained sulfonamide residues that were sufficiently nucleophilic >pH 10.5 to undergo Michael addition with the activated double bonds of the cross-linker. In fact, many of the aminosulfonyl dyes selected as Basazol dyes were already available as 2:1 premetallized dyes for dyeing wool (Ortolan—BASF). The following simplified scheme, describing the covalent fixation of the sulfonamide dye to cotton is relevant, although it should be noted that Baumgarte (42) describes up to nine different possible reaction products from such a system (Fig. 26).

Clearly, the above species contains an unreacted double bond that is capable of undergoing further reaction with either the nucleophilic sulfonamide residue or with the nucleophilic cellulosate anion. This system was highly novel, but the dyes were withdrawn from the market place, because of its restriction to padding and printing processes due to the nonsubstantive character of the cross-linker and possible toxicity problems. The clear advantage of such a system was that the dyes were not susceptible to hydrolysis and thus, in theory, very high levels of fixation should be achievable, provided sufficient cross-linker was present.

It is of interest that the above cross-linking agent has been found to efficiently fix dyes containing pendant nucleophilic amino groups on both wool and nylon (44,45). In the former case, very good results were obtained, providing the cross-linking agent was predispersed with the anionic dispersant Matexil DA-AC (ICI). Thus wool could be dyed, from long-liquor baths set at pH 6,

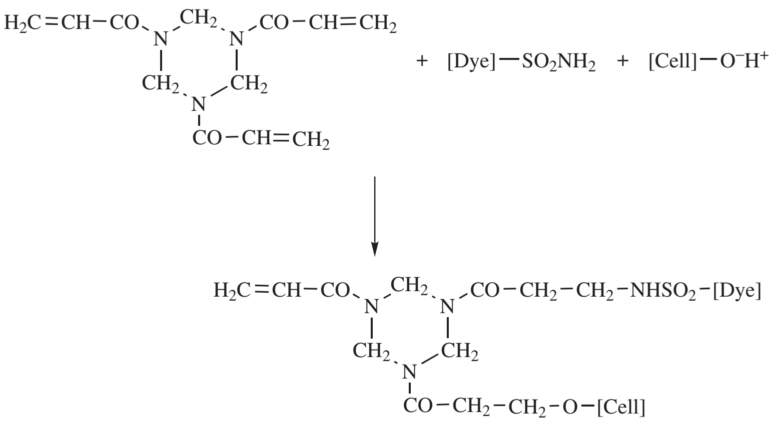


Fig. 26. Fixing Agent P/sulfonamido dye–cellulose reaction.

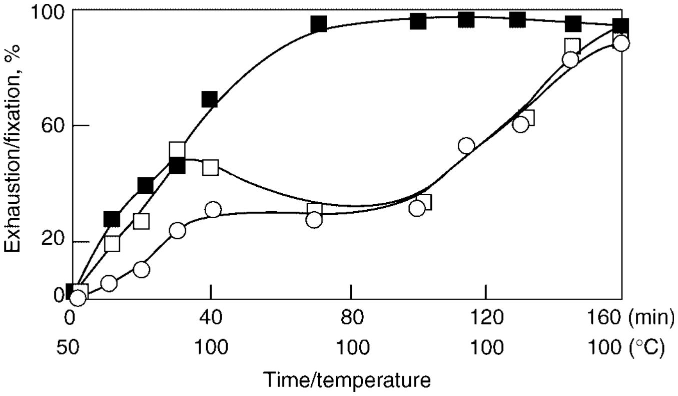
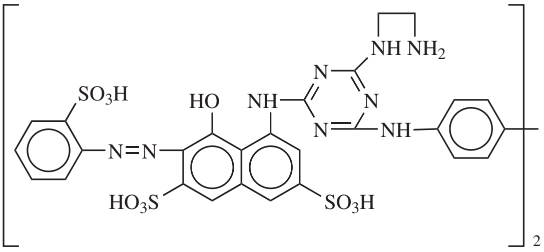


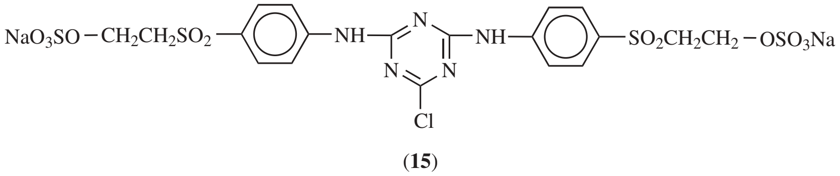
Fig. 27. Exhaustion–fixation curves from the aminoalkyl dye–FAP method, using 4% o.w.f. bis(aminoalkyl) dye. Filled Squares—Exhaustion (E), Open Squares—Fixation (F), Open Circles—Fixation (T).

using aminoalkylamino-*s*-triazine dyes along with the above cross-linking agent. Very high exhaustion values were obtained and fixation values of 95% were recorded. This system had the advantage of low reactivity until the boil was reached, giving the dye an excellent opportunity to level before covalent bonding became significant. Typical results for the aminoalkyl dye (**14**) are shown in Figure 27.



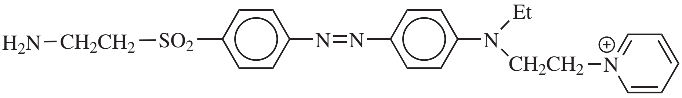
(**14**)

If such systems are to be further developed for covalently fixing dyes on cellulosic materials, the Basazol experience appears to indicate that fiber-substantive cross-linking agents should be developed along with suitably nucleophilic dyes. Another system (46,47) has described the promising covalent fixation to cellulose of sulfonated chromophores containing pendant aminoalkyl groups by reaction of the dye and the cellulose with the cross-linking agent, disodio-2-chloro-4′,6-di(aminobenzene-4-sulfatoethylsulfone)-*s*-triazine (XLC) (**15**):



(**15**)

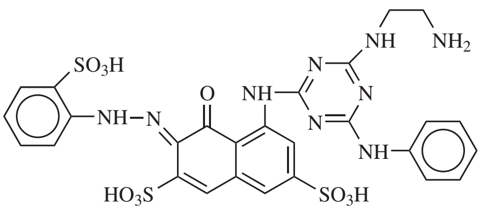
This agent (XLC) has also been investigated as a cross-linking agent to covalently fix amino-nucleophile containing dyes to wool (48) and nylon (49–51). In the case of wool, a very high degree of covalent fixation was recorded, either by coapplying dye and cross-linker at pH 6 (100°C) or by dyeing first and then adding the cross-linker to the exhausted bath. Nylon, owing to its paucity of nucleophilic amino sites, represented a bigger problem. However, promising results were obtained by synthesizing the aminoalkyl cationic dye shown (**16**) and applying it to nylon at pH 9 at the boil. Subsequent aftertreatment, at the boil, with XLC resulted in promising levels of dye-fiber covalent bonding, even in deep shades.



(**16**)

Cyanuric chloride (52) has even been proposed as a cross-linking agent for fixing dyes containing pendant amine groups to cellulosic fibers. Clearly, from a health and safety point of view, this approach is flawed; cyanuric chloride is a primary skin irritant and is known to cause severe allergic reactions in certain individuals.

A very simple cross-linking system to fix aminoalkylamino-*s*-triazine dyes on wool, based on hexamethylene tetramine (or hexamine), was studied by Lewis and co-workers (53). This agent, when coapplied to wool with nucleophilic dyes (Fig. 28) at pH 5 and at the boil, promoted covalent fixation of the dye to the fiber. Hexamine breaks down under such conditions, to produce formaldehyde, which is the active cross-linking species. Since covalent fixation does not commence until the boil is reached, the dyes have an excellent opportunity to migrate and produce level dyeings. Figure 29 shows typical exhaustion/fixation rate curves for dyeings produced with a monochloro-*s*-triazine reactive dye and dyeings produced with the aminoalkylamino-*s*-triazine derivative (**17**), in the presence of hexamine.



(**17**)

3.7. Modern Reactive Dye Systems for Wool Fibers.

In the light of increasing environmental concerns with heavy metals, it is desirable to use reactive dyes to match deep shades of black and navy blue in order to offer the dyer a

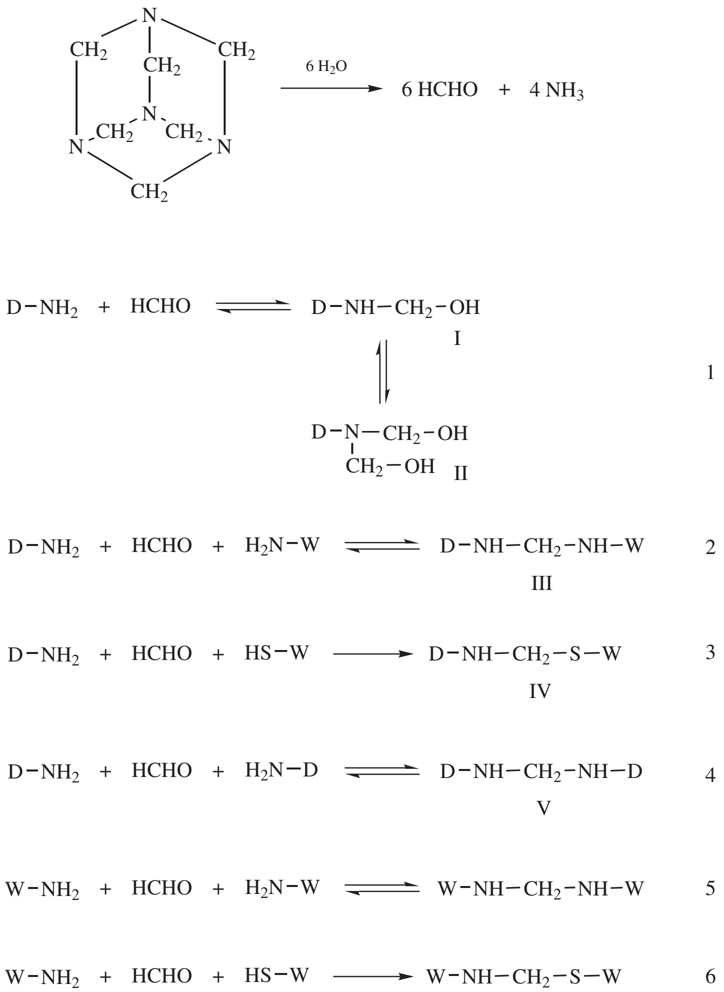


Fig. 28. Covalent bondings of nucleophilic dues to wool using hexamine.

real alternative to chrome dyes. In this context, dye-manufacturers have increased their efforts to offer wool dyers ranges of reactive dyes that are attractively priced; examples include Lanasol CE dyes from Ciba, Realan dyes from DyStar, and Drimalan F dyes from Clariant.

Black and navy blue shades are often based on the popular and widely available dye, CI Reactive Black 5. This dye is a bifunctional sulphatoethylsulfone, which activates to vinylsulfone on boiling at pH 5.5.

Müller (54) has studied AOX residues from various reactive dye systems and clearly there are advantages in selecting dyes containing only sulfatoethylsulfone residues as the reactive group.

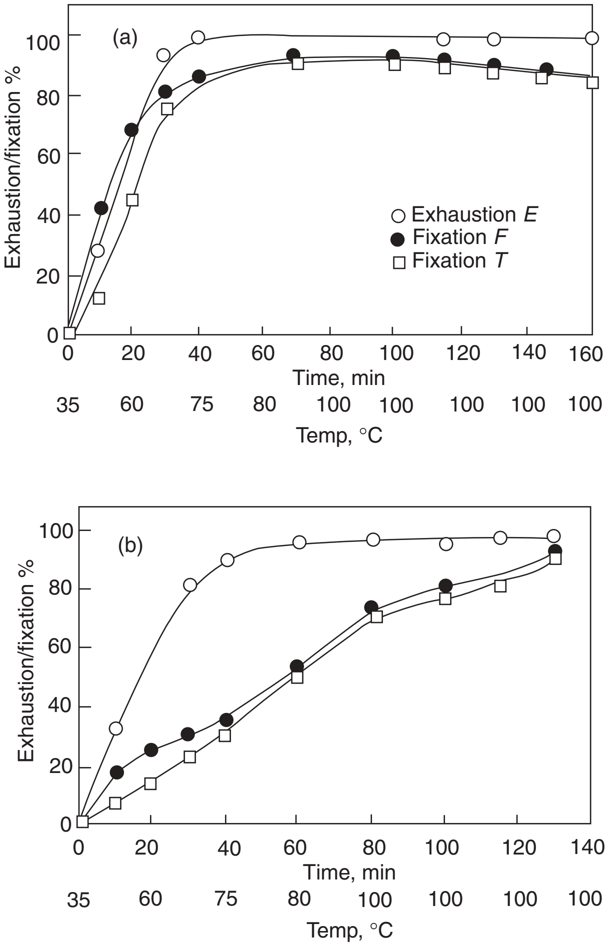
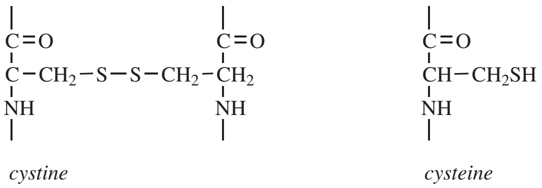


Fig. 29. Comparison of conventional reactive dyeing method (**a**) with the aminoalkyl dye plus HMTA dyeing method (**b**).

4. Developments with Reactive Dyes and Antisetting Agents

The chemistry of reactive dyes for wool has been fully reviewed (55,56). Of particular interest is the ability of certain reactive dyes to interfere with setting.

Permanent setting is a contributory factor to loss in wool fiber strength during dyeing, is the main cause of increased hygral expansion of wool fabrics following piece dyeing, is the reason for surface marks such as “crows-feet” in piece dyeing, and is the source of reduced bulk or yarn leanness following package dyeing (57–59). Apart from the above wholly negative effects, permanent setting can sometimes be seen as beneficial: such instances include the setting of wool yarn in hank form when using hank dyeing machines—this gives extra bulk and resilience to yarns and explains why this dyeing route remains popular for the



$$\begin{array}{lll}
| & | & | \\
C{=}O & C{=}O & C{=}O \\
| & | & | \\
C{-}CH_2{-}S{-}S{-}CH_2{-} & CH_2 & CH{-}CH_2SH \\
| & | & | \\
NH & NH & NH \\
| & | & |
\end{array}$$

Fig. 30. Representation of bound cystine and bound cysteine.

production of wool carpets. It is necessary to summarize the various chemistries involved in the production of permanent set in wool dyeing.

Wool is a heterogeneous material made up of keratin proteins, a small amount of non-keratinous proteins, and even smaller amounts of lipid and fatty acid materials. It is the keratinous or cystine disulfide cross-linked proteins that are responsible for most of wool's physical properties and the reactivity of the cystine disulfide residue is of paramount importance. The cystine content of wool varies, but an appropriate average value is 450 μmol/g and for its reduced form, cysteine, 30 μmol/g. Cystine and its reduced form cysteine are particularly sensitive to elimination reactions in water, the extent and nature of which depend especially on the parameters of pH, temperature, and time (60–62). The chemistry of these residues bound to the protein chains through the amide linkage can be drawn according to Fig. 30.

These amino acid residues can readily undergo a *trans*-1,2-β-elimination reaction to form the dehydroalanine residue that contains an activated double bond capable of subsequent Michael addition with suitable nucleophiles. The above elimination reactions are activated by the electron-withdrawing character of the adjacent amide carbonyl residue. In general, the thiol form, cysteine, more readily undergoes β-elimination than the disulfide form, cystine. Figure 31 summarizes these reactions.

The hydrogen sulfide or hydrosulfide anion produced in the above reaction is capable of ready reaction with cystine disulfide residues to produce further cysteine thiol residues that will undergo rapid β-elimination to dehydroalanine and hydrogen sulfide in boiling dyebaths even at pH 3; this is clearly the start of a runaway degradation reaction. The reactive entity, dehydroalanine, will undergo Michael addition with amino nucleophiles present in histidine and lysine residues and with thiol nucleophiles present in cysteine; in this way, more stable cross-links such as histidino-alanine, lysino-alanine, and lanthionine are formed (63,64). The extent and exact composition of these new cross-linking amino acids varies greatly with pH and temperature of treatment, since the nucleophilicities of amino and thiol residues increase with pH and temperature increases. The chemistry of these cross-linking reactions is exemplified, for lysine and cysteine residues, in Figure 32.

The above cross-links will not undergo degradation or elimination reactions under conditions normally encountered in wool dyeing and are thus likely to be of great importance in explaining the phenomena of permanent setting during wool dyeing. Also of some importance in setting is the so-called thiol-disulfide interchange reaction (65,66).

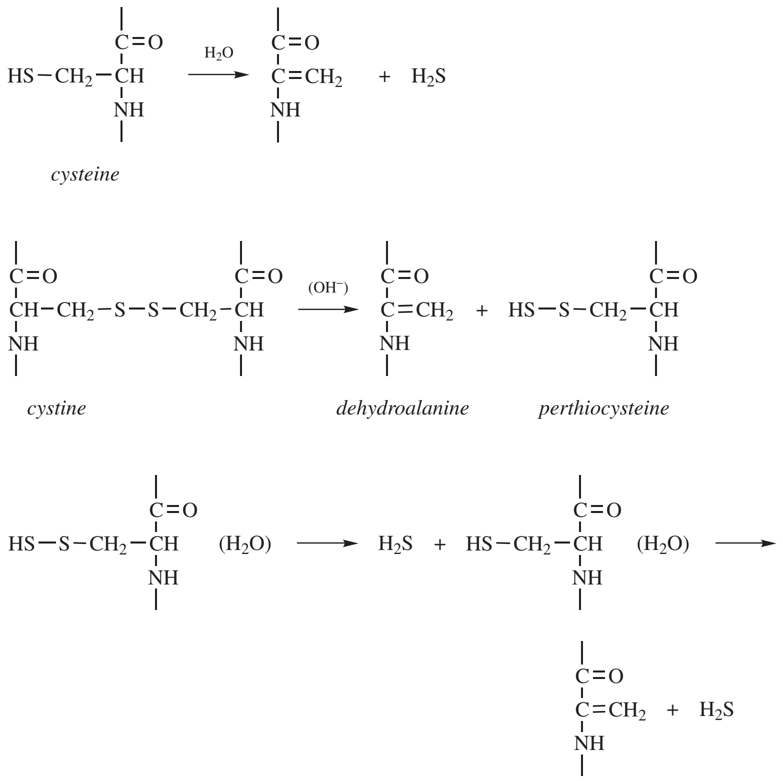


Fig. 31. Elimination reactions of cystine and cysteine.

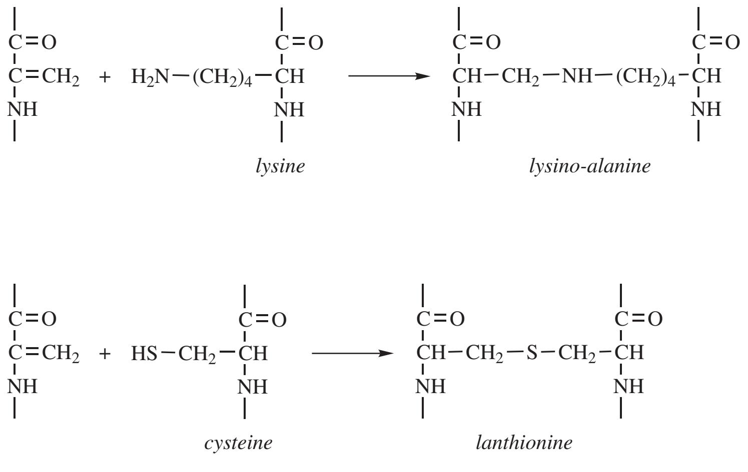


Fig. 32. Formation of lysino-alanine and lanthionine cross-links.

It is clear from the above discussion that control of setting in dyeing can be achieved in two ways:

1. Inclusion of oxidants in the dyebath.
2. Inclusion of fiber-substantive electrophiles in the dyebath.

   Most of the published research in this area uses Køpkes crease angle method for measuring set (67); typically including an antisetting agent in a pH 5 dyeing for 1 h at the boil; will reduce set from ~70 to ~30%.

Reactive dyes actively prevent damage in wool dyeing (68) especially those dyes that contain activated carbon–carbon double bonds and that thus react with fiber nucleophiles via a Michael addition mechanism (these dyes include acrylamido dyes and vinylsulfone dyes). The magnitude of this effect increases with increasing amounts of reactive dye applied being optimum at ~3% dye omf. The importance of this effect when dyeing wool fabric at pH 4 with the α-bromoacrylamido reactive dye, Lanasol Red 6G—4% omf, is demonstrated in Figure 33.

It is interesting to reflect why reactive dyes based on reactive halogenated heterocycles, which react with wool fiber nucleophiles by a nucleophilic substitution reaction are less effective in controlling wool damage in dyeing than are the

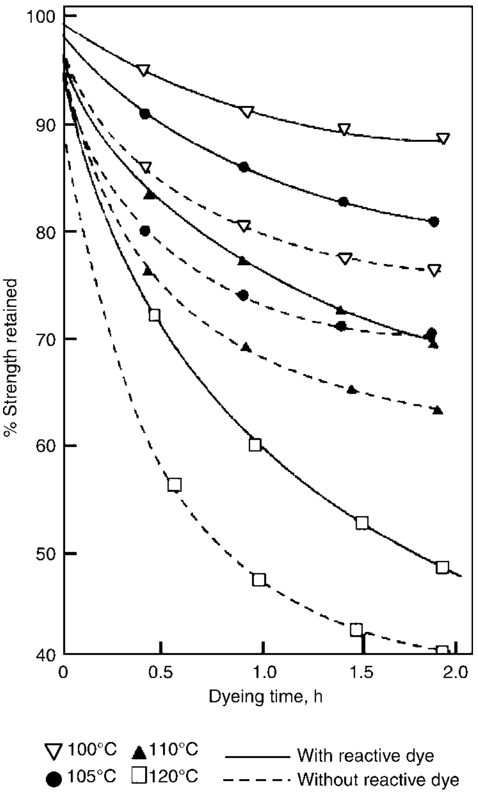


Fig. 33. Effect of time and temperature on fabric strength (68).

activated carbon–carbon double-bond type of reactive dye. From the above discussions, it is clear that successful control of damage and set go hand-in-hand and it is thus necessary to look carefully at the reactivity–stability of the reactive dye–cysteinyl residue covalent bond. Thioether derivatives of triazine or pyrimidine heterocycles will react further with amines to form bonds of greater stability; the leaving group in this reaction being the substituted thiol (69). The thioether formed from reaction with an activated carbon–carbon double bond is, however, resistant to nucleophilic attack or β-elimination under the mildly acidic conditions pertaining in wool dyeing (70).

When set was measured from wool fabric dyeings produced at pH 5 from the activated halogenated heterocycle type of reactive dye, Drimalan Red F-2G–Clariant (3% omf), a value of 74% was obtained; in contrast when the above dye was replaced with a reactive dye containing an activated carbon–carbon double bond, Lanasol Red 6G–CIBA (3% omf), a set value of 41% was obtained (71).

The reactions responsible for these differences are summarized in Figure 34.

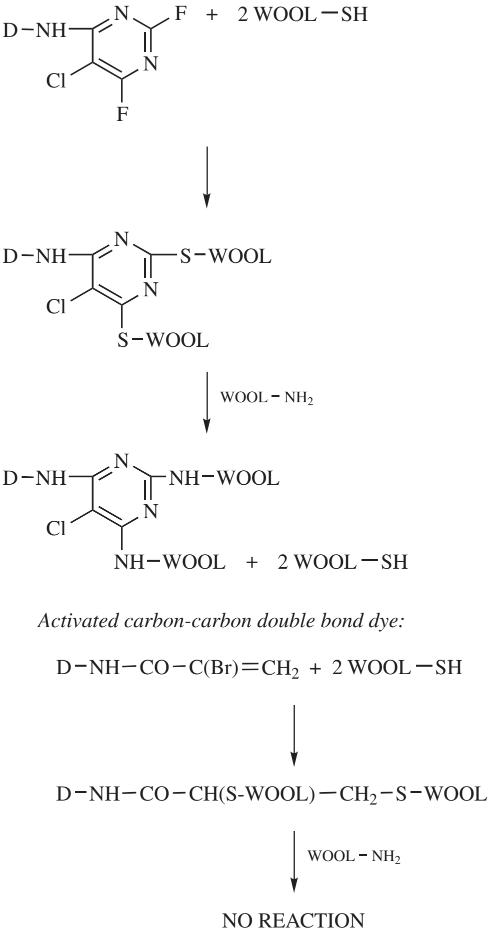


Fig. 34. Cysteinyl reactions with active hetercyclic and double-bond types of reactive dye.

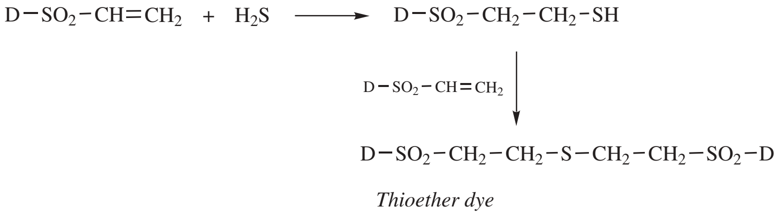


Fig. 35. Thioether dye formation in wool dyebaths.

The importance of hydrogen sulfide as a catalyst to promote setting–wool damage under dyeing conditions was proven by Lewis and Smith (72) who demonstrated the presence of a bis(dye-sulfonylethyl)-thioether dye after dyeing with a model vinylsulfone dye. This dye arises from the reaction of the vinylsulfone with free hydrogen sulfide, according to the mechanism shown in Fig. 35.

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