

COLOUR AND TEXTILE CHEMISTRY—A LUCKY CAREER CHOICE

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Introduction

In presenting this Olney lecture, I am conscious that it should cover not only scientific detail, but also illustrate, from a personal perspective, the excitement and opportunities offered through a scientific career in the fields of colour and textile chemistry.

The author began this career in 1959 by enrolling at Leeds University, Department of Colour Chemistry and Dyeing; the BSc course was followed by research, leading to a PhD in 1966. The subject of the thesis was "the reaction of ω -chloroacetyl-amino dyes with wool"; this study was responsible for instilling a great enthusiasm for reactive dye chemistry, wool dyeing mechanisms, and wool protein chemistry. It was a natural progression to work as a wool research scientist at the International Wool Secretariat (IWS) and at the Australian Commonwealth Scientific Industrial Research Organisation (CSIRO) on such projects as wool coloration at room temperature, polymers for wool shrink-proofing, transfer printing of wool, dyeing wool with disperse dyes, and moth-proofing.

Moving into academia in 1987 led to wider horizons bringing many new research challenges. Some examples include dyeing cellulosic fibres with specially synthesised reactive dyes or reactive systems with the objective of achieving much higher dye-fibre covalent bonding efficiencies than those produced using currently available systems; neutral dyeing of cellulosic fibres with reactive dyes; new formaldehyde-free crosslinking agents to produce easy-care cotton fabrics; application of leuco vat dyes to polyester and nylon substrates; cosmetic chemistry, especially in terms of hair dyeing and bleaching; security printing; 3-D printing from ink-jet systems; and durable flame proofing cotton with formaldehyde-free systems. The lecture will attempt to capture the exciting nature of the challenges faced in using chemistry and chemical technology to tackle the above wide variety of projects and underline the great satisfaction such a career provides. In this paper, I propose to detail developments in reactive dyes and dyeing processes, advances in ink-jet printing processes, reactive arylating agents to allow disperse dye application to wool and cotton, and new textile crosslinking agents for easy-care finishing of cotton.

In 2004 the author partially retired but became more involved in two companies: Inovink Ltd., a security printing business that has specialised in infra-red absorbing pigments, and Green Chemicals plc, which is developing new flame-proofing processes, new hair dyes, activated bleaches, and new treatments to dye and shrink-proof wool. This latter company was 'spun' out of the university following a patent covering the use of percarbamic acid [$\text{NH}_2\text{-CO-OOH}$] as an activated bleach [1].

Reactive Dyes and Dyeing Processes

Reactive Dye History

The history of reactive dyes is a fascinating story [2-4]. In 1938, IG Farben launched the first reactive dye, Supramine Orange R (Fig. 1), but at that time the excellent wet-fastness properties on dyed wool were not attributed to the formation of a dye-fiber covalent bond.

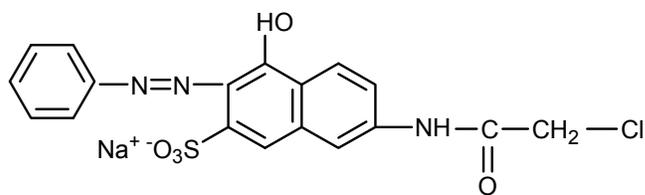


Fig. 1. Supramino Orange R.

The author's first encounter with reactive dyes involved synthesis of the above dye, applying it to wool, hydrolyzing the keratin proteins to their constituent amino acids, and estimating the carboxymethyl-amino acids present in the hydrolysate to identify the fiber nucleophiles involved in reaction with the dye. Cysteine thiol was most important, followed by histidine secondary amino and finally lysine ϵ -amino [5,6]. This work formed a significant part of the author's PhD thesis.

In 1948 Heyna and Schuhmacher [7] and the Hoechst Company patented dyes that contained a β -sulfatoethylsulfone side-chain and that gave wool dyeings of excellent wet-fastness—these dyes were marketed as Remalan Fast dyes for wool. It is difficult in hindsight to believe that the patentees did not realize that these were, in fact, fiber-reactive dyes and perhaps company policy did not wish such ideas to be common currency. This groundbreaking 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.

Guthrie published an important paper in 1952 [8] in which it was shown that a sulfatoethoxyphenylazo dye could be applied and fixed on cotton by an 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 led to the dyeings showing poor rub-fastness, especially in deep shades; however, this problem was absent in those dyes that contained sulfonate groups directly attached to the chromophore (e.g., the bluish-red dye prepared by diazotizing 2-(p-aminophenoxy)ethylsulfuric acid and coupling to 1,8-dihydroxy-naphthalene-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 water-soluble chromophore containing a pendant reactive group.

In 1956, the first range of fully water-soluble reactive dyes for cellulosic fibres was launched by ICI and named Procion MX. Work by Rattee and Stephen [9], who were subsequently awarded the Perkin medal of the Society of Dyers and Colourists, 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, 40C).

There are many texts which describe the subsequent explosive development of reactive dye systems [e.g. 2,3,10-12]. Today, the reactive dyes occupy a vital place for dyeing cellulosic fibres to a wide gamut of shades and their use on polyamide fibres is rapidly increasing.

Reactive Dyes Giving Improved Levels of Fixation on Cellulosic Fibres

Reactive dyes are applied to cellulosic fibres 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 about 30% of the market,

the residual, most popular application method being "exhaust" dyeing. The reason for the current popularity of the latter method lies in the short-run, high fashion nature of the textile industry, which 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 [13] who published the following table (Table I) 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 I: The fixation yield of various reactive red dyes (from Douthwaite, et al. [13])

Dye-reactive group	3% o.m.f.	6% o.m.f.
MCT/VS	76	68
MFT	64	56
MFT/VS	61	50
DFMCP	74	67
VS	68	58
MCT/MCT	57	49

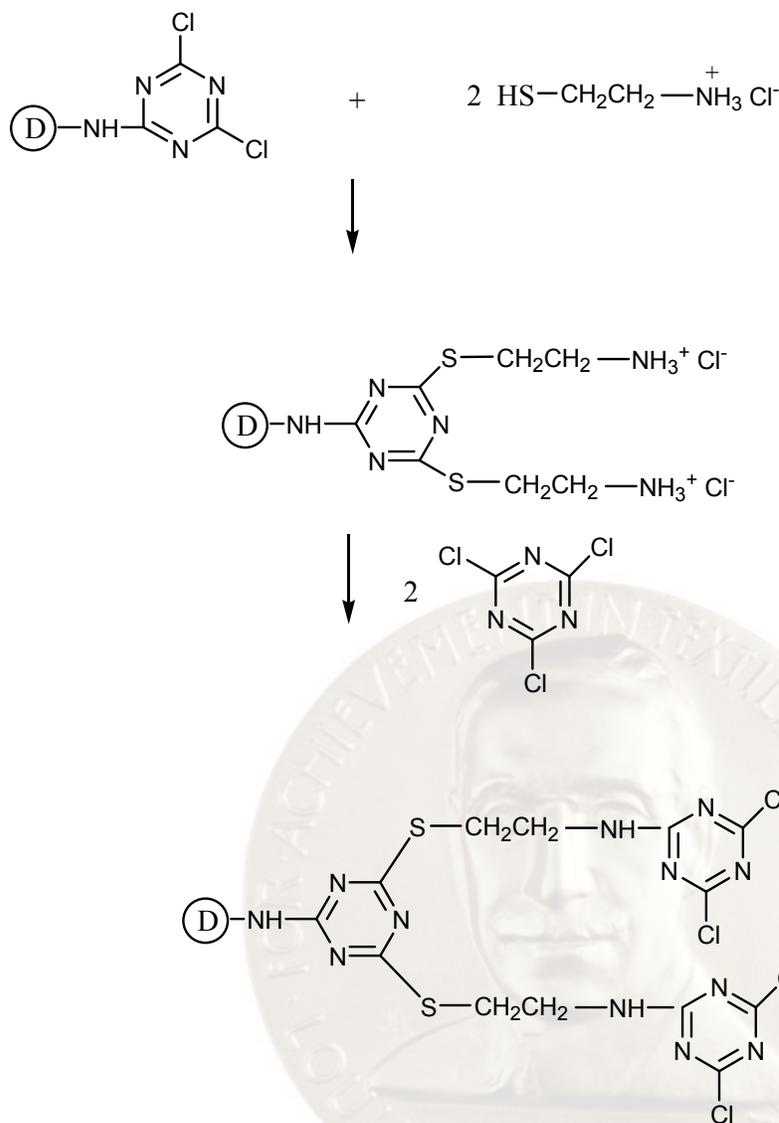
In the above Table, MFT = monofluoro-*s*-triazine, MCT = monochloro-*s*-triazine, VS = vinylsulfone, and DFMCP = difluoro-monochloro-pyrimidine.

The above table 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 washed away. Given that reactive dyes are highly water soluble and thus difficult to remove from dye-house effluent at the water treatment works, colour in rivers is a problem associated with the practice of cellulose fiber dyeing using reactive dyes.

It is well known that increasing the number of reactive groups attached to the dye molecule increases fixation yields and as a consequence, there are many bi-functional dyes on the market. If tri- or tetra-functional dyes could be economically manufactured then it might be expected that improved cotton reactive dyeing efficiencies would result.

As early as 1975 Hoechst launched the tri-functional dye, Remazol Red SBB (C.I. Reactive Red 181), which contained a monochloro-*s*-triazine group plus two divinylsulfone groups linked through an aliphatic amine to the triazine residue; Hoechst also patented other dyes of this type [14].

Tetra-functional reactive dyes have been claimed in the patent literature; for example, chromogens containing two vinylsulfone/monohalo-triazine residues [15]. In a Proctor and Gamble patent [16], the author and his co-workers describe tetra-functional reactive dyes prepared from the reaction of dichloro-*s*-triazine dyes (or difluoro-monochloro-pyrimidine dyes) with cysteamine and subsequent reaction of the two pendant primary amines with cyanuric chloride. The preparation is shown in Fig. 2.



where (D) is a sulphonated chromophore

Fig. 2. Preparation of tetra-functional halo-triazine dyes.

When applied, in medium shade depths by long-liquor processes at 50C in the presence of 40 g/dm³ sodium sulfate and then fixed with sodium carbonate additions, these dyes gave total fixation efficiencies greater than 95%. In addition, the large hydrophobic side-chain gave the dyes very good combinability properties in tertiary mixture 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 to enhance water solubility of the dyes.

The author and his research group [17] further developed the above concept by replacing cysteamine with ethylenediamine. The two amine groups in protonated ethylenediamine show differing pK_a values (pK_{a1} is 6.86 and pK_{a2} is 9.92 at 25C [18]), which makes possible simple control of its selective substitution reactions with halo-heterocycles. Using this information, the following tetra-functional dye was synthesized (Fig. 3):

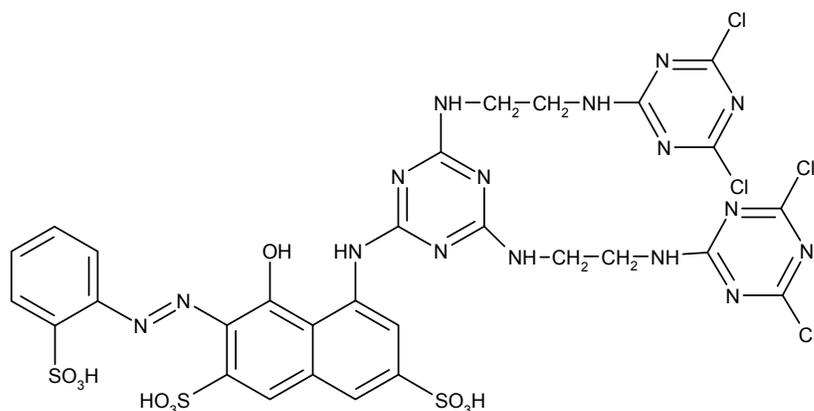


Fig. 3. Structure of a tetra-functional reactive dye [17].

The above dye was applied to cotton fabric by both long-liquor, exhaustion dyeing and by cold pad-batch (24 hr)—total efficiency values for dye-fiber fixation are shown in Tables II and III.

Table II. Total dyeing fixation efficiency (T) values from long-liquor application of dichloro-s-triazine (DCT) dye and bis-dichloro-s-triazine (bis-DCT) dye in the presence of various alkalis at different dye-bath temperatures—dyes used at 2% o.m.f.

%T								
Alkali Used (20 g/dm ³)	TSP		Na ₂ CO ₃		NaHCO ₃		Na ₂ HPO ₄	
Dyeing Temperature	DCT	Bis- DCT	DCT	bis- DCT	DCT	bis- DCT	DCT	bis- DCT
40C	68.4	88.9	73.5	92.8	72.3	33.8	80.9	35.5
50C	68.6	89.6	68.6	93.0	72.8	44.4	76.2	46.5
60C	62.4	84.3	62.9	90.9	65.5	51.3	65.3	47.8

Table III. Total fixation efficiencies values from pad-batch application of DCT dye and bis-DCT dye in the presence of various alkalis—dyes used at 2% o.m.f.

TSP 20 g/dm ³		Na ₂ CO ₃ 20 g/dm ³		NaHCO ₃ 20 g/dm ³		Na ₂ HPO ₄ 20 g/dm ³	
DCT	bis-DCT	DCT	bis-DCT	DCT	bis-DCT	DCT	bis-DCT
60%	95%	59 %	96%	27%	71%	71%	82%

In exhaust dyeing [Table II] optimum fixation efficiency was recorded at pH 10.5 using Na₂CO₃ at 50C. Overall, the fixation values obtained for the bis-DCT dyes are very good and, surprisingly, the dyeings produced are not sensitive to boiling in dilute acetic acid; this is in contrast to the poor acid-bleed resistance of comparative dyeings produced from the unmodified DCT dye. Undoubtedly, in the case of the bis-DCT dye, this is due to deactivation of the triazine reactive group by the aliphatic amino bridge linking triazine to the chromophore.

Neutral Fixation of Reactive Dyes on Cellulosic Substrates

The traditional method of dyeing reactive dyes on cotton from long-liquors, commonly termed "exhaust dyeing," relies on a two stage process: firstly, "exhaustion" of the sulfonated dye in the presence of salt and secondly, dye-fiber covalent bond formation or "fixation" in the presence of alkali (usually sodium carbonate or in some cases a sodium hydroxide/silicate mixture). If this two-step dyeing method could be replaced by a process that involves adding sufficient salt to the bath and raising the dye-bath to a temperature sufficient to achieve dye-fiber covalent bonding *without* adding alkali, the following benefits should emerge: cheaper dyeing processes, better reproducibility of the final dyeings, reduced reactive dye hydrolysis, and one-bath dyeing of cotton/polyester blends without the need to select alkali-stable disperse dyes. It is noteworthy that Nippon Kayaku, with their Kayacelon React range of nicotinic acid quaternary triazine dyes, has promoted the concept of neutral fixation [19,20]. In recent publications [21,22], we have demonstrated that many other reactive dye systems, in particular bifunctional dyes containing mono-fluoro-*s*-triazine groups and dyes containing free vinylsulfone groups, will fix efficiently to cellulosic fibres when applied at the boil under neutral conditions.

The dye-fiber covalent bond formation reaction depends on the interrelation between physico-chemical and electro-chemical forces at the cellulose/solution interface; major parameters affecting these interactions include bath pH, electrolyte concentration, and dyebath temperature. At the aqueous solution interface, the surface of the cotton cellulosic fiber acquires a negative charge, mainly because of the dissociation of accessible cellulose hydroxyl (Cell-OH) groups as expressed in Fig. 4.



Fig. 4. The dissociation of cellulose hydroxyl groups.

In the above scheme, K_a is the dissociation constant of the weak acid, Cell-OH; K_a is calculated according to the equilibrium concentrations of the various ionic species in Eq. 1.

$$K_a = \frac{[\text{Cell-O}^-][\text{H}_3\text{O}^+]}{[\text{Cell-OH}]} \quad \text{Eq. 1}$$

The higher the K_a value, the greater the acid strength; clearly the acid strength of cellulose hydroxyl groups is low (according to Neale [23] K_a for Cell-OH is 1.84×10⁻¹⁴ at 25C). The ease of dissociation of an acid is often expressed as its pK_a value which is the negative logarithm of its K_a value – the smaller the value of pK_a the stronger the acid. Cellulose-OH can be regarded as a very weak acid which has a pK_a value of 14.27, which means that at 25C and at the *theoretical* pH of 14.27, the concentration of the highly

nucleophilic species, Cell-O⁻, is equal to that of the extremely weak nucleophilic species, Cell-OH. Thus in classical reactive dyeing processes, alkali additions are used to increase the concentration of nucleophilic Cell-O⁻ groups. Temperature increases can achieve the same result since raising temperature from 25C to 100C can lower the pK_a values of conjugate acids by up to two units [24]—i.e. increasing the concentration of Cell-O⁻ one-hundredfold. Moreover, dissociation of acids is also affected by ionic strength—thus an increase in salt concentration will increase the dissociation of the proton from the cotton cellulose hydroxyl residue. The dependence of the rate of reaction on the ion concentration of the reactive medium is known as the primary salt effect [25]. Sumner [26] also showed that salt additions to the cellulose-dye system increased the internal pH value of the fiber.

By way of example [21], cotton samples were dyed with 2% o.m.f. pre-activated (vinylsulfone form) Remazol Black B at different holding temperatures (20C to 100C) for 60 min. The dyebaths contained Na₂SO₄ (80 g/dm³) as electrolyte and the liquor ratio adjusted to 10:1; subsequent exhaustion/fixation values are plotted in Fig. 5.

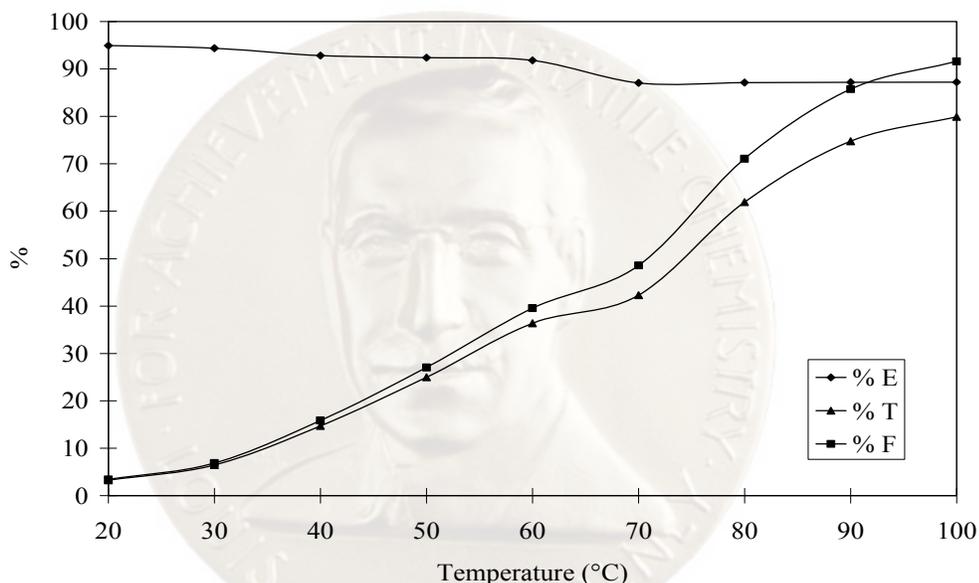


Fig. 5. Dye exhaustion, fixation and total fixation efficiency of activated Remazol Black B dyed 1hr at different holding temperatures under neutral conditions [from ref. 21].

As the temperature of dyeing increased, the amount of cellulosate anion formed increased and thus the absorbed dye fixation values improved. The rate of vinylsulfone group hydrolysis is both pH and temperature dependent and hydrolysis will increase with increasing temperature. The effects of varying the sodium sulfate concentration on the neutral dyeing properties of activated Remazol Black B (2% o.m.f.—dyed 1hr at the boil) are summarised in Table IV.

include acrylamido dyes and vinylsulfone dyes). The magnitude of this effect increases with increasing amounts of reactive dye applied being optimum at circa 3% dye o.m.f. The importance of this effect when dyeing wool fabric at pH 4, at and above the boil, with the α -bromoacrylamido reactive dye, Lanazol Red 6G – 4% o.m.f., is demonstrated in Fig. 7.

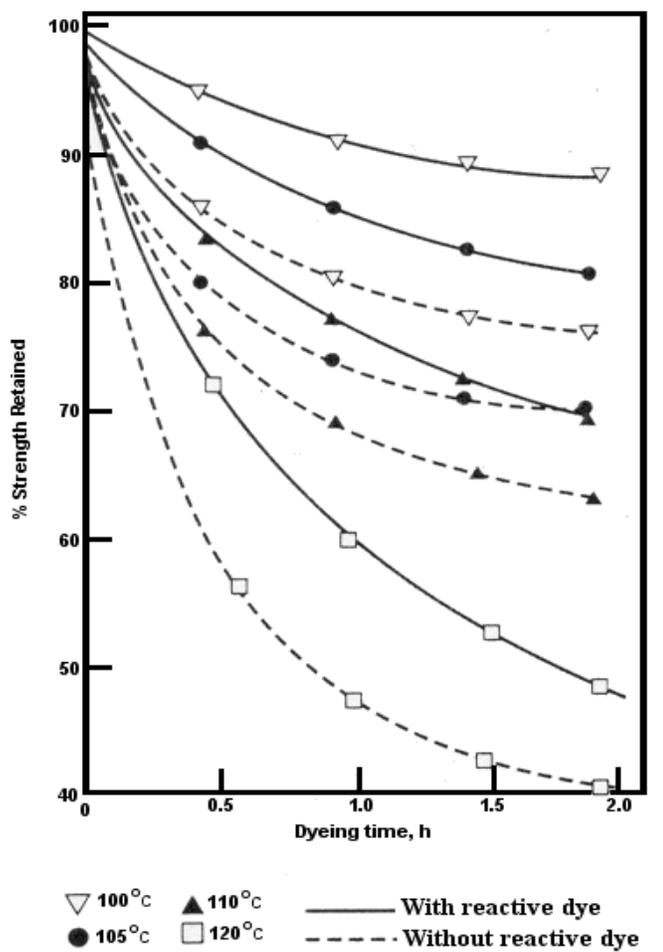


Fig. 7. Effect of dyeing time and temperature on wool fabric strength.

It is interesting to reflect why those 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 activated carbon-carbon double bond type of reactive dye. Wool damage and wool setting reactions occur during dyeing because of β -elimination of cysteine thiol residues to produce new, more stable crosslinks. Reactive dyes by reacting rapidly with cysteine thiol interrupt this elimination mechanism; it is thus necessary to look carefully at the reactivity/stability of the reactive dye-cysteinyll residue covalent bond. Thioether derivatives of triazine or pyrimidine heterocycles will react further with wool amino residues to form bonds of greater stability; the leaving group in this reaction being the substituted thiol [28]. The thioether formed from reaction with an activated carbon-carbon double bond is, however, resistant to nucleophilic attack by wool amines or β -elimination under the mildly acidic conditions pertaining in wool dyeing [29].

When set was measured from dyeings on wool fabric produced at pH 5 from an activated halogenated heterocycle type of halo-pyrimidine reactive dye dyed at (3% o.m.f.), a set value of 74% was obtained; in contrast when the above dye was replaced with a reactive dye containing an activated carbon-carbon double bond (3% o.m.f.), a set value of 41% was obtained [30].

The reactions responsible for these differences are summarized in Figs. 8 and 9.

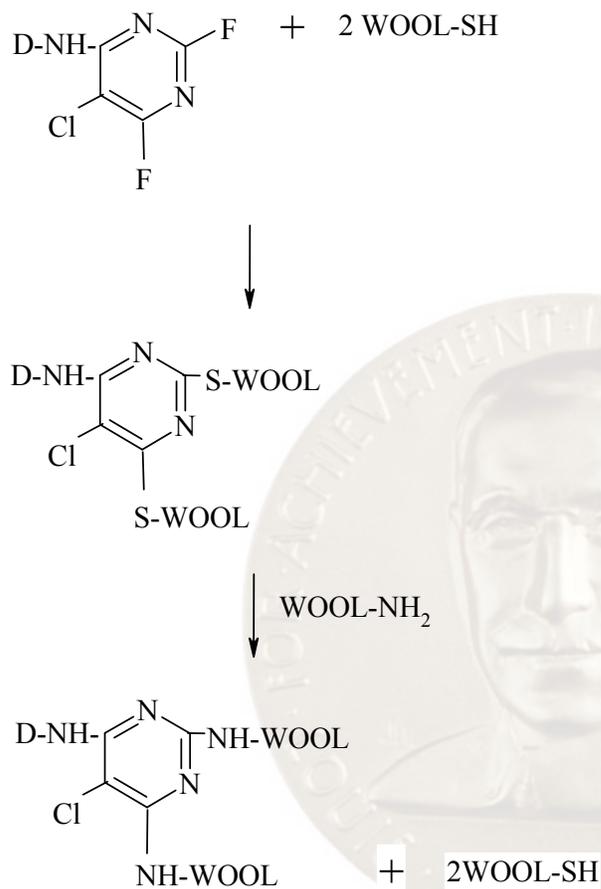


Fig. 8. Cysteinyl reactions with activated heterocycle dye.

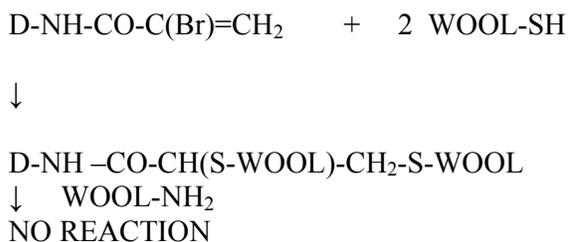


Fig. 9. Cysteinyl reactions with activated carbon-carbon double bond dye type of reactive dye.

Hydrogen sulfide, produced from β -elimination of cysteine thiol, acts as a catalyst to promote setting/wool damage under dyeing conditions; this mechanism was proven by Lewis and Smith [31] who demonstrated that a bis-(dye-sulfonylethyl)-thioether dye was present in the bath 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. 10.



Thioether dye

Fig. 10. Thioether dye formation in wool dye-baths.

Dyeing Nylon with Cationic Reactive Dyes [32,33]

When nylon is dyed with anionic reactive dyes, usually by exhaust dyeing at pH 5, there is a rapid build up of fixed negative charge, which combined with the large negative contribution from excess carboxylate groups in the fiber, leads to difficulty in achieving build-up of anionic dye. If cationic reactive dyes were to be prepared, then this situation will not pertain and deep shades of excellent wet-fastness should be achievable. Thus we prepared a vinylsulfone disperse dye and solubilised it in water by reaction with thio-choline (Fig.11).

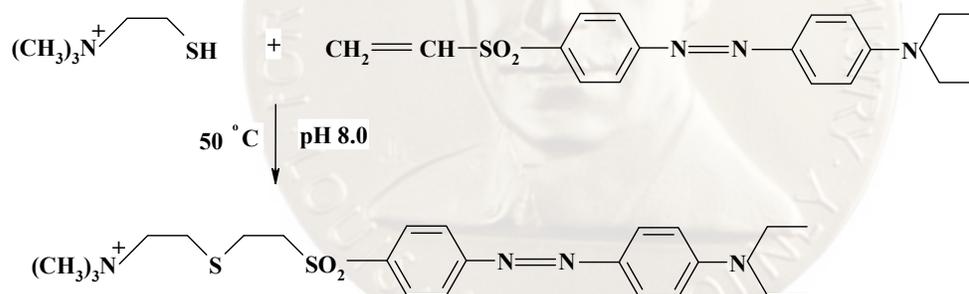


Fig. 11. Preparation of a cationic reactive dye.

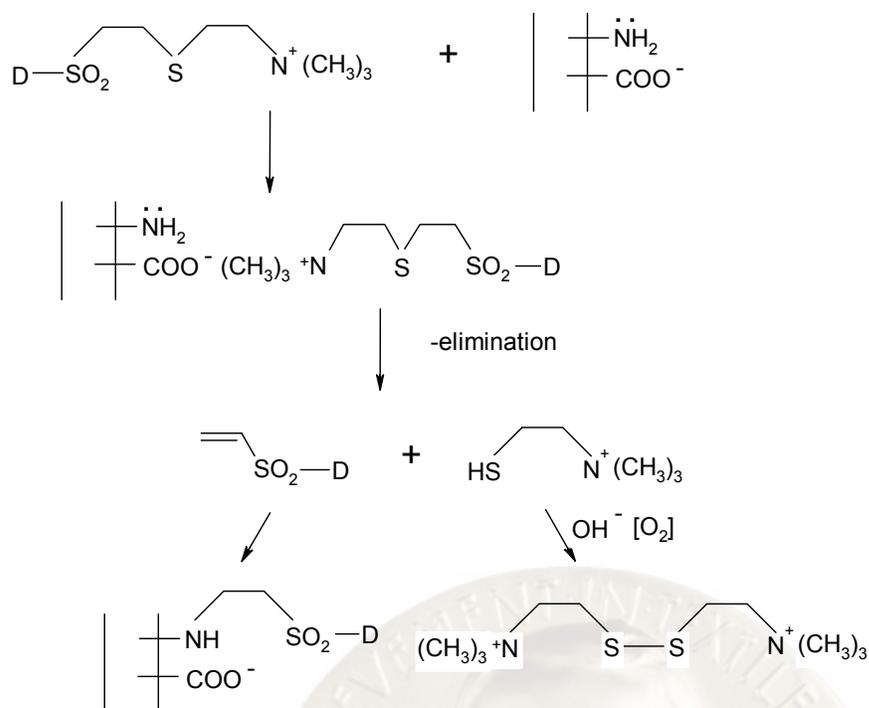


Fig. 12. Application of a cationic reactive dye to nylon.

The novel dye was cationic and was substantive to nylon at pH 10; at the boil it readily eliminated the thio-choline residue to reform the reactive vinylsulfone disperse dye and dye-fiber covalent bonding thus proceeded smoothly (Fig.12). Fixation efficiency values for a 2% shade were determined and are reproduced in Table V.

Table V. Fixation (F) and Total fixation efficiency (T) when dyeing the cationic reactive dye on nylon (2% pure dye o.m.f.) [33].

pH (dyebath)	A ₄	F (%)	T (%)
3	0.00	1.88	0.07
4	0.00	11.53	1.56
6	0.124	46.63	22.76
7	0.138	89.18	82.99
8	0.188	91.30	86.22
9	0.163	92.37	88.16
10	0.133	95.21	92.85

The above table shows that the cationic dye when applied to nylon at pH 10, gave excellent uptake and fixation; the wash-fastness and light-fastness of the dyeings produced were found to be very good.

Ink-jet Printing of Textiles

The advent of practically useful ink-jet printing systems has brought about an exciting technological revolution in such diverse fields as paper printing, electronic device printing, textile printing, micro-fabrication and even printing living tissue scaffolds. Not all of these areas are fully mature and some such as the tissue engineering area can only be described as fledgling. This paper discusses the status of textile printing using ink-jet, along with a description of some new studies in our laboratories; these include new methods to activate cotton fabrics towards ink-jet printing with reactive dyes, and the development of "all-in" inks containing an 'activator' which avoid the necessity to pre-treat fabrics. The latter approach is novel since the activators allow almost full fixation of reactive dyes on unmodified cotton even at pH 6.5 further reinforcing the value of neutral conditions to covalently fix reactive dyes on cotton. Studies aimed at producing resist print styles on cotton by ink-jet printing will also be described.

Ink-jet Printing of Textile Substrates with Reactive Dye Based Inks

Currently, commercial ink-jet textile printing operations require the pre-treatment of cellulosic fabrics with pad liquors containing a thickener and alkali (such as sodium carbonate or sodium bicarbonate). We have found [34] that this procedure can also use a neutral fixation "activator", such as sodium acetate, sodium formate, sodium trichloroacetate, sodium cyanate, or sodium borate. The results indicated that fabrics pre-treated, even at pH 6.5, with such an 'activator' resulted in subsequent ink-jet prints that exhibited much higher levels of reactive dye fixation than corresponding prints produced on alkali pre-treated fabrics.

The "activators" found to be of most use as pre-treatments were: sodium acetate, sodium formate, sodium cyanate, and sodium trichloroacetate. The following "activators" were suitable for inclusion in the *all-in* ink formulations: lithium acetate, lithium formate, and lithium trichloroacetate. In the ink formulation, lithium acetate was found to give best results in terms of dye fixation with minimum effect on dye solubility. A typical "all-in" ink, containing both a reactive dye and the dye "activator" in the same cartridge, was prepared as follows: 100-200 g/dm³ reactive dye, 100 g/dm³ lithium acetate, 200 g/dm³

N-methylmorpholine-N-oxide, 20 g/dm³ 2-pyrrolidinone, 25 g/dm³ propan-2-ol, and 20 g/dm³ Ludigol (BASF) (adjust to pH 6.5 with an appropriate carboxylic acid and make up to 1 L with distilled water).

The reactive dyes used in the inks were selected from Remazol (sulfatoethylsulfone), Cibacron F (monofluorotriazine), Cibacron C (monofluorotriazine, vinylsulfone), Sumifix Supra (monochlorotriazine, sulfatoethylsulfone), Procion (monochlorotriazine), Drimarene K (difluoromonochloropyrimidine), and Sumifix HF (modified vinylsulfone).

All-in Prints on Polyamide Fibres

Chlorinated wool, silk, and nylon 6,6 fabrics were printed with the reactive dye/lithium acetate pH 6.5 formulation developed for cotton fabrics; following steam fixation (10 min, 104C), the colour in the wash-off solutions indicated that the reactive dyes fixed very well on wool but less well on silk and nylon. The colours on chlorinated wool were less

brilliant than on cotton due to the propensity of chlorinated wool to thermal yellow in steaming.

Resist Printing Cotton with Sodium Sulfite

Discharge printing provides a method of producing either a white or coloured image on a solid ground fabric; unfortunately, the print shade range from this process is limited. An alternative approach to discharge printing is resist printing. In resist printing, the resist agent prevents fixation of the background colour by chemical means (resist agent inhibits dye fixation) or physical means (resist agent inhibits dye absorption), in both cases giving a white print against a solid colour background. A coloured print may be achieved by incorporating a suitable dye or pigment in the resist ink. In all cases it is *extremely important* that the ground shade reactive dye(s) do not fix during the drying process prior to the printing process, otherwise white images cannot be produced following printing with the resist agent, then steam development and washing-off. A suitable process includes the following steps: pad the fabric with a pad liquor containing a sulfatoethylsulfone reactive dye (Remazol) and the metal salt of an organic acid (sodium formate to pH 6.5), dry at 70C-80C, overprint with a print paste containing either the sodium sulfite resist agent, or for illuminated prints sodium sulfite plus a monochloro-*s*-triazine reactive dye (Procion P/PX); fixation is achieved by steaming at 102C for 8-10 min, finally soap-off to yield either a white and/or a coloured print on a coloured background.

The reactions occurring during the process are represented in Figs. 13 and 14.

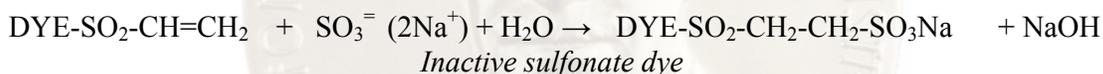


Fig. 13. Reaction of sulfatoethylsulfone dye with resist agent.

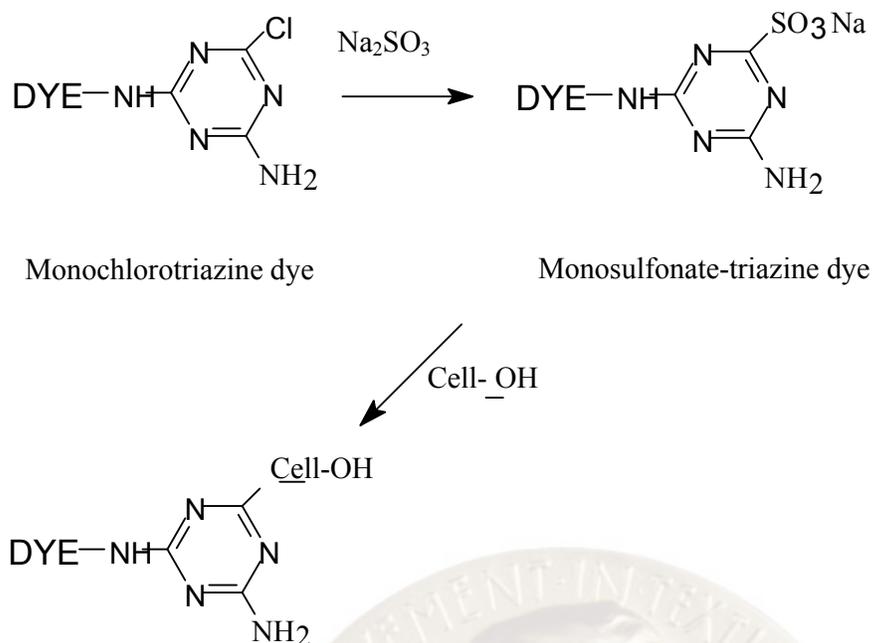


Fig. 14. Reaction of monochlorotriazine dye with resist agent and cellulose.

Background fabrics for use in the ink-jet sulfite resist process could be prepared by padding and drying cotton fabric with a dye liquor containing Remazol dyes (either in the sulfatoethylsulfone or the vinylsulfone form), an activator (sodium formate or sodium acetate) and a thickening agent so as to achieve a wet pick-up of 100%; to inhibit possible background dye reduction by liberated SO₂ in subsequent steaming, an anti-reductant, such as Ludigol (BASF), was incorporated in the ground pad liquor. After padding, the fabrics were dried at 50C for 3 min to yield coloured ground fabrics that could be used for subsequent resist printing operations. When using sodium formate as an activator, high levels of dye fixation were achieved for pad liquors possessing the Remazol dye in its pre-activated vinylsulfone form, whilst pad liquors containing sodium acetate gave equivalent results even when the Remazol dye was still in its sulfatoethylsulfone form. Weakly acidic pad liquors (pH 6.5) enabled the production of ground-shade fabrics having 4 to 5 days stability (i.e. no dye-fibre bonding or dye hydrolysis), whereas ground fabrics prepared using alkaline pad liquors require immediate printing to prevent unwanted ground dye fixation occurring. White image areas can be achieved by printing these prepared grounds with resist inks formulated from sodium sulfite. The addition of a tertiary amine, such as DABCO, to the resist ink formulation resulted in improved ground-shade dye deactivation (ground containing sodium formate) and so lower levels of sodium sulfite were necessary. However, inks containing reduced sodium sulfite concentrations were not successful in fully resisting ground fabrics containing sodium acetate; such ground fabrics still requiring the higher sodium sulfite concentrations to achieve total dye inactivation. Such inks could also be used to produce photographic quality images on sepia or black coloured ground fabrics; the resulting prints exhibit images of high definition, clarity, and sharpness.

Illuminated resist inks contained both a resist agent (sodium sulfite) and a suitable sulfite-stable monohalo-*s*-triazine reactive dye. On ground fabrics containing sodium formate, it was observed that illuminating inks containing monofluoro-*s*-triazine dyes

provided greater colour yields than corresponding inks containing monochloro-*s*-triazine dyes.

Resist Printing with Secondary Amines

In terms of the dye class selection, this system covers the opposite situation to the above; in this case, monohalo-*s*-triazine reactive dyes are padded on cotton fabrics and then ink-jet printed with a suitable secondary amine based ink formulation to produce a white image on a solid ground colour after appropriate fixation and soap-off procedures have been undertaken. A coloured image can be achieved by over-printing the resist printed areas with a coloured ink formulation containing either a vinylsulfone or a sulfatoethylsulfone reactive dye; such dyes are capable of forming a new reactive dye via reaction with a secondary amine and so are not deactivated towards subsequent covalent reaction with the cotton substrate. The processes involved may be summarised by the following steps:

- (1) pad the fabric with a pad liquor containing a monohalotriazine reactive dye and the metal salt of an organic acid,
- (2) dry at 70C-80C,
- (3) overprint with an ink containing N-methyltaurine and, if coloured resists prints are required, a sulfatoethylsulfone reactive dye,
- (4) steam at 102C for 8-10 min,
- (5) soap-off to yield either white only or coloured/white prints on a coloured background.

The reactions occurring during the process are represented in Figs. 15 and 16:

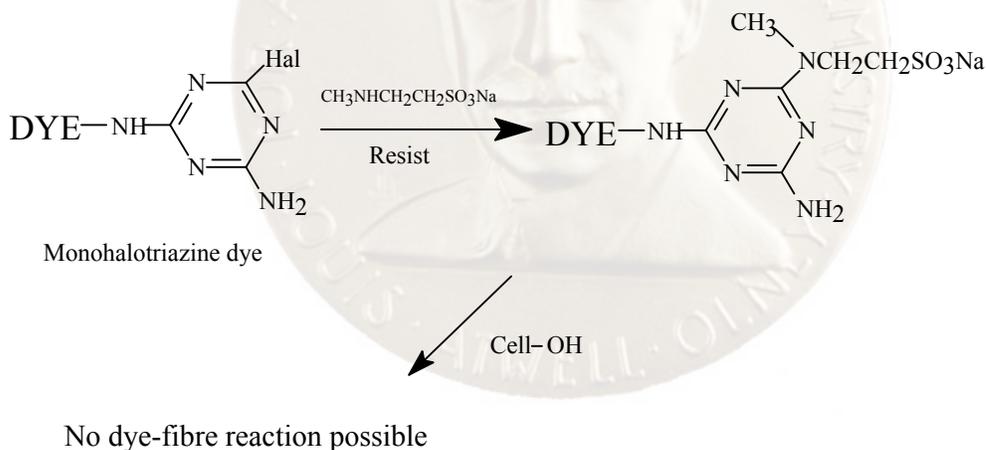


Fig. 15. Reaction of monohalo-*s*-triazine dye with N-methyltaurine.

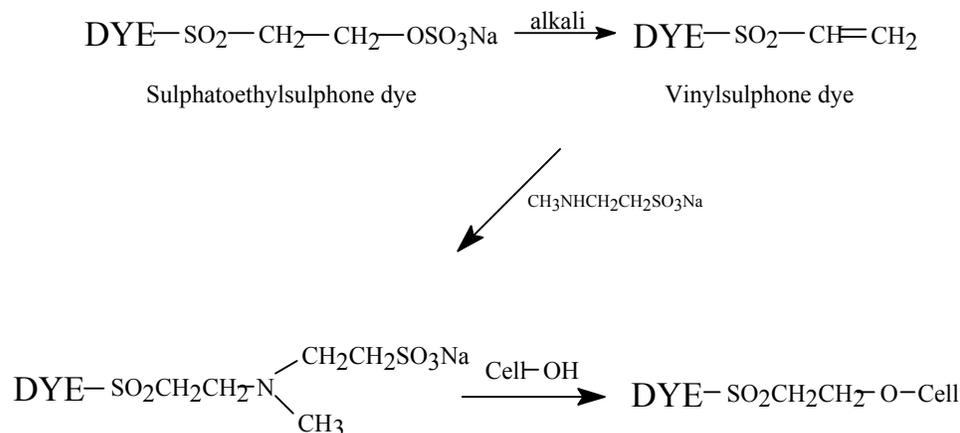


Fig. 16. Reaction of sulfatoethylsulfone dye with N-methyltaurine.

The ground shade for use in the secondary amine resist process may be produced by padding the cotton fabric with liquors containing a monofluoro-*s*-triazine dye, a thickening agent, an anti-reductant (Ludigol (BASF)) and a dye activator such as sodium formate. In particular, sepia ground shades were prepared using the following pad liquor: 8 g/dm³ Cibacron Red FN-R, 5 g/dm³ Cibacron Blue FN-R, 12 g/dm³ Cibacron Yellow F-3R, 8 g/dm³ Cellcosan 2000, 20 g/dm³ Ludigol, and 50 g/dm³ sodium formate (adjust to pH 5 with formic acid). The fabrics were padded and dried at 50C for 3 min on a Mathis laboratory drier—this low drying temperature ensured that no fixation of the reactive dyes occurred at this stage.

A dye activator, such as sodium formate, is added to promote the fixation of the ground dye under the mildly acidic conditions used. The activator also promotes the fixation of the illuminating dye when coloured images are being printed on resisted ground fabrics. Ground fabrics prepared by the above processes could be stored at room temperature for 4 to 5 days without any unwanted ground dye-fibre fixation occurring. After such storage times, the prepared ground fabrics could still be printed with secondary amine based resist inks and processed to produce white images on a coloured ground.

White (secondary amine resist process) ink formulations may be prepared using 10-100 g/dm³ N-methyltaurine (secondary amine), 150 g/dm³ ethylene glycol, 20 g/dm³ 2-pyrrolidinone, and 25 g/dm³ propan-2-ol (adjust to pH 5 via the addition of formic acid and make up to 1 L with distilled water); the process of ground dye inactivation by N-methyltaurine is indicated in Fig. 13. Such inks enabled white images to be produced on coloured ground shades. Alternatively, coloured images can be prepared by either including an illuminating dye, such as a Remazol (Dystar), Sumifix Supra (Sumitomo), Sumifix HF or Cibacron C dye, in the resist ink formulation, or by over-printing image areas previously printed with the white resist ink formulation.

Illuminated resist ink formulations capable of producing multi-coloured images on a coloured ground were formulated in accordance with the following recipe: 50 g/dm³ N-methyltaurine, 100 g/dm³ Remazol dye, 200 g/dm³ N-methylmorpholine-N-oxide, 20 g/dm³ 2-pyrrolidinone, and 25 g/dm³ propan-2-ol (adjust to pH 5 via the addition of acetic acid and make up to 1 L with distilled water).

The vinylsulfone-containing dyes used to prepare the illuminating inks included the following: Sumifix Supra Red 3BF, Sumifix Supra Yellow 3RF, Sumifix Supra Turquoise Blue BGF, Sumifix Supra Blue BRF, Remazol Red BS, Remazol Turquoise Blue G, Remazol Golden Yellow RNL, Remazol Brilliant Blue R, Remazol Brilliant Red F-3B, Sumifix HF

Yellow 3R, Sumifix HF Red 2B, Sumifix HF Blue 2R, Cibacron Red C-R, Cibacron Blue C-R, and Cibacron Yellow C-2R.

The Use of a Novel Water-soluble Arylating Agent to Dye Wool and Wool Blends with Disperse Dyes

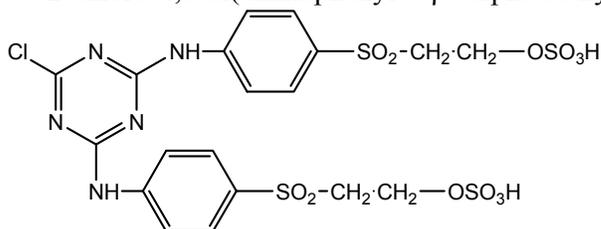
The covalent incorporation of bulky aryl residues in wool fibres, at a level of *circa* 13% o.m.f., results in the following interesting properties: disperse-dyeable wool [35], shrink-resist wool [35], and heat-settable wool [36]. Undoubtedly the above effects are due to an increase in the number of aromatic interactions [37], which arise from the negatively charged π -electrons in aromatic systems interacting with the less negative σ -electrons; these aromatic interactions are geometric in action and are seen as very important in determining crystal orientation [38].

Most of the successful early laboratory-scale work used benzoic anhydride as the electrophile to modify pre-dried wool fabric from dimethylformamide, typically at 70C for 2-3 hr; the modified wool fabric was of good colour and strength and was resistant to felting under machine washing conditions; in addition the wool could be dyed or printed with disperse dyes to a high standard of brilliance with disperse dyes offering the opportunity to develop the wool/polyester market by simplifying the coloration process. It would also be of interest to investigate the possible advantages of using novel bright chromophores available only in disperse dye ranges to reproduce such shades on wool. Clearly the disadvantages of this procedure, hindering its acceptance by the wool processing industry, are the necessity to work from organic solvents and the relatively high degree of fibre modification required to get the optimum effects.

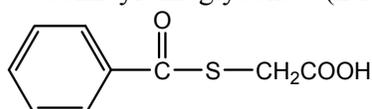
It is interesting to reflect that a similar procedure was developed in Japan for modifying cellulosic fibres so as to render them transfer-printable with existing disperse dye printed papers; this was the so-called Shikibo-Uni process and involved a pad pre-treatment of the cotton fabric with sodium hydroxide solution, passing the alkaline wet fabric through benzoyl chloride and finally washing-off with sodium hydroxide [39]. Such a process using the acyl chloride did not work well on wool fabric as it produced unacceptable yellowness.

Due to the above restrictions, there has been concerted activity within our research group to develop water-soluble acylating/arylating agents capable of incorporating covalently-bound bulky aromatic residues in either wool or cotton fibres. The leaving group in the reaction with fibre nucleophiles has to be the water-solubilising group. Some examples of the compounds evaluated are given in Fig. 17:

2-chloro-4,6-di(aminophenyl-4- β -sulphatoethylsufone)-1,3,5-triazine (XLC) [40]



benzoyl-thioglycollate (BTG) [41]



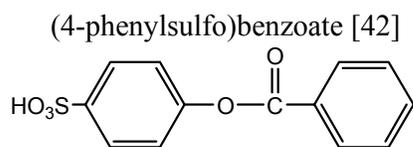


Fig. 17. Water-soluble fiber-reactive arylating agents.

The above compounds all contained water-solubilising groups that acted as leaving groups in nucleophilic substitution reactions; all were anionic and hence potentially co-applicable with commercially-available disperse dyes that contain anionic dispersing agents. In the case of cotton fabrics, most promise was shown by the BTG system applied by padding from an aqueous pad-liquor containing Na_2CO_3 , followed by steaming to fix. However this system could not be used on wool since the leaving group, thioglycollate, would damage the fibre at the high temperatures involved in the disperse dyeing process. In addition the thioglycollate leaving group reduced many disperse dye chromophores and hence this procedure was necessarily a two-step process involving pre-treatment followed by disperse dye application.

In order to achieve a one-bath, one-dye system for dyeing wool-polyester blends, it was decided to develop a water-soluble acylating agent for wool which was applicable from long liquor, had good solubility, was compatible with commercial disperse dye dispersions and which formed covalent bonds with the fiber in the region of pH 5-6; in addition, the agent should significantly protect the fiber from damage even when the dyebath temperature was raised to 120°C to fix the disperse dye on the polyester component. A number of compounds, based on the *s*-triazine/*p*-base system (*p*-base is anilino-4- β -sulfoethylsulfone) were thus synthesized, and as a result, one compound was selected since it gave promising disperse dyeings when included in a dyebath containing commercial disperse dye (virtually 100% dyebath exhaustion even at 2% disperse dye o.m.f.); this compound was coded as FAA 200 (Fig. 18) [43].

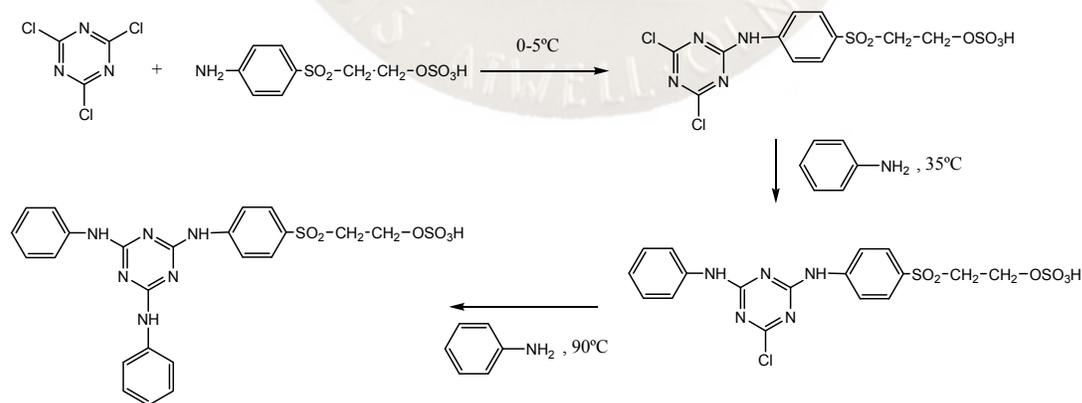


Fig. 18. Preparation of FAA 200.

This agent is fiber substantive and, when absorbed, reacts covalently with wool fiber nucleophiles (Wool-XH, where X is NH or S) to give Wool-X-(Ar)_n where (Ar)_n represents a residue of FAA 200. FAA 200 was applied to all-wool at pH 6.0 with selected disperse dyes

at 120C and for comparison the same disperse dye selection dyed on pure polyester fabric—the exhaustion of the wool dyebaths approached 100% when 10% o.m.f. FAA 200 was present, but in its absence very little disperse dye was taken up by wool. The results are summarized in Table VI.

Table VI: Colour yield values from dyeings produced with selected disperse dyes applied to all-wool fabric and polyester fabric (PES)

Disperse Dye	Colour Yield (f_k) Values			PES
	Wool No FAA	5% FAA	10% FAA	
C.I. Disperse Red 50	50	120	170	160
C.I. Disperse Orange 25	23	42	83	93
C.I. Disperse Violet 26	14	21	28	39
C.I. Disperse Red 167:1	48	106	128	127
C.I. Disperse Blue 79:1	37	81	117	136
C.I. Disperse Red 60	15	21	32	72
C.I. Disperse Yellow 119	12	51	60	73

The excellent colour yields of the disperse dyeings on wool and their promising wet-fastness properties are worthy of comment. Lewis and Pailthorpe [35] showed that wool acylated with benzoic anhydride showed high substantivity for disperse dyes and good wash-fastness (ISO2) properties, but similar acylations with propionic anhydride, although producing wool substrates having good substantivity for disperse dyes, gave dyeings of poor wash-fastness. Even more interesting perhaps was the observation that the benzoylated wool did not felt at all when tested to the Superwash standard (IWS-TM193) whereas the propionylated wool showed some felting (5% Area Felting Shrinkage - AFS); the acetylated wool gave 35%AFS and the untreated gave 65% AFS. Milligan and Wolfram [36] in an evaluation of heat setting properties (Hoffman press for 15 sec) of acylated wools showed a remarkable difference between aromatic acylations versus aliphatic acylations; benzoylated wool gave a crease angle of 63° whereas propionylated wool gave a value of 137°, and non-acylated wool gave a crease angle of > 170°. Clearly, the above observations indicate that the covalent incorporation of aromatic residues into wool fibres is highly desirable, since they increases significantly the forces of interaction between adjacent protein chains and also between the modified proteins and the disperse dye. These interactions are clearly being played out in the FAA 200 modified wool. Lewis [37] points out that multiple aromatic interactions have their basis in the relatively "positive" σ -electron system interacting with the strongly negatively-charged π -system on the benzene ring or in the extended π -electron system in the chromophore of the disperse dye; Hunter [38] has reviewed the nature of such aromatic interactions, along with their geometry-determining properties, in influencing molecular assembly and shape.

In the case of wool/polyester blends, varying from 60:40 to 40:60 wool:polyester, it was very feasible to disperse dye with just 5% o.m.f. FAA 200 in the dyebath; thus a 60:40 wool/polyester blend fabric was dyed with a variety of commercially-available disperse dyes at 2% dye o.m.f., in the presence and absence of FAA 200. The dyebaths were buffered to pH 7 using a sodium acetate (3 g/dm³)/acetic acid buffer; hydrogen peroxide (2 cm³/dm³ of 27%

w/v) plus Briquest 422-33N ($2 \text{ cm}^3/\text{dm}^3$) were also added to prevent reduction of the sensitive disperse dyes. The baths were raised to 129C at 2C/min. and the dyeing continued for 40 min at this temperature. At this stage, it was noted that the dye bath exhaustion was virtually complete for those baths containing FAA 200. Finally the fabrics were washed thoroughly in hot (50C) soapy water to remove any surface deposited dye. Results from these dyeings are shown in Table VII.

Table VII. Colour yield values from dyeings produced with selected disperse dyes on 60:40 wool:PES blend fabric

Disperse Dye	Colour Yield (f_k) Values		PES
	Wool/PES		
	No FAA	5% FAA	
C.I. Disperse Red 202	70	109	139
C.I. Disperse Orange 30	64	80	120
C.I. Disperse Yellow 114	28	54	69
CI. Disperse Violet 26	35	47	78
C.I. Disperse Red 167:1	73	121	127
C. I. Disperse Yellow 218	50	79	78
Dispersol Navy XF	72	129	150
Dispersol Navy G PC	62	130	110
Dispersol Rubine 3B PC	48	125	106
C.I. Disperse Red 60	19	23	40

This table reveals that the best results, in terms of colour yield on wool/PES substrates, are achieved using azo-based disperse dyes.

Dry rub tests on all the above dyeings produced on wool/PES gave values of 4-5 in all cases, indicating that there was little deposited surface dye. ISO2 washing results gave change of shade values in the region of 4-5 with nylon adjacent stain ratings of 3-4.

The fibre-protective effect of FAA 200 when dyeing wool at high temperatures was assessed by carrying out the following treatments on the 100% wool fabric: 0% and 5% o.m.f. FAA 200, pH 5.5, 100C for 60 min; 0%, 5%, and 10% o.m.f. FAA 200, pH 5.5, 120C for 30 min. The wet burst strength of the fabrics was measured according to IWS TM 29 and the results are shown in Table VIII:

Table VIII. Wet burst strength (WBS) of untreated and treated fabrics

Fabric	WBS (kg/cm^2)	% Strength Loss
Untreated	5.63	0.0
No FAA 200, 100C, 60'	4.75	15.6
5% FAA 200, 100C, 60'	5.82	0.0
No FAA 200, 120C, 30'	3.97	29.5
5% FAA 200, 120C, 30'	5.15	8.5
10% FAA 200, 120C, 30'	5.41	3.9

The above table demonstrates the remarkable ability of the reactive vinylsulfone group present in FAA 200 to block free thiolate anions as they are formed, thus limiting wool setting in the high-temperature treatment processes used; these results are similar to those achieved with vinylsulfone dyes [31]. When dyeing at 120C without FAA 200, the wool after 30 min treatment was brittle and yellow in contrast to its excellent condition when including FAA 200. Therefore, FAA 200 achieves two important effects when dyeing wool polyester blends above the boil with a single dye class: aryl sites are covalently incorporated for the disperse dye and fiber damage is reduced to less than that produced during conventional wool dyeing at the boil.

Cotton Crosslinking Agents

The crosslinking of cotton cellulose to achieve good wrinkle recovery properties is one of the triumphs of 20th-century textile chemistry. Recently, the class of compounds usually used in this procedure has been criticised from the point of view of free formaldehyde emission propensity; this class is typically represented by N,N'-di-methylol-di-hydroxy-ethylene urea (DMDHEU). Efforts have been made to replace this compound with polycarboxylic acids, which react with cotton cellulose via acid catalysis to form ester crosslinks. In all the latter work, success is judged not only on easy care performance of the treated fabrics but on the substitute chemical having a competitive market price to DMDHEU and also on the level of damage produced during processing.

Use of Triethanolamine-trisulfate (TES)

Cotton cellulose may be successfully etherified by reaction with organic sulfates in aqueous sodium hydroxide solution [44]. Padding cotton with 2-aminoethyl hydrogen sulfate (AES) in aqueous sodium hydroxide solution, followed by heat curing, is a useful treatment to produce aminised cotton fabric [45,46]. With this etherification chemistry in mind, we synthesised [47] the tri-functional agent, triethanolamine-trisulfate (TES), which, being multi-functional, should react to form new ether linkages with cotton and thus impart anti-wrinkle properties; in addition, a tertiary amine residue will be incorporated by these reactions changing subsequent dyeing properties. Since TES is formaldehyde-free and is synthesised from cheap intermediates, it offers the potential to compete with DMDHEU.

TES (potassium salt) was synthesised by reacting triethanolamine with chlorosulfonic acid (Fig. 19).

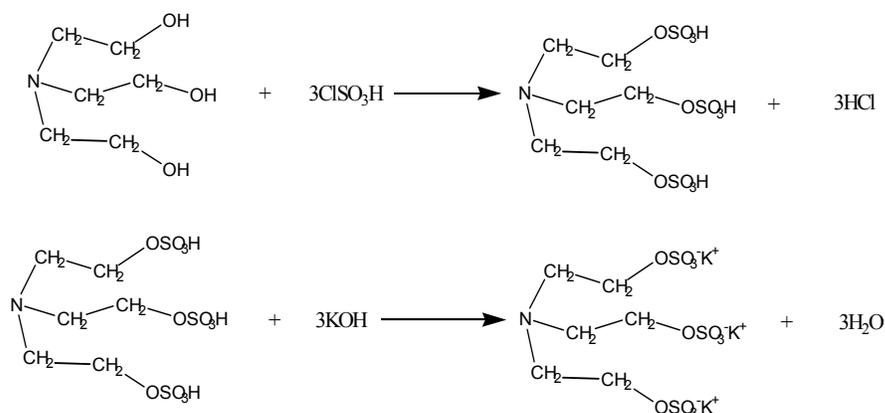


Fig. 19. Synthesis of TES (potassium salt) from triethanolamine and chlorosulfonic acid.

The reaction of TES with cotton is considered to involve intermediate aziridine formation. The TES aziridinium cation is highly activated and will ring open under alkaline conditions to add on to the nucleophilic cellulosate anion, as shown in Fig. 20. Alternatively, TES can undergo direct nucleophilic substitution reactions with cellulosate anions, eliminating sulfate ion, under strongly alkaline conditions (Fig. 21).

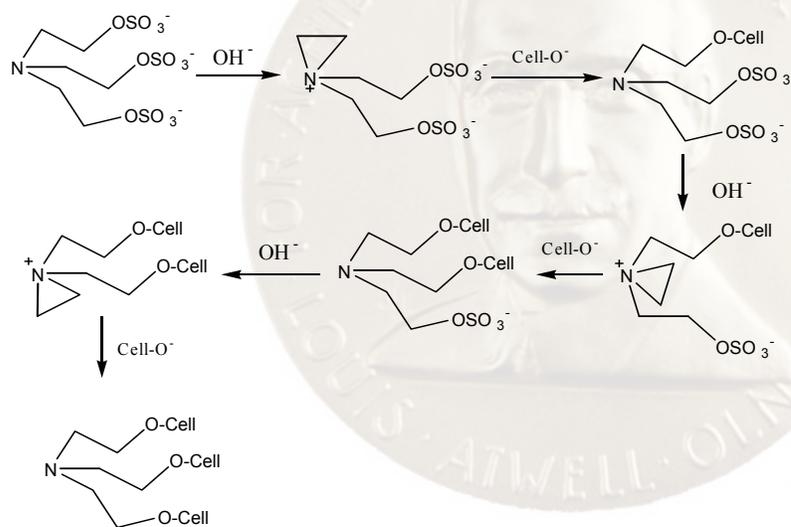


Fig. 20. The aziridinium cation mechanism for the reaction of TES with cellulose under alkaline conditions.

At room temperature (20C), TES is quite stable in weakly acidic aqueous solution, but not stable in neutral or alkaline aqueous solutions. Hydrolysis of TES ultimately forms the original triol, tri-ethanolamine. As expected, TES was found to hydrolyze less rapidly under neutral conditions than under alkaline conditions. It was found that TES is not stable in aqueous solution at any pH when heated over 80C. However, TES was found to be sufficiently stable for pad application to cotton fabric even when the pad-liquor contained sodium hydroxide; stability was also sufficient to allow intermediate drying at 80C for 5 to 15 min.

Application of TES to Cotton Fabric [47]

Cotton fabrics were impregnated with pad-liquors containing 100 g/dm³ or 200 g/dm³ of TES and various alkalis such as sodium carbonate, sodium phosphate, and sodium hydroxide. Following various fixing procedures, the treated fabrics were thoroughly rinsed in tap water and dried at ambient temperature.

Capillary electrophoresis (CE) was used to prove that covalent fixation of TES to cotton occurs; the treated cotton fabrics were extracted with water and the extracts analysed. Without steaming or baking the fabrics, TES was recovered quantitatively with only a trace of sulfate anion (even after drying the padded fabric at 80C); after steaming or baking the fabrics, sulfate anion was the main species detected plus very small amounts of hydrolysed TES. The presence of significant amounts of sulfate anion in the latter solutions confirms covalent reaction of TES with cotton cellulose since sulfate is the leaving group.

Fig. 21 indicates that high temperature steaming imparted a slightly higher dry Wrinkle Recovery Angle (WRA) to cotton fabric than did dry curing at the same temperature (130C). In every process, except high temperature steaming, the stronger the alkali employed, the better the WRA. There was hardly any WRA increase in those fabrics treated by the pad-batch method.

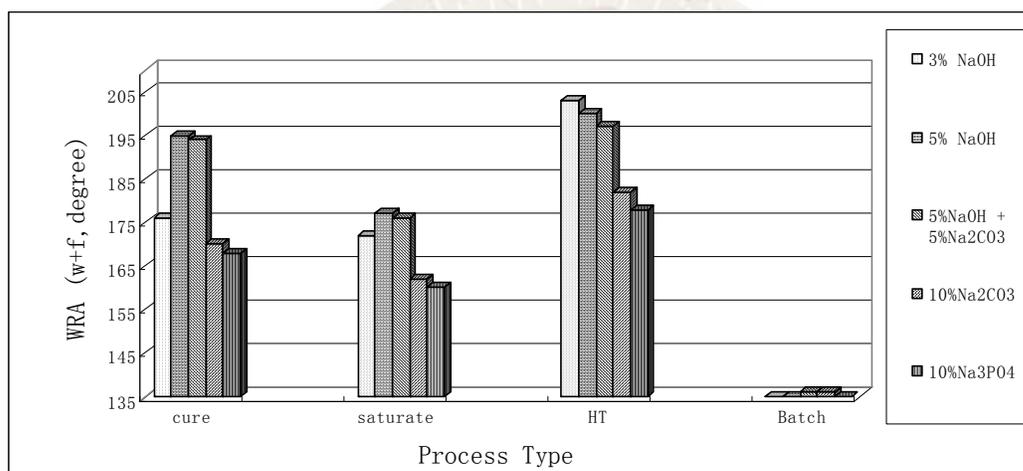


Fig. 21. Effect of alkali and finishing process on dry WRA.

In summary, a strongly alkaline pad-liquor is essential to maintain a sufficiently high pH during the TES reaction with cellulose; pad-dry-curing imparts a good dry wrinkle recovery angle to cotton but fabric yellowing is a problem.

The best WRA value obtained was 260°; achieved by employing 20% (o.m.f.) TES and 5.0 % (o.m.f.) NaOH. However, the whiteness index was -45 units. Under the same conditions, whiteness index was improved to 62.1 by adding 1% (o.m.f.) sodium borohydride, but wrinkle recovery angle decreased to 242°. Strength losses were up to 29.0%. The possible reason is that NaBH₄ may react with the intermediate aziridine [48] as shown in Fig. 22. Clearly if one of the reactive sites in TES reacts with borohydride, the chance to react trifunctionally with cotton cellulose will be reduced.

Due to the mole mass of the three sulfate ester groups, a loading of 10% o.m.f. TES is equivalent to 2% o.m.f. of triethanolamine, which is quite low compared to the normal amount of cotton finishing agent used to obtain easy-care effects. Fabric treated with TES is very smooth, probably due to finishing in strong base.

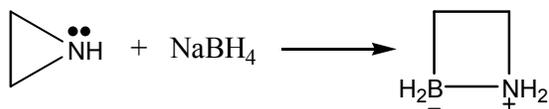


Fig. 22. The reaction of sodium borohydride with aziridine [48].

In summary, TES reacts covalently and crosslinks cotton cellulose in the presence of NaOH. Dry curing at high temperature may alleviate TES hydrolysis under strong alkaline conditions since water is evaporated very quickly. The major problem is yellowing; although sodium borohydride additions can overcome this, the extent of crosslinking decreases due to the reducing agent being involved in a side reaction which reduces TES functionality. Strong alkali additions to the pad-liquor impart high fabric strength retention and a smooth fabric surface since chain degradation may be avoided by using alkaline conditions.

TES is also a tertiary amine and is a possible agent to introduce permanent tertiary amine sites to cotton. Thus cotton pre-treated with TES can be dyed with anionic dyes under slightly acidic conditions which protonate the fixed tertiary amino residue. To achieve sufficient tertiary amine bonding to cotton, a steaming process suffices, presumably because only one of the three functional groups needs to react with cotton; to achieve an easy-care finish at least two or three of the functional groups need to react with cotton—hence the need for the high temperature baking process; fixing TES by steaming means that the whiteness can be maintained without adding reducing agent.

The Use of 1,3,5-Triacrylamino-hexahydro-s-triazine (FAP) to Crosslink Cotton Cellulose[49]

Fixing Agent P (FAP or 1,3,5-triacryloylamino-hexahydro-s-triazine) was developed to crosslink sulfonamide containing Basazol dyes (BASF) with cotton to give covalent dye-fibre bonds sufficiently stable to produce dyeings of very high wet-fastness [50,51]. The dyes used in this process did not contain electrophilic groups, but possessed pendant nucleophiles. The crosslinking agent acted as a bridge joining the nucleophilic dyes to the nucleophilic fibre (Fig. 23).

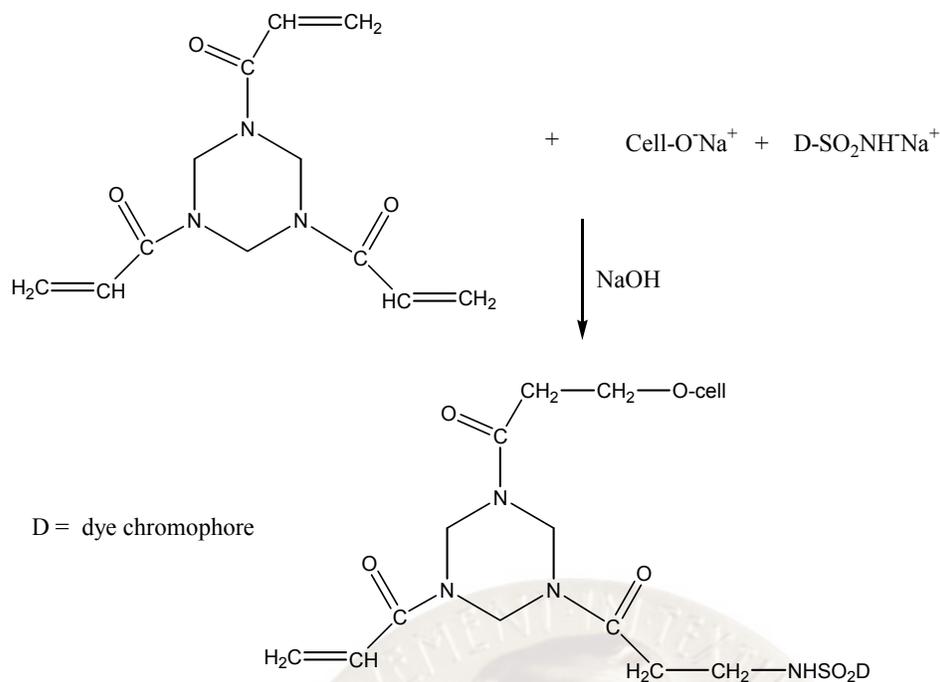


Fig. 23. Nucleophilic addition of sulfonamide dye with FAP to cellulose.

FAP has since found practical application as a crosslinking agent for Lyocell fibres to reduce fibrillation [52].

A major disadvantage of FAP is its low cold-water solubility and its lack of substantivity for cotton; FAP quickly dissolves in water as soon as the temperature reaches 75C. We modified FAP by reaction with ammonia [49], thus incorporating amino residues to give a derivative of enhanced cold water solubility. This derivative would react with cotton, when applied by pad-heat curing, from aqueous alkaline pad-liquors as shown in Fig. 24.

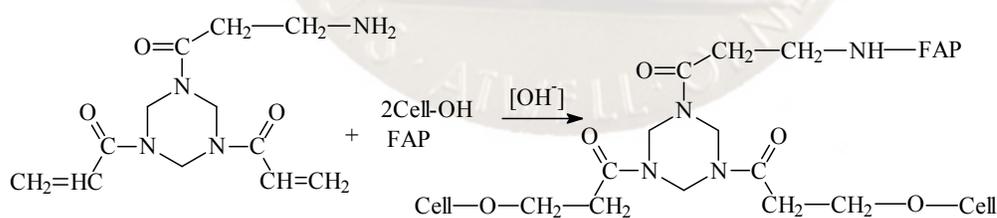


Fig. 24. Reaction between FAP-amine adduct mixture and cotton.

The treated fabrics showed very promising easy-care properties (Table IX).

Table IX. Effect of different process variables on properties of FAP treated fabrics

Sample No.	Na ₂ CO ₃ g/dm ³ (pH)	Treatment Condition	Temp. (C)	Treatment Time (min)	Whiteness Index	Dry WRA (w+f) °	DP Rating	Tensile Strength (kg)
Control					79.5	130	1.0	49.9
P1	20 (11.4)	Cure	130	3	46.5	240	3.1	32.3
P2	20 (11.4)	Saturated steaming	104	10	76.0	180	4.3	33.3
P3	20 (11.4)	HT steaming	120	5	72.3	247	4.0	32.5

Sample P3 was treated by a high-temperature steaming process, so a good wrinkle recovery angle (247), good DP rating (4.0) and good whiteness (72.3) properties were achieved. Good WRAs were achieved when the pH was 11.

The performance properties from the FAP system were compared to those achieved from the DMDHEU system (Table X).

Table X. Performance properties of cotton fabric treated with FAP/FAP-amine adduct mixture or DMDHEU

Finish Formulation, (% o.m.f.)	Temp. (C)	Time, (sec)	Whiteness Index, CIE	DP Rating	WRA (w+f) °	Tensile Strength (f, kg)
FAP/FAP-amine (8.0) Na ₂ CO ₃ 20g/dm ³	120	240	72.3	4.2	254	32.5
DMDHEU(8.0), MgCl ₂ (2.0)	160	90	75.4	3.7	260	32.3
	200	15	76.8	3.2	250	34.1
Control			79.5	<1.0	130	49.9

There are two explanations for the strength loss following FAP-amine treatment of fabric. Firstly, the fabric treatment with FAP/FAP-amine was performed in a moist environment, which favours the production of good dry and wet wrinkle recovery angles. Although wet wrinkle recovery was not tested, the better smoothness was proof that good wet wrinkle recovery ability had been improved significantly. Under moist conditions, the dry wrinkle recovery ability may be reduced. However in this experiment, high dry wrinkle recovery values had been achieved which indicated a great amount of FAP should be needed. But in fact, only the same amount of FAP as DMDHEU was necessary. The differences must be related to the three functional groups in FAP (one more functional group than DMDHEU); crosslink formation could account for the slightly greater strength loss. From this deduction, the conclusion can be drawn that FAP reacts very efficiently with cotton. The second explanation for the strength loss pattern with FAP-amine was that there was no polymer formed during the FAP-amine crosslinking reaction with cellulose, thus higher strain occurred in the cellulose chain through an increase in crosslinking points.

The fabric treated by both DMDHEU and FAP/FAP-amine adduct was tested using 20 household washing (HLDW) cycles (Table XI).

Table XI. The durable press performance of the cotton fabric treated with FAP/FAP-amine adduct mixture and DMDHEU during 20 HLDW cycles

Finish Agent Temperature (C) × Time (min)	WRA (w+f) °				DP Rating			
	Number of HLDW cycles				Number of HLDW cycles			
	0	5	10	20	0	5	10	20
FAP/FAP-amine 120 × 4	256	251	249	240	4.3	4.2	3.9	3.5
DMDHEU 160 × 1.5	261	256	250	241	3.7	3.5	3.3	2.9

The covalent bond formed between FAP and cellulose is an ether bond, which is clearly resistant to alkali attack during household washing. After 20 household washing (HLDW) cycles the FAP-amine treated cotton fabrics still maintained WRA values above 240° and DP ratings of 3.5, DMDHEU-treated fabric showed similar WRA values, but lower DP ratings after 20 HLDW cycles.

To summarise the FAP/FAP-amine mixture formed by reacting FAP with 1/4 mole of ammonia has good water solubility and imparts wrinkle resistance properties to cotton fabric when applied and cured under alkaline conditions. The most suitable application process was padding followed by steaming at 120C for 4 min at a steam-moisture content of 65%. The covalent bonds formed between the agent and cotton cellulose are very durable to alkaline washing conditions. Since the FAP crosslinking reaction is carried out under alkaline conditions, it might have been expected that the strength losses after processing would be less than those obtained using DMDHEU—in fact they were slightly worse due to the absence of polymer formation in the FAP case and also due to greater crosslink density since FAP is three functional.

Shrink-resist Finishing of Wool Fabrics by Application of Bunte Salt (S-thiosulfate) Polyether Polymers

The author patented both the synthesis and application of the above polymers [53, 54]; these polymers are water soluble, anionic, and yet readily curable to give water-insoluble, highly crosslinked polyether-poly-disulfides which protect the wool fabric from felting, yet have minimum effect on handle. The best process to apply these polymers was by pad-batch [55] in the presence of 2% w/w sodium sulfite—excellent soft-handling fabrics were produced, which resisted felting in machine washing. This process was used for many years on an industrial scale especially for shrink-resist treatment of Vyella wool/cotton (40/60) blend fabrics—untreated fabric would typically felt 60% in area when machine washed five times in the Wascator, whereas the treated would give zero felting. A further development allowed simultaneous dyeing and shrink-proof finishing of wool fabrics by incorporating halo-s-triazine reactive dyes in the pad-liquor [56]. The curing mechanism leading to poly-disulfide formation is shown in Fig. 25.

P – {O-(C=O)-SSO₃⁻}₃ + **Wool-SH** (generated from sulfite reaction with cystine)

↓

Wool-{S-S-O-(C=O)}-**P** + 3SO₃⁼
(mixed disulfide)

↓ (disulfide rearrangement)

P-{O-(C=O)-S-S-O-(C=O)}-**P** + **Wool-S-S-Wool**

Where P represents polyether polymer

Fig. 25. Curing reaction of Bunte Salt polyether polymer on reaction with wool thiol.

In the above, the mixed disulphides are only stable under acidic conditions and rapid rearrangement to the corresponding symmetrical disulfides occurs especially on water rinsing.

Concluding Remarks

As noted in the introduction, this lecture cannot incorporate all my past and present interests. Not detailed are the following items: work on bank-note security printing; the use of ink-jet to print Braille and other 3-D effects; the use of ink-jet to print conductive circuitry; the development through Green Chemicals PLC of formaldehyde-free wash-durable flame retardant process for cotton, paper and wool; reactive fibres rather than reactive dyes; crosslinking nucleophilic dyes on wool, nylon and cotton; new 'permanent' hair dyes, which are not based on hydrogen peroxide oxidation of aromatic amines; and new reactive dyes for cotton based on alkyl phosphonates.

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