The Early Work on Reactive Dyes for Cellulose

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Although it is not difficult to make a dyestuff which will colour fibres it is a much more complex matter to make one which will withstand repeated washing or laundering. The ideal way of achieving this has long been recognised to be by formation of a covalent bond with the fibre so that the dye in fact becomes part of the fibre itself. The potentially rich rewards of developing a practical process for dyeing fibres, particularly cellulose, in a variety of fast, bright shades by a dye-fibre reaction have intrigued research workers for some sixty years, but although earlier attempts often produced interesting results they entailed the use of expensive and complicated processes that were unsuitable for technical and commercial exploitation.

Of the existing fibres, apart from cellulose, wool has often been a natural choice because it contains easily reactable amino and mercapto groups. The author was working on this topic in the early 1950's and prepared several types of dyestuffs including some containing 2 : 4-dichloro-triazin-6-ylamino groups for assessment as reactive dyes. It was hoped that by virtue of the high reactivity resident in such groups almost complete reaction with the fibre might be attained. About this time Warren, Reid and Hamalainen[1] published a paper which assessed an S.C.I. patented method for reaction of soda cellulose with cyanuric chloride. Following on this, I.D. Rattee and the author, turning aside from their work on wool dyes, collaborated in investigating the possibility of achieving reaction between such dyestuffs containing a 2,4-dichlorotriazin-6-ylamino group and cellulose. It was found that when cotton yarns which had been treated with 15% caustic soda solution were immersed in a cold aqueous solution of such a dye and washed off, the resultant dyeing was exceptionally fast to washing. Thus, some fifty years after C.F. Cross, E.J. Bevan[2] and G.J. Briggs[3] had achieved the first chemical combination of a dye with cellulose by a complicated process involving benzoylation of soda cellulose, nitration, reduction, diazotisation and coupling to form an azo dye chemically bound with the fibre, the germ of a practical and commercially viable system for achieving the objective was found. This resulted in the first reactive dyes for cellulose, namely Procion dyes, being marketed in 1956. These early members of the range were dichlorotriazines; marketing of the less reactive monochlorotriazinyl dyes being delayed until the optimum application conditions had been finalised.

In the intervening period subsequent to the work of Cross and Bevan, many attempts were made to achieve chemical combination of cellulose with dyestuffs mainly by formation of either an ester or an ether link between the dye and the cellulose but all failed for a variety of reasons to provide a method suitable for commercial exploitation. Often the synthetic routes to the finished dyeings were too laborious, involving as for example in the Cross and Bevan method, the nitration of a benzoylated cellulose and, in others, the reaction of a nitro aromatic intermediate carrying a suitable reactive group such as chloro-, chloromethyl-, chlorosulphonyl- or chlorocarbonyl- with so-called soda cellulose, followed by reduction of the nitro group, diazotisation and finally coupling with suitable components to produce a coloured cellulose. The treatment of cotton fabric with concentrated solutions of caustic alkali in water or ethanol in order to form alkali cellulose, which was usually considered to be a necessary step in forming a dye-fibre bond, had the disadvantage of leading to marked deformation of the fibre unless carried out under mercerisation conditions. Furthermore, the use of solvents such as chloroform or toluene, employed as carriers for the reactive intermediates was impractical and hazardous on the large scale. A further disadvantage of such methods was that the production of coloured cellulose was very inefficient, although McLaughlin and Mutton[4] did claim a greater efficiency than was obtainable with systems previously tried, by washing soda cellulose with ethanol prior to reaction with *p*-amino-ω-chloroacetophenone in boiling ethanol.

Some attempts were made to achieve reaction of intermediates or dyes in aqueous solution without preformation of soda cellulose. Gunther of I.G. Farben[5] used derivatives of isatoic anhydride (e.g. the azo dyestuff sulphanilic acid → isatoic anhydride) in attempted reaction with cotton from aqueous solution, maintained mildly alkaline by the addition of sodium carbonate. The cotton was stated to be dyed an intense yellow despite the fact that the dyestuff molecules had very low substantivity for the fibre. The reasons why this system was not further developed are a little obscure but may be due to the ready hydrolysis of the dye-fibre bond.

[1] J. Warren, J.D. Reid and C. Hamalainen, *Text. Res. J. 22* (1952) 584.
[2] C.F. Cross and E.J. Bevan, *Researches on Cellulose 1895–1900*, published 1907 by Longmans, Green, London, p. 39.
[3] G.J. Briggs, *Z. angew. Chem. I* (1913) 255.
[4] R.R. McLaughlin and D.B. Mutton, *Can. J. Chem. 33* (1955) 647.
[5] U.K. Pat. 259,634 to Badische Anilin- und Soda-Fabrik.

GUTHRIE[6] obtained ether linkages with cellulose by use of sulphuric esters of alcohol side chains in the dyestuff. A solution of 2-*p*-aminophenoxyethylsulphuric acid → *p*-cresol in warm caustic soda was padded onto cotton which was dried and baked at 110 °C but unless long heating periods were used only pale yellow fixed dyeings resulted. The dyeings, however, had good fastness to washing but only moderate light fastness.

PEACOCK[7] claimed the formation of nitrobenzyl ethers of cellulose when cotton was treated with dilute solutions of compounds of the type *p*-nitrobenzylphenyldimethyl ammonium chloride containing the stoichiometrical amount of sodium carbonate. The reacted cotton was put through a colour forming process of reduction, diazotisation and coupling to give dyeings of varying shades stated to be fugitive to light. Other workers used intermediates or dyes carrying onium groups both as part of the reactive system and as temporary solubilising centres. S.C.I.[8] used quaternary compounds obtained from aromatic carboxylic acid amides with formaldehyde and a salt of a tertiary amine while Russian workers[9] used compounds derived from benzyloxymethylpyridinium chloride. In both cases the fixation of either a nitrated intermediate or a dye was achieved by baking cotton padded with the solutions. The Russian workers postulated the formation of an ether linkage by their process.

One further method of historical interest in view of subsequent developments was the outcome of work in the laboratories of S.C.I. in the early 1930's. By this time this firm had already initiated their extensive research on cyanuric dyes, in the formation of which the well known stepwise reaction behaviour of cyanuric chloride towards amines was used to build up mainly substantive types for cotton, some purely azo, others containing mixed chromophores and with at least two of the three chlorine atoms replaced. In this work,[10] partly the subject of reassessment already mentioned, HALLER and collaborators obtained a cyanurated cellulose still containing reactive chlorine which could be made to react with amino derivatives of chromophores or their precursors. Alternatively a chlorotriazinyl dye dissolved in organic solvent could be reacted with soda cellulose, but as in earlier work using similar technique these methods gave considerably degraded cellulose of little value for textile purposes. No water soluble dyes containing dichlorotriazinylamino groups were employed.

The dominating feature of most of this early work, GUNTHER's[5] and PEACOCK's[7] apart, was the use of severe conditions such as very strong caustic soda to prepare soda cellulose or the use of inert solvents. There was little study of the use of the mild conditions necessary to render a colouration process both reasonably efficient and technically feasible. The reasons for this were probably two-fold. Firstly, the belief that cellulose was relatively inert—probably a logical consequence of the work on the preparation of cellulose derivatives for textiles and other purposes, where it is necessary to achieve a reasonably high degree of substitution in the cellulose chain on secondary as well as primary alcohol groupings—and secondly, the belief that the use of a highly reactive system in aqueous solution would mainly result in hydrolysis because the reaction with water is a homogeneous phase reaction and that with cellulose, heterogeneous.

Work by the author and I.D. RATTEE showed that if highly reactive dyes were suitably introduced into the fibre from an aqueous solution e.g. by padding and treated with aqueous alkali they then fixed rapidly. Although the degree of substitution was not high, the efficiency of the reaction or ratio of the degree of fixation with cellulose to the degree of hydrolysis with water was sufficiently great to provide the basis of simple attractive dyeing processes yielding fast dyeings over a satisfactory range of shades and depths of shade. That portion of the dyestuff which had hydrolysed and was not chemically bound to the fibre was removed by rinsing. The dye chosen for the early work was of the constitution of No. 1 in Table 1. Further work on this dye showed that reaction between the dye and cellulose could be complete in as little as 5 seconds at 100 °C using alkali no stronger than sodium carbonate. Furthermore, it was found that by varying the *p*H or the temperature the reaction could be controlled so that the dye could be applied under most conditions likely to be encountered in dyeing practice, to give deeply coloured bluish-red shades.

Further examples of chlorotriazinylamino dyes, as listed in Table 1, were then prepared and the application methods more widely assessed. The dyes evolved were chiefly analogues of monoazo and anthraquinone acid wool dyes but were designed to study the effect of various structural changes on the efficiency of dye fixation. As an instance of this Dye 6 was closely analogous in structure to the direct dye Durazol Red 2B (Colour Index Direct Red 81) and was included to determine the degree of substantivity that would be tolerable in this type of dye. Different techniques were necessary in the preparation of these dyes. With the azo dyes the chlorotriazinyl nucleus was either attached directly to one of the azo components prior to forming the dye or in cases where coupling conditions could cause undue hydrolysis of the triazinyl chlorine atoms the aminoazo body was preformed and subsequently condensed with cyanuric chloride. This latter method had the advantage that where isomeric coupling was prone to occur, for example with alkaline coupled J-acid derivatives, reworking to remove the undesired isomer was possible before reaction with cyanuric chloride.

[6] J.D. GUTHRIE, *Amer. Dyestuff Rep. 41* (1952) 13 and 30, also U.S. Pat. 2,741,532 to J.D. GUTHRIE.
[7] D.H. PEACOCK, *J. Soc. Dyers Colourists 42* (1926) 53.
[8] U.K. Pat. 533,073 to S.C.I. BASLE.
[9] KURSANOV and SOLODKOV, *Zh. Prik. Khim* (U.S.S.R.) *16* (1943) 351.
[10] U.K. Pat. 363,897, to S.C.I. BASLE.

Table 1. Dyes prepared for first assessment of Pad/Dry/Caustic Soda Fixation process

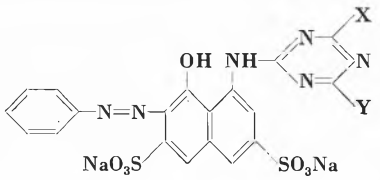
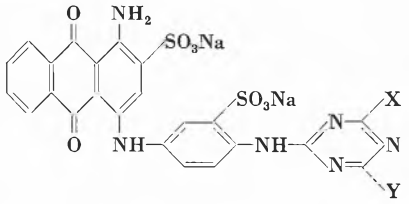
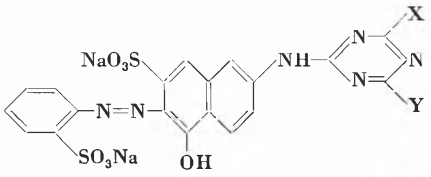
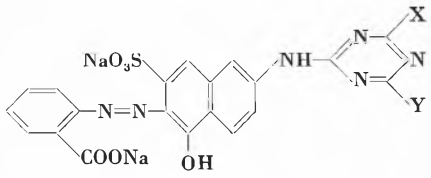
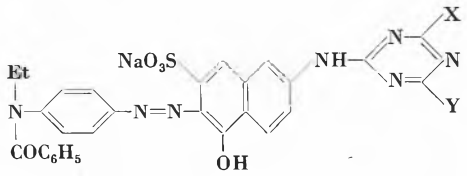
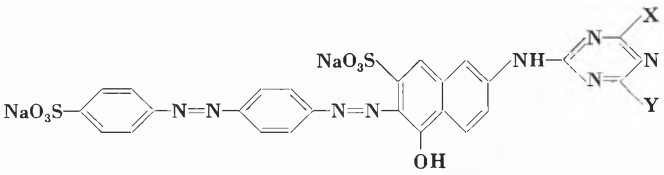
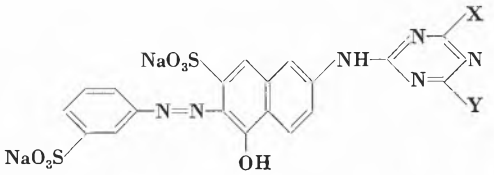
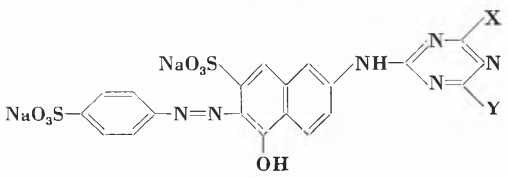
Dye No.	Constitution	No. of chlorine atoms on triazine nucleus (X + Y)	Shade of fixed dyeings on cotton	Light Fastness (1–8 scale) 1 to 2.5 % shades
1		1.83	Bright bluish-red	4
2		1.91	Blue	5–6
3		1.92	Bright orange	5–6
4		1.87	Bright reddish orange	6 after coppered 6–7
5		2.0	Pale pink	4
6		1.93	Maroon in deep shades	3
7		1.92	Bright orange	6
8		1.66	Bright orange	6

Table I (continued)

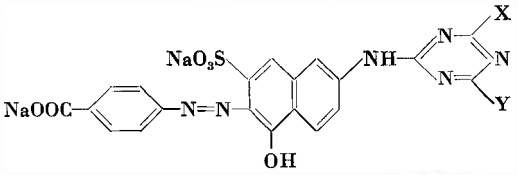
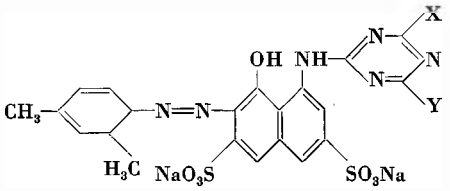
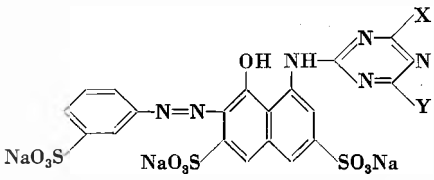
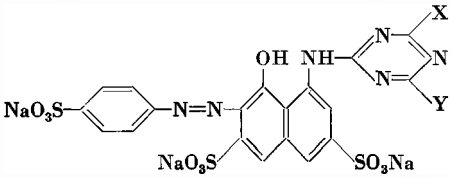
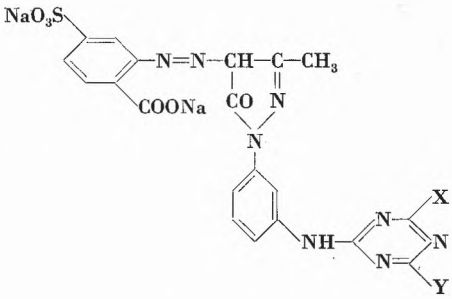
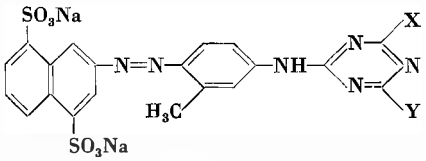
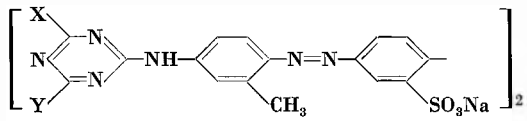
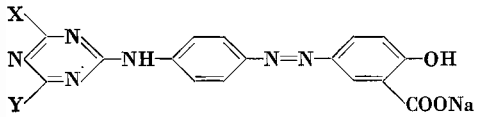
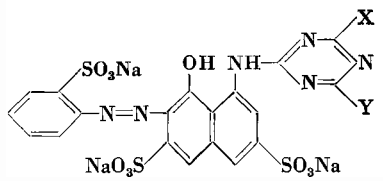
Dye No.	Constitution	No. of chlorine atoms on triazine nucleus (X + Y)	Shade of fixed dyeings on cotton	Light Fastness (1–8 scale) 1 to 2.5% shades
9		1.93	Redder orange than 7 or 8	5–6
10		1.73	Bright bluish red Bluer than I	3–4
11		1.83	Bright red	4–5
12		1.68	Bright bluish red	5
13		1.84	Very pale yellow	–
14		1.97	Bright orange Yellow	6–7
15		3.78 for 2X + 2Y	Weak Yellow	4
16		1.84	Greenish Yellow	4
17		1.8	Bright Red	5

Table 1 (continued)

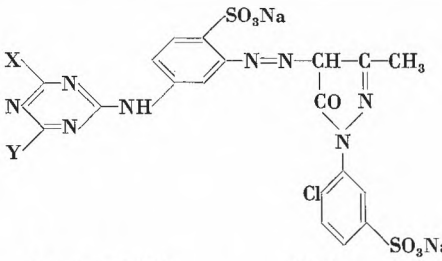
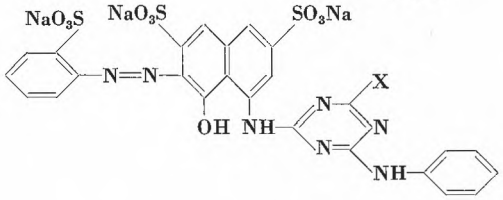
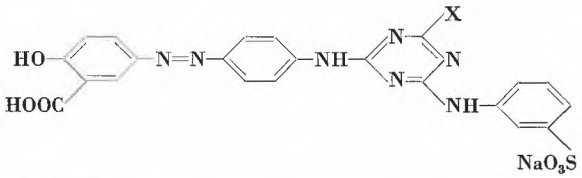
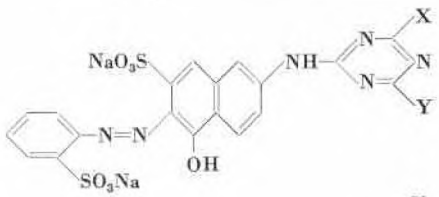
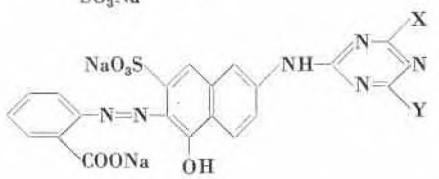
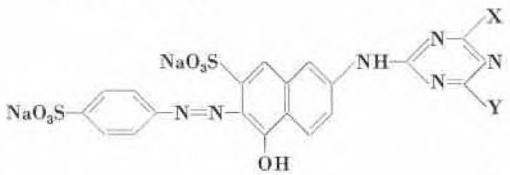
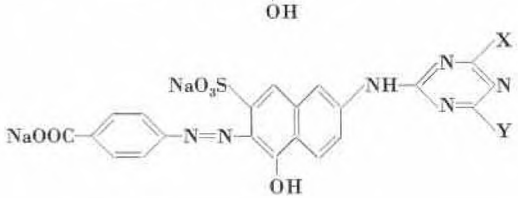
Dye No.	Constitution	No. of chlorine atoms on triazine nucleus (X + Y)	Shade of fixed dyeings on cotton	Light Fastness (1–8 scale) 1 to 2.5 % shades
18		2.0	Yellow	6 – 7
19		0.93	Bright bluish-red	6
20		0.90	Yellow	–

Table 2. Loss of reactive chlorine by dyes on storage

Dye No.	Constitution	No. of chlorine atoms on triazine nucleus (X + Y) When first isolated	After storage days	X + Y
3		1.92	28 89	1.7 0.39
4		1.87	62 149 190	1.7 1.48 1.44
8		1.66	33 76	1.48 0.62
9		1.93	28 70 107	1.93 1.87 1.87

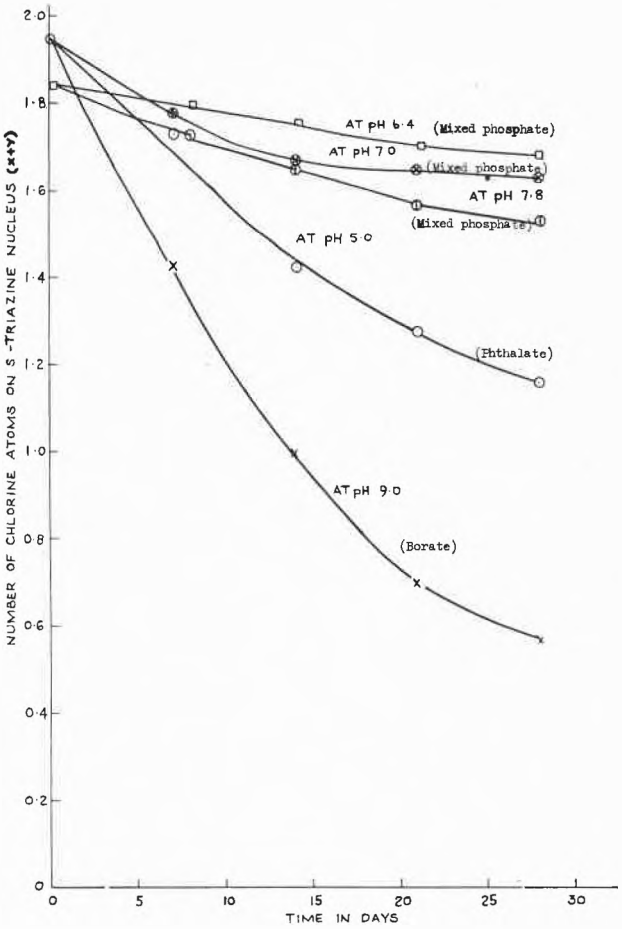
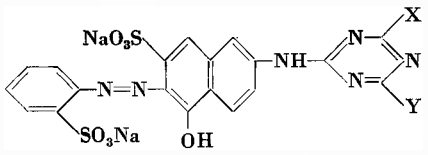


Figure 1. Rates of hydrolysis of dye 3 in aqueous solutions buffered at different *p*H values



When the dyes 1 to 18 in Table 1 were applied to cotton by the padding process it soon became evident that adequate water solubility was essential. Solutions of dyes 2 and 6 tended to gel and, in consequence, did not fix as efficiently as dye 1 at room temperature, but fixed at 95 °C gave much improved results, presumably due to the increased mobility of the dye within the fibre. In most cases it was found that fixation was improved at 95 °C but the improvement with those dyes based on dichlorotriazinyl H-acid was small. All the other dyes except 15 and 16 had adequate solubility in cold water and most of the dyeings obtained were bright and had good fastness to severe washing and soda boiling. Often the fastness properties were of the same order as those obtainable from vat dyestuffs. This work formed the basis of the first patented application method.[11]

[11] U.K. Pat. 797,946 and 798,121 to I.C.I. Ltd.

A comparison was made of the efficiency of the new colour fixing process using a 2% solution of dye 10 with that of the method described in Ex. 3 of U.K. Patent 363,897 giving the same fixed dyestuff by reacting cyanurated cellulose with H-acid and then with diazo *m*-xylidine. Of the 1.9% of pure dye 10 padded on to the fibre 1.6% was fixed, representing an 83% efficiency whereas only 2% of the cyanuric chloride employed for reaction with soda cellulose ultimately became fixed as dyestuff by the patented method.

The varying chlorine contents of the dichlorotriazinyl dyes listed in Table 1 illustrated that the extent of hydrolysis during preparation and drying varied from dye to dye. Commercial usefulness of these dyes demanded that they should retain close to two chlorine atoms per triazine nucleus for considerable periods and in consequence storage stability was investigated. No such difficulties arose with the less reactive monochlorotriazinyl dyes such as dye 19 which, however, required more vigorous application conditions. Samples of the dichlorotriazinyl dyes were kept in glass stoppered bottles and analysed for varying periods up to 12 months. As expected a wide variety of behaviour was observed. The most interesting results arose with the two pairs of dyes 3 and 4 and 8 and 9 which differed in constitution only in that one of the sulphonic acid groups was replaced by a carboxylic acid group in the other dye of each pair. As illustrated in Table 2, the dyes with carboxylic groups were much the more stable on storage and it was considered that this increase in stability was due to an internal buffering effect which could be assigned to these groups.

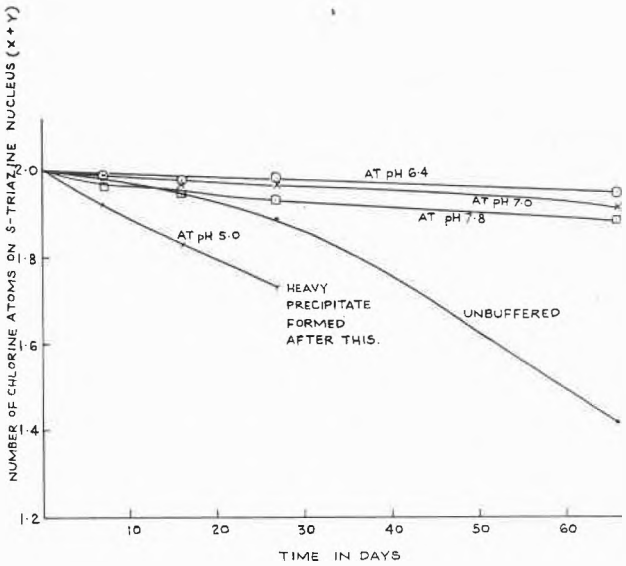
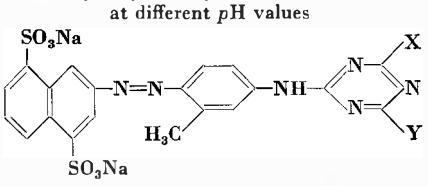


Figure 2. Rates of hydrolysis of dye 14 in aqueous solutions buffered at different *p*H values



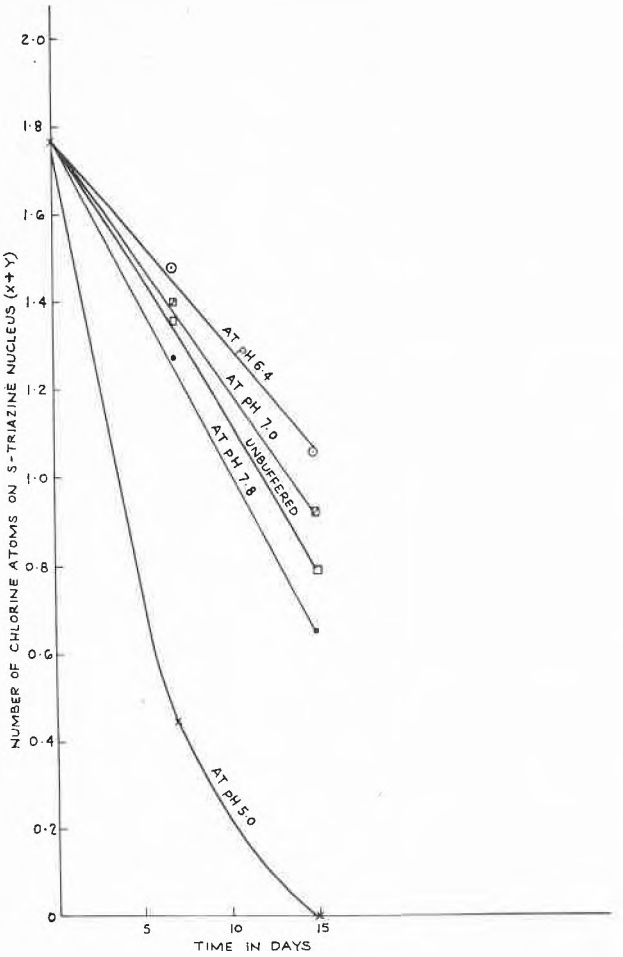
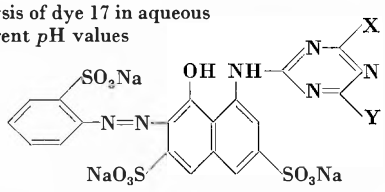


Figure 3. Rates of hydrolysis of dye 17 in aqueous solutions buffered at different *p*H values



Other factors such as lower solubility of the more stable dyes could have been of equal or greater importance but the idea of internal buffering suggested the possibility of controlling hydrolysis on storage by admixture with external buffers. Dye 3 was chosen for detailed investigation of the effect of external buffers because of its high solubility and fairly rapid hydrolysis on storage. Solutions stored over a range of *p*H and analysed after various times of storage—the results are plotted in Figure 1—showed clearly that the minimum rate of hydrolysis occurred at *p*H 6.4. The rate of hydrolysis at *p*H 7 was only slightly higher whereas at *p*H 9 the rate of hydrolysis was high. A sample of dye 3 was intimately mixed with a mixture of anhydrous potassium dihydrogen phosphate and anhydrous disodium hydrogen phosphate in proportions to give *p*H 6.8 when dissolved and stored alongside an unbuffered control. The reactive chlorine content of the dye in the two samples over varying periods up to 14 months are illustrated in Table 3.

Table 3. Reactive chlorine content of buffered and unbuffered samples of dye No. 3 after varying periods at 20 °C

No. of days Samples stored	Reactive chlorine atoms on triazine residue In unbuffered sample	In buffered sample
14	1.84	1.92
21	1.84	1.92
43	1.85	1.92
62	1.74 (Acid to Congo Red paper)	1.92
107	0.86	1.94
252	0.6	1.94
429	0.58	1.83

These results indicated that hydrolysis of the buffered sample was greatly retarded and patent protection was obtained for this important development in overcoming instability of dichlorotriazinyl dyestuffs.[12] Further systematic study showed that wide differences in the rate of hydrolysis between the dyestuffs such as are represented in Figures 1 to 4 was largely reflected in wide differences in reactivity. In consequence, an appreciable amount of work was necessary in an endeavour to link reactivity with constitutional variation.

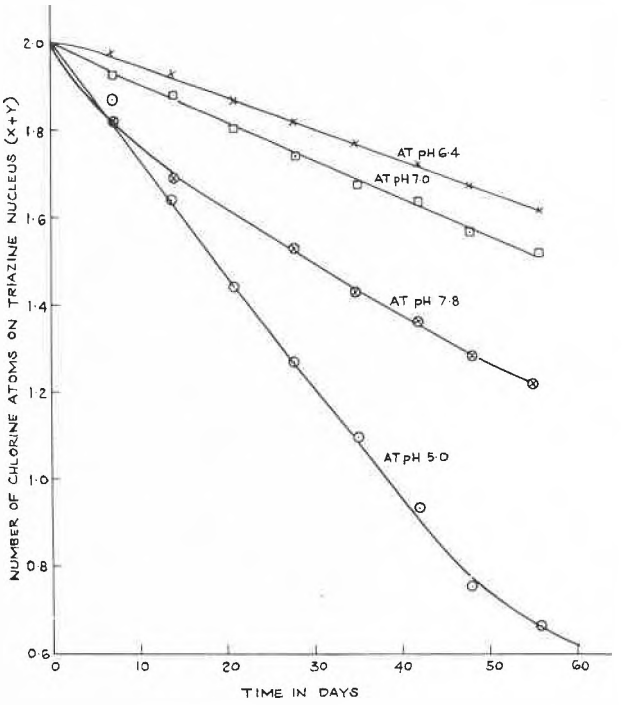
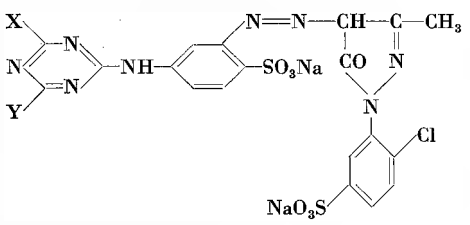


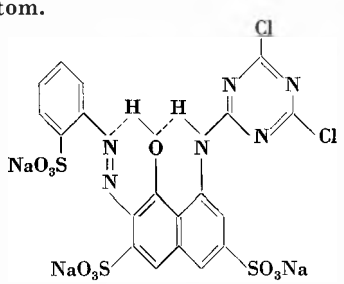
Figure 4. Rates of hydrolysis of dye 18 in aqueous solutions buffered at different *p*H values



[12] U.K. Pat. 838,337 to I.C.I. Ltd.

While synthetic work was undertaken in this direction a more detailed kinetic study of the hydrolysis of cyanuric chloride itself and various 2-arylamino-4,6-dichloro- and 2,4-diarylamino-6-chloro-*s*-triazines was undertaken by my colleague S. HORROBIN.[13] This work emphasised that the reactivity of the chlorine atoms in the triazine nucleus was greatly dependent upon the electron density on the nitrogen atom linking the triazine residue with the dyestuff. When this link was an unsubstituted imino group this was mainly dissociated as a negatively charged anion under alkaline conditions and the reactivity of the chlorine atoms was considerably less than in the analogous compounds using alkylated imino linking groups which prevented dissociation.

Since both dyes 3 and 17 contained an unsubstituted imino linking group the reasons for the considerable difference in their reactivities was not clear. Nevertheless, in the cases of dyes derived from dichlorotriazinyl H-acid there is an opportunity for hydrogen bonding, not only between the hydroxy group and the azo group, but more particularly between the linking imino group and the peri oxygen atom.



Hydrogen bonded form of dye 17

This hydrogen bonding possibly impedes ionisation of the linking imino group. Such a possibility of hydrogen bonding with the linking imino group does not arise with dyes of type 3. There was some evidence (see Figures 2 and 3) that the rates of hydrolysis at *p*H 5 outstripped those in unbuffered solutions suggesting that the hydrolysis was catalysed by the use of phthalate buffer. Kinetic studies confirmed the adverse catalytic effect of carboxylate buffers[13] and it was unfortunate that the region of minimum hydrolysis rate (*p*H 3–6) required this type of buffer. Buffering in the required *p*H range was satisfactorily achieved by use of aminoarylsulphonic acids in which the amino group is twice substituted by alkyl (other than methyl), cycloalkyl or aralkyl.[14] In a few cases this type of buffer had decided advantages over phosphate buffers in conferring stability to dye powders. Examination of other buffering systems failed to reveal any superior to those based on phosphates and disubstituted arylamine sulphonic acids.

Following the satisfactory solution of the stability problem, a range of three Procion dyes, the first commercial range of reactive dyes for cellulose, was developed. The principle had been demonstrated that reactive groups can be chosen which are reasonably stable in aqueous solution but which will react under very mild conditions with cellulose rather than with water provided that the dye can penetrate into the cellulose. Further application methods, particularly for printing and batchwise dyeing, required to be worked out and it was also evident that many other reactive groups with equally interesting possibilities had yet to be evaluated. It is of interest that over 200 different reactive groups were examined in subsequent work.

It was found by F. ALSBERG[15] that chlorotriazinyl dyes could be satisfactorily printed by use of a sodium alginate thickener, urea and sodium bicarbonate in the print paste. This obviated the undesirable effect of cross linking with the usual starch thickeners. Prints with this composition were fixed to the cloth by steaming or alternative means of heating for a very short time. The practical success of alginate thickeners is probably due to the lack of primary alcohol groups, the lower reactivity of the secondary hydroxyl groups and repulsion of the anionic dye molecules by the ionised carboxyl groups in the alginate.

A satisfactory batchwise dyeing method was also evolved. This required the dye to be applied to the fabric from long liquors (e.g. liquor to goods ratio of 30 : 1) and was achieved by application from a neutral bath containing salt until the dye had been absorbed by the fibre when sodium carbonate was added to achieve fixation. Dye fixation required some 90 minutes for optimum effect. Table 4 tabulates for several of the dyes already mentioned the degree of dye bath exhaustion (E_s), on adding 30 g/litre of salt, (E_f) dye-bath exhaustion after adding 1 g/litre of soda ash and F_a the percentage fixation relative to the total dye present originally in the dye-bath.

Table 4. Fixation of dyes by batchwise dyeing

Dye	E_s	E_f	F_a
3	61%	98%	92%
14	91%	99%	70%
17	30%	74%	60%
18	17.5%	48%	48%

From these results it was evident that better fixation efficiency was being achieved with dyes which were more readily absorbed by the yarn, namely the more substantive dyes. Dyes 3 and 14 would both be expected to have an inherent substantivity in view of their structural relation to direct dyes whereas dyes 17 and 18 would be expected to be deficient in substantivity. In general, the fastness properties of these dyeings were similar to those obtained by the pad-fix method.

[13] S. HORROBIN, *J. Chem. Soc. 1963*, 4130.
[14] U.K. Pat. 842,933 to I.C.I. Ltd.
[15] F. ALSBERG, W. CLARKE and A.S. FERN, *J. Soc. Dyers Colourists 75* (1959) 89.

The evolution of these new methods of application serves to emphasise the versatility of the Procion dyes and makes it possible for them to be used not only in dyehouses equipped with modern machinery for continuous application but also by less well-equipped establishments using simpler batchwise methods. The main attraction of Procion dyes lies in their brightness of shade, hitherto unobtainable on cotton, high fastness properties and ease of application. As time progressed the end uses of Procion dyes have been extended and they have also, for example, found considerable outlet in the dyeing of leather.

In order to provide a wider range of shades new members to add to the first three Procion dyes were sought utilising the various types of azo combinations and other chromophores known to be associated with particular shades.[16]

One particular aspect was the provision of bright turquoise shades. The easiest way of achieving such dyes was by use of copper phthalocyanine sulphonic acid chlorides condensed, for example, with phenylene diamine sulphonic acids and subsequently with cyanuric chloride,[17] or by condensation of phthalocyanine polysulphonyl chlorides with amines of the type $NH_2CH_2CH_2X$ where X may be chlorine, bromine or sulphate,[18] or with ethyleneimine[19] or with an amine containing at least one 3-chloro-2-hydroxypropylamino group.[20]

Orange to red azo dyes with good bleach fastness were obtained by use of 2-naphthylamine-1-sulphonic acid or 1,5-disulphonic acid as diazo components.[21] The improvement of bleach fastness can probably be ascribed to the displacement of the sulphonic acid in the 1-position of the naphthalene residue by halogen(cf. ref. [22]).

Concurrently with work on dichlorotriazine dyes, application methods for the less reactive monochlorotriazine dyes such as dyes 19 and 20 in Table 1 were worked out. It was found that these dyes could be fixed on cellulose at high temperatures by either dyeing or printing techniques and, moreover, had the advantage of greater stability in the print paste than the more reactive dichlorotriazine dyes. In consequence, a range of such dyes for high temperature application (Procion H dyes) was evolved and marketing commenced in early May, 1957.

In search of dyes approaching in reactivity those with either dichlorotriazinyl or monochlorotriazinyl groups, several other alternative replaceable groups and reactive systems were of necessity examined and this work has continued well beyond the period that this paper covers.

With triazine dyes, it was found that several replaceable groups alternative to chlorine could be introduced, namely bromo, fluoro, sulpho, thiocyano and other groups of the type SR where R is an electro-negative group. Another useful labile system disclosed by this early work was a phenoxy group with an electro-negative substituent such as sulpho.[23] The replacement of the chlorines in cyanuric chloride by other labile groups was usually relatively straightforward, involving direct reaction with HX where X is the labile group under suitable ionising conditions. To introduce a sulphonic acid group[24] reaction was obtained between the chlortriazine and sodium sulphite. Analysis showed the dyes now contained sulpho groups in place of chloro groups. The fact that these were sulpho groups and not sulphite esters was established by making the corresponding mercapto compounds, oxidising to the sulphonic acid compounds and proving identity of the two products.

Replacement of one chlorine atom in a dichlorotriazinyl dye by a non-labile substituent offered a wide possibility of varying the reactivity of the resulting monochlorotriazinyl dye. This also enabled one to vary the properties such as affinity and solubility of the dye to suit required end applications. In this connection the use of amines was important since the solubility and affinity of a particular dye could be varied appreciably by using, for example, many primary arylamines, N-methylarylamines and sulphonated arylamines. It was soon realised that the reactivity of monochloromonohydroxytriazinyl dyes is depressed in alkaline media, probably due to ionisation of the hydroxyl.

The chlorine atoms of chlorotriazinyl derivatives are readily removed by nucleophilic agents because they are activated by the three electro-negative nitrogen atoms as well as by other substituents present in the triazine. Chlorine containing diazines were found to be less reactive than the chloro-s-triazine but nevertheless 2:4:6 trichloropyrimidine reacted satisfactorily with amino dyestuffs to give products capable of being fixed on cellulose.[25] Since then commercially important ranges of reactive dyes derived from either 2:4:6-trichloro- or 2:4:5:6-tetrachloropyrimidines have appeared under the Reactone (Geigy) and Drimarene (Sandoz) labels.[26] Although the di- and trichloropyrimidyl dyes devoid of more electronegative groups than chlorine in the 5-position are much less reactive than dichlorotriazinyl dyes and are of little value for cold dyeing they are quite well suited to printing and hot continuous dyeing. Because of their lower reactivity the times for fixation may be somewhat longer and the temperatures somewhat higher. Some enhancement of the reactivity of the chlorine atoms in chloropyrimidinyl dyes was achieved by introduction of a nitro group in the 5-position but the resulting dyeings were deficient in fastness to severe

[16] U.K. Pat. 785,120, 785,222, 826,405, 838,340, 838,341, to I.C.I. Ltd.
[17] U.K. Pat. 805,562, to I.C.I. Ltd.
[18] U.K. Pat. 826,689, to I.C.I. Ltd.
[19] U.K. Pat. 830,246, to I.C.I. Ltd.
[20] U.K. Pat. 830,847, to I.C.I. Ltd.
[21] U.K. Pat. 836,248 and 837,990, to I.C.I. Ltd.
[22] A.G. Green and K.H. Vakil, *J. Chem. Soc. 113* (1918) 40.
[23] U.K. Pat. 846,765, to I.C.I. Ltd.
[24] U.K. Pat. 849,772, to I.C.I. Ltd.
[25] U.K. Pat. 822,047, to I.C.I. Ltd.
[26] (a) M. Capponi, E. Metzger and A. Giamara, *Amer. Dyestuff Rep. 50* (1961) 505; (b) H. Ackermann and P. Dussy, *Melliand Textilber. 42* (1961) 1167.

washing. This was possibly traceable to over-activation by the nitro group weakening the dye-fibre bond since further work at a later date[27] has illustrated that such dyes containing a cyano group in the 5-position of the pyrimidinyl ring have high reactivity and give satisfactory dyeings.[27] Of several halogeno heterocyclic groups examined during the early stages as possible replacements for halogenotriazinyl groups, few showed promise, either on grounds of cost or low reactivity, although subsequent work has shown the efficacy of 2,3-dichloroquinoxaline-6-carbonyl as a reactive group. This group has been utilised in a commercial range of dyestuffs in recent years by Farbenfabriken Bayer AG.[28]

Among other reactive systems evaluated during this early work one of the most interesting was the use of sulphon fluoride groups which had sufficient reactivity to approach closely the properties of dichlorotriazinyl groups.[29] Of other groups evaluated at that time there may be mentioned ω-chloropropionyl, chloroacetyl, chloroalkylsulphamyl, β-sulphatoethyl, γ-chloro-β-hydroxypropyl.

The above account has been concerned primarily with some of the work done on reactive dyes for cellulose by the author and his collaborators prior to 1957. Since that time both I.C.I. and other dye manufacturers have been very active in the field of reactive dyes for cellulose and it appears likely that this research will continue for many years to come. Of ranges other than Procions, Reactones and Drimarenes that are interesting by virtue of the reactive group utilised, particular mention should be made of that using the β-sulphatoethylsulphonyl group, as represented by Remazol (Hoechst) range of reactive dyes. Remazol dyes are interesting in reacting via a generated vinyl sulphonyl group to form an ether type linkage with the cellulose. The true ether-like nature of this compound is, however, a little suspect in that the resulting dyeings are less fast to alkaline washing than the ester type linkages formed with Procion dyes or Drimarene dyes.

At the time the above work was done, evidence for the reaction of reactive dyes with the fibre was only indirect. Thus, dyeings of Procion Yellow R could be reduced on the fibre and after thorough washing, the fabric could be diazotised and coupled with a naphthol sulphonic acid to yield a dyeing with similar fastness properties. Further work by VICKERSTAFF,[30] WEGMANN[31] and others gave indirect evidence but final proof was eventually achieved by ZOLLINGER, STAMM and others[32] by means of microbiological degradation of cellulose dyed with reactive dyes and identification of glucose in the hydrolysate state of a dyed, soluble degradation product.

One of the surprising features of Procion dyes is their preferential reaction with cellulose rather than with water. This subject has been investigated by my colleagues PRESTON and FERN[33] and SUMNER *et al.*[34] and they have shown that the Procion reaction takes place with ionised cellulose and with hydroxyl ions of water, the ratio of the bimolecular reaction constants of a dye for cellulose ions to that for hydroxyl ions being constant at varying alkali concentrations. The preferential reaction for cellulose is attributed firstly, to the affinity of the dye for the fibre causing the concentration of the dye in that phase to be as much as 500 times greater than in the water and secondly to the lower dissociation constant of cellulose compared with water causing a greater proportion of cellulose-O^- ions than of hydroxyl ions at any given *p*H. These factors will of course be equally applicable to dyeing systems using groups less reactive than the dichlorotriazinyl and the extent of reaction between fibre and dye will be dependent upon the reactivity of the dye. It is in the matter of high reactivity that the dyes of the Procion range are outstanding for it endows them with their great versatility, allowing them to be fixed efficiently on cotton by a wide variety of methods employing varying degrees of alkalinity and fixation times. The failures of the previous methods tried were probably due to a great extent to the lack of sufficient reactivity in intermediates or dyes used even though the cellulose used was in its most highly ionised form.

The discovery of the first system for achieving chemical combination between dyestuff and cellulose suitable for commercial use has been followed by world-wide research on reactive dyes not confined only to those suitable for application to cellulose. Work on dyes for other fibres has been revitalised and catalysed. Simultaneous with the development of the Procion dyes a range of reactive dyes for nylon called Procinyls has been introduced by I.C.I. Ltd. and of later date their range of reactive dyes for wool—the Procilans, has been marketed.

The author wishes to acknowledge the collaboration of many colleagues in much of the work outlined in this paper and to thank Dr. N.S. CORBY and Dr. R.R. DAVIES for their help in preparing the paper for publication.

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Procion and Durazol are the registered trade marks of Imperial Chemical Industries Limited.
Reactone is the registered trade mark of J.R. Geigy, S.A.
Remazol is the registered trade mark of Farbwerke Hoechst AG.

[27] U.K. Pat. 917,780, to I.C.I. Ltd.
[28] K.G. KLEB, E. SIEGEL and K. SASSE, *Angew. Chem. 76* (1964) 423.
[29] U.K. Pat. 819,320, to I.C.I. Ltd.
[30] T. VICKERSTAFF, *J. Soc. Dyers Colourists 73* (1957) 237.
[31] J. WEGMANN, *Melliand Textilber. 39* (1958) 1006.
[32] (a) O. STAMM, H. ZOLLINGER, H. ZAHNER and E. GÄUMANN, *Helv. Chim. Acta 44* (1961) 1123; (b) R.C. SENN, O. STAMM and H. ZOLLINGER, *Melliand Textilber. 44* (1963) 261.
[33] C. PRESTON and A.S. FERN, *Chimia 15* (1961) 177.
[34] W. INGAMELLS, H. SUMNER and G. WILLIAMS, *J. Soc. Dyers Colourists 78* (1962) 274.