Dyes and Pigments 14 (1990) 239–263

Synthesis and Application of Reactive Dyes with Heterocyclic Reactive Systems*

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(Received 15 December 1989; accepted 19 January 1990)

ABSTRACT

Synthetic methods are described for the preparation of the reactive dyes of the general formula 4.

The dyestuffs have been used for dyeing cotton according to a uniform dyeing process. Parameters such as the most favourable dyeing temperatures, exhaust and fixing values have been determined.

Investigations have been carried out for estimation of the stabilities of bonding between dyestuff and fibre under both acidic and alkaline conditions.

Among the triazine dyes, the highest average relative fixation values (70%) are exhibited by the 2-aryl and 2-heteroaryl derivatives. Among the reactive dyes based on pyrimidine, the 5-cyano-2,4-dichloro derivatives show a higher level with 73% while the 2,4-difluoropyrimidines show the highest level with 84%.

The 2,4-difluoropyrimidine dyes also show the best overall picture with respect to hydrolysis fastness properties, permitting the conclusion that the dye-fibre bonds are stable under both acid and alkaline conditions. The other pyrimidine dyes can be generally regarded as moderate, while the reactive dyes based on triazine showed poor results.

1 INTRODUCTION

Reactive dyes are coloured compounds containing a chromophore and particular groups known as reactive systems or anchors, which in the course

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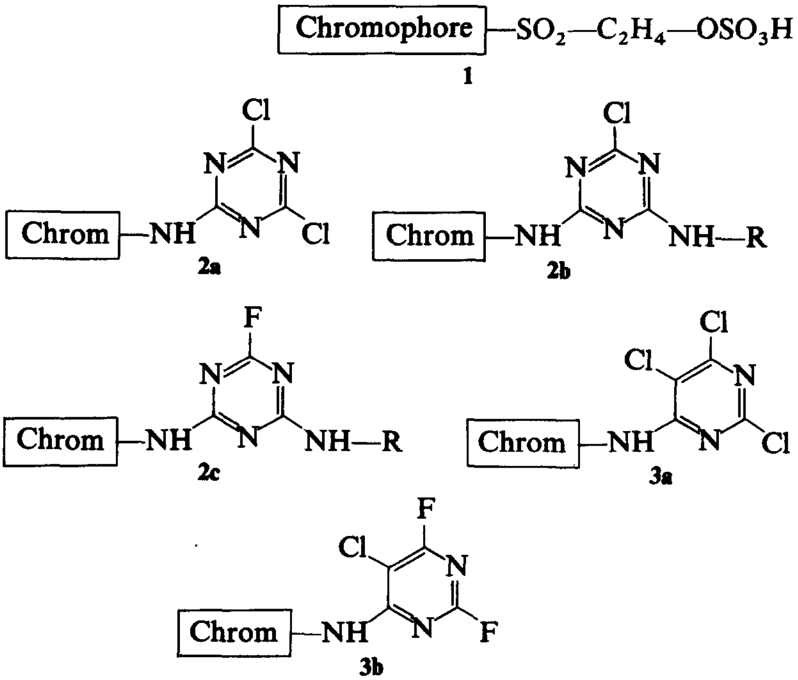
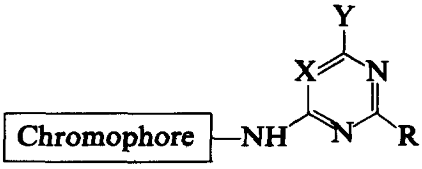
* Presented at the SCI-Symposium on Colour Chemistry, May 11, 1989, London



Scheme 1. Commercially available reactive dyestuff classes.

of the dyeing process, form a covalent chemical bond with the substrate.[1-16] Scheme 1 shows a selection of commercially available reactive dyestuff classes.[9]

Important reactive dyes are the sulphate esters of the hydroxyethylsulphones **1**.[5] A second group of reactive dyestuffs are based on triazines, e.g. the 2,4-dichlorotriazines **2a**,[6,7] the 2-amino-4-chlorotriazines **2b**[8,10] and the 2-amino-4-fluorotriazines **2c**.[6,7] A third group are pyrimidines, e.g. the trichloropyrimidines **3a**[7] and chlorodifluoropyrimidines **3b**.[12]



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The objectives of our investigation were as follows:

(i) The synthesis of additional reactive dyes with different heterocyclic reactive systems and containing several more recently available chromophores; i.e. with a wide variation of. X, Y and R in the general formula **4**.

(ii) Their application on cotton according to a uniform dyeing process, in order to make a comparison between the performances of the different systems synthesized.

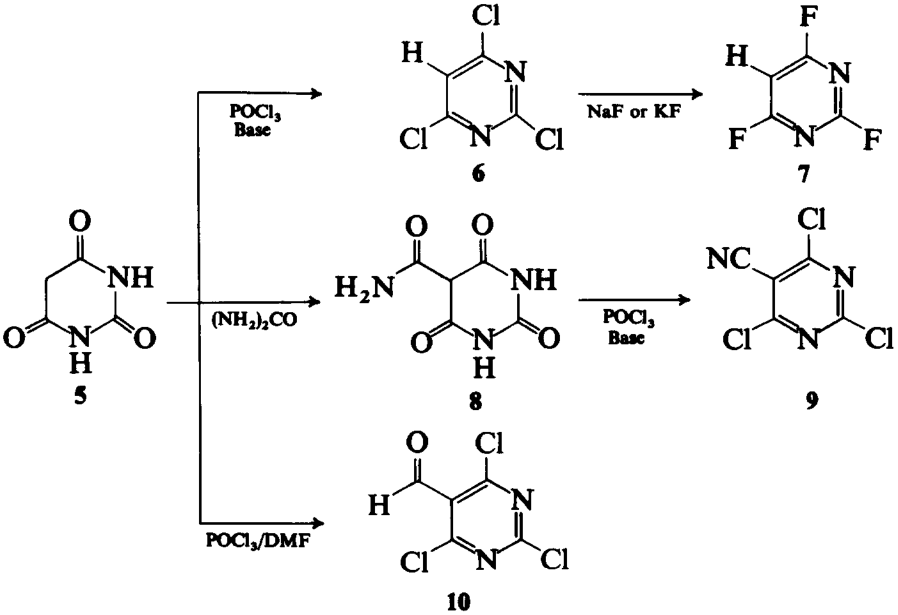
(iii) The determination of some important dyeing parameters, such as the most favourable dyeing temperature as well as exhaust and fixing values.

(iv) A study of the stability of the dye–fibre bond under both acid and alkaline conditions.

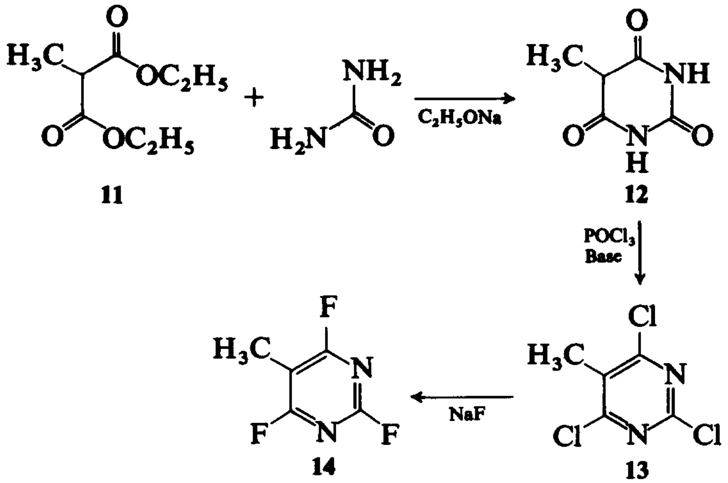
2 SYNTHESIS OF REACTIVE SYSTEMS AND REACTIVE DYESTUFFS

The syntheses were carried out using known methods or by analogous procedures. The yields were not optimized.

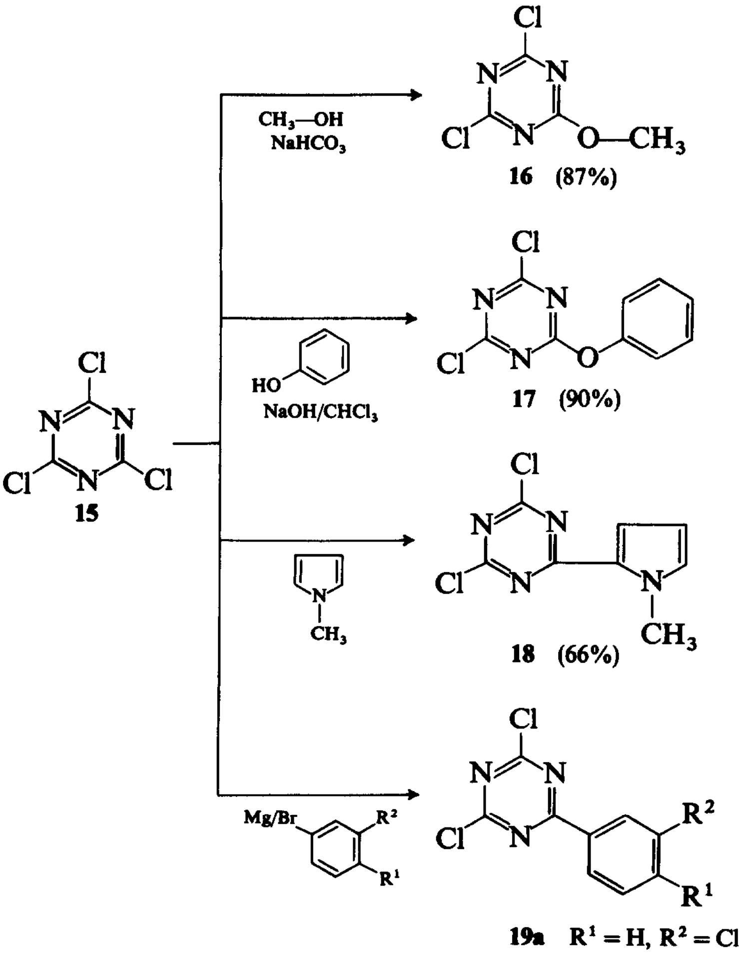
Scheme 2 describes the preparation of reactive systems based on pyrimidine. The starting material in each reaction is barbituric acid **5**. Chlorination with phosphorus oxychloride gives trichloropyrimidine **6**,[17] which when treated with sodium or potassium fluoride produces trifluoropyrimidine **7**.[18,19] Barbituric acid reacts with urea in aqueous suspension to form the carbonic acid amide derivative **8**,[20] which can be converted to 2,4,6-trichloro-5-cyanopyrimidine **9** with phosphorus oxychloride.[6] It is also possible to prepare the trichloro-5-formylpyrimidine



Scheme 2. Synthesis of reactive pyrimidine components.



Scheme 3 Preparation of 2,4,6-trifluoro-5-methylpyrimidine 14.

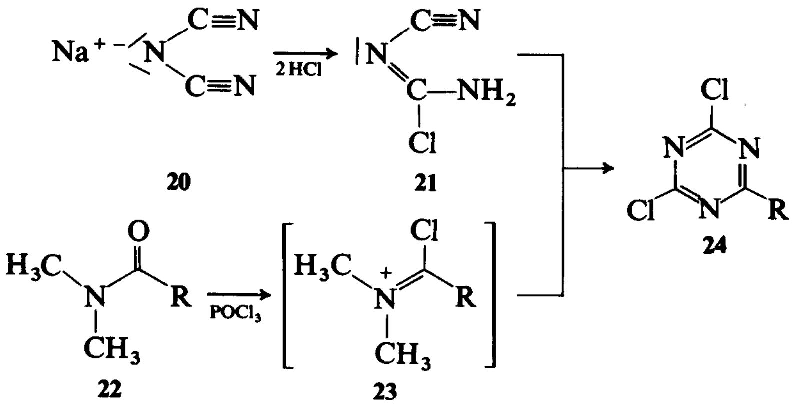


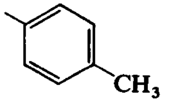
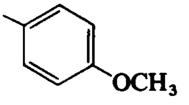
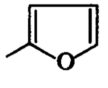
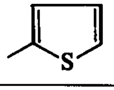
Scheme 4. Reactive systems prepared from cyanuric chloride 15.

derivative **10** by treating barbituric acid with phosphorus oxychloride in DMF.[21-23]

The synthesis of 2,4,6-trifluoro-5-methylpyrimidine **14** is outlined in Scheme 3. Condensation of diethyl 2-methylmalonate **11** with urea in ethanol produces 5-methylbarbituric acid **12**[24] which is successively converted to the trichloro[25] and finally the trifluoro derivative **14**.[18,19]

For the synthesis of reactive components based on triazine, cyanuric chloride **15** is a versatile, low-priced starting material (Scheme 4). Reaction with methanol in the presence of sodium bicarbonate leads to 2,4-dichloro-6-methoxytriazine **16**.[26] Reaction with sodium phenolate in chloroform produces the 6-phenoxy-triazine derivative **17**.[27] Cyanuric chloride reacts with N-methylpyrrole in toluene to form **18**.[16,28] Products **19a** and **19b** are



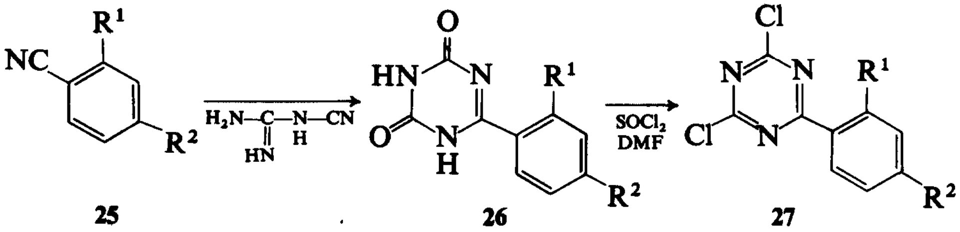
No.	R	Yield (%)
24a	$-CH_3$	28
24b	$-C_2H_5$	32
24c		33
24d		27
24e		20
24f		19

Scheme 5. Synthesis of triazine derivatives **24a–f.**

accessible by reaction with the Grignard reagents prepared respectively from *m*- and *p*-chlorobromobenzene.[16]

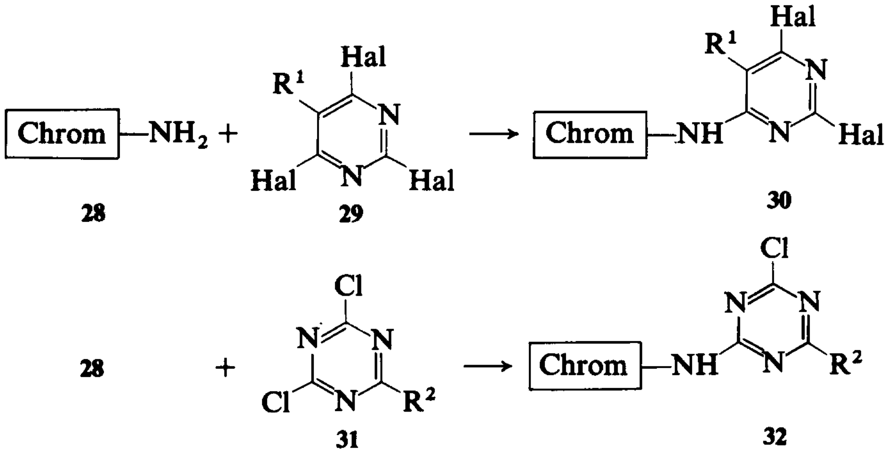
Scheme 5 shows a versatile method for producing triazine derivatives **24**.[29,30] R can be methyl, ethyl, substituted aryl, furyl and thienyl.[16] However, the yields are low. The appropriately substituted N,N-dimethylcarbonic acid amide **22**[31] reacts with phosphorus oxychloride to form the intermediate salt **23**, which cyclizes with N-cyanochloroformamidine **21** to form the triazine derivative **24**.[29,30] Compound **21** is produced from sodium dicyanamide **20** and hydrochloric acid.[32]

The synthesis of several aryl-substituted dichlorotriazine derivatives **27** (Scheme 6)[16] occurs in better yields. The appropriately substituted



No.	*R*^{1}	*R*^{2}	*Yield* (%)
27a	—H	—H	58
27b	—Cl	—H	51
27c	—CH_3	—H	30
27d	—CH_3	—CH_3	57
27e	—O—CH_3	—H	46

Scheme 6. Preparation of 2-aryl-4,6-dichlorotriazines **27a–e**.

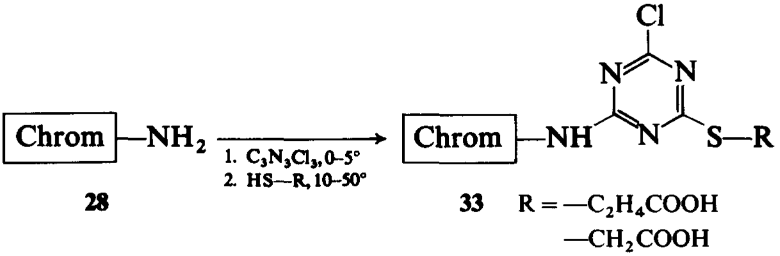


Scheme 7. Formation of reactive dyestuffs.

benzonitriles **25** are treated with dicyandiamide to give the 6-aryltriazine-2,4-diones **26**,[33] which are converted into the dichloro derivatives **27** with thionyl chloride.[34]

Scheme 7 outlines the conversion of chromophores to reactive dyes using reactive systems. The chromophores **28** here are amino azo dyestuffs containing sulphonic acid groups.[35-43] Condensation of **28** with reactive components **29** based on pyrimidines produces the reactive dyestuffs **30**; reactions of **28** with triazine derivatives **31** give reactive dyes of general formula **32**.[16] These condensation reactions are carried out in aqueous suspension at temperatures ranging from 5 to 70°C, depending on the reactive system.

The mercapto substituted chlorotriazine dyes **33**[44] are synthesized according to eqn (1):

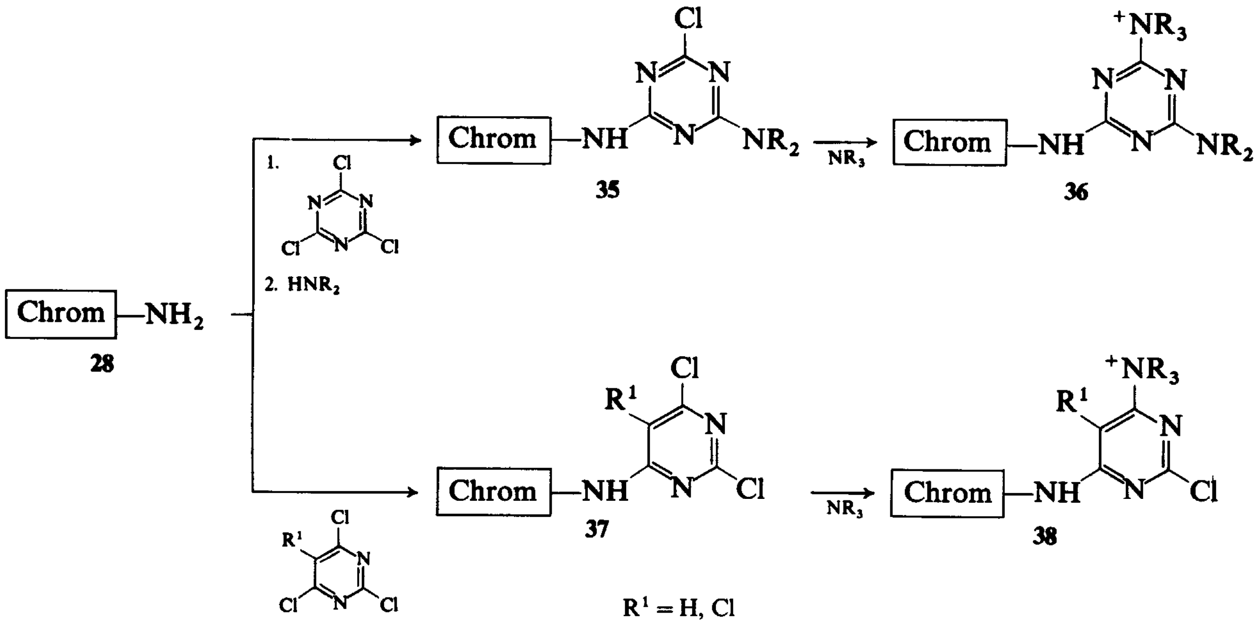


(1)

Treatment of the chromophores **28** with cyanuric chloride in aqueous suspension at 0–5°C leads to the corresponding dichlorotriazine dye intermediates which then can be converted to dyes of type **33** by reaction with 3-mercaptopropionic acid or 3-mercaptoacetic acid at 10–50°C.

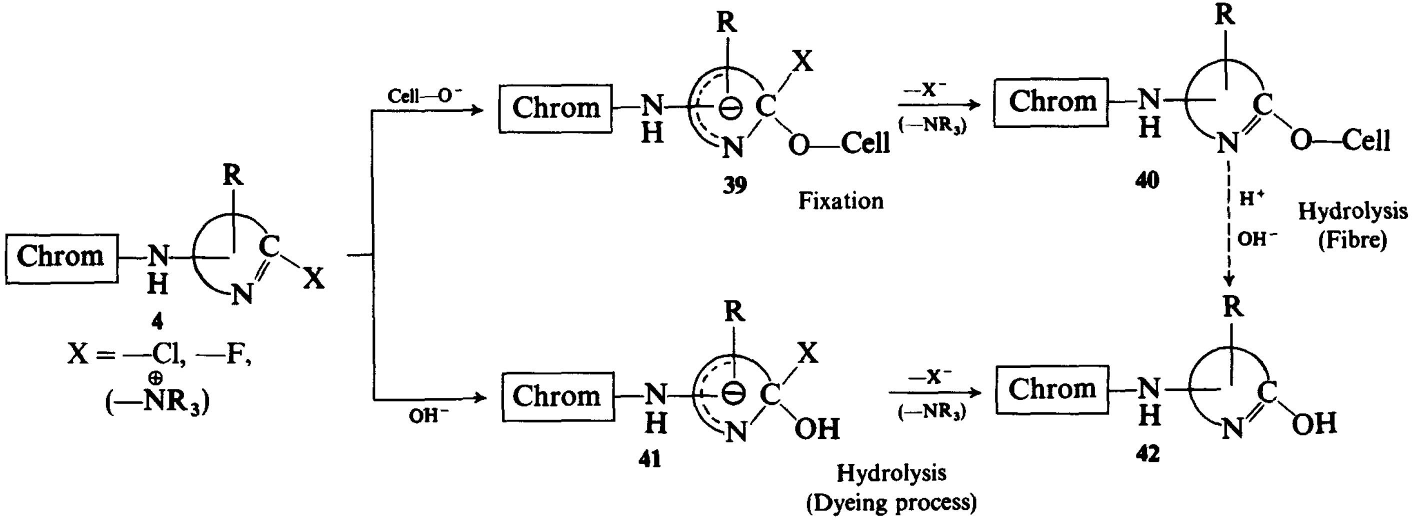
Scheme 8 shows the syntheses of reactive dyes **36** (triazines) and **38** (pyrimidines) containing quaternary ammonium substituents[45] which are also good leaving groups in nucleophilic substitution reactions. The chromophores **28** react first with cyanuric chloride and then with ammonia, primary or secondary amines to form the corresponding dyes **35**. Final treatment with tertiary amines at *c.* 40–50°C leads to the quaternary ammonium triazine dyes **36**. Similarly, the chromophores **28** on treatment with trichloropyrimidine or tetrachloropyrimidine at *c.* 20–50°C form dyes **37**, which can be nucleophilically substituted with tertiary amines at *c.* 40–60°C to form the positively charged pyrimidine dyes **38**.

Scheme 9 shows the reaction mechanism of dyeing with reactive dyes; the process is considered a nucleophilic biomolecular heteroaromatic substitution.[6,15] The general formula **4** covers all reactive dyes with the triazine and pyrimidine reactive components described above. Under alkaline dyeing conditions, the cellulose anion nucleophilically adds to the polarized C-atom of the reactive system to form the intermediate **39**, followed by elimination of the halo atom or the tert. amine to yield **40**. A competing



Scheme 8. Reactive dyestuffs with quaternary ammonium substituents.

Nucleophilic bimolecular heteroaromatic substitution



Scheme 9. Reaction mechanism.

reaction is always the hydrolysis of **4** commencing with the nucleophilic hydroxyl anion and ultimately forming **42**.

When the dyed cellulose **40** is treated, e.g. in washing processes with acid or alkaline reagents, the dye–fibre bond may cleave, also forming dye **42**.

3 APPLICATION AND PROPERTIES OF THE REACTIVE DYESTUFFS ON COTTON

3.1 Application and fastness properties

The reactive dyes described above were applied on cotton[10–14] according to the procedure shown in Chart 1. To determine the optimum dyeing temperature, four aqueous dye-liquors were prepared, each containing the cotton fabric, 2% dyestuff (based on the substrate) and 50 g/litre common salt. Soda ash (10 g/litre) was added after 20 min and 30 min dyeing at 30°C. The temperatures of the four dye-liquors were then raised over 30 min to 40, 60, 80 and 98°C respectively. After dyeing for 60 min at these temperatures, the woven fabric was rinsed with hot water, soaped at the boil and then dried.

Charts 2 and 3 show application test results for two dyes chosen at random. The reactive dye **45e** contains a monoazo chromophore and a chlorotriazine reactive component with a furyl substituent. In the first row of the chart, the 2% dyeings obtained at 40, 60, 80 and 98°C are illustrated.

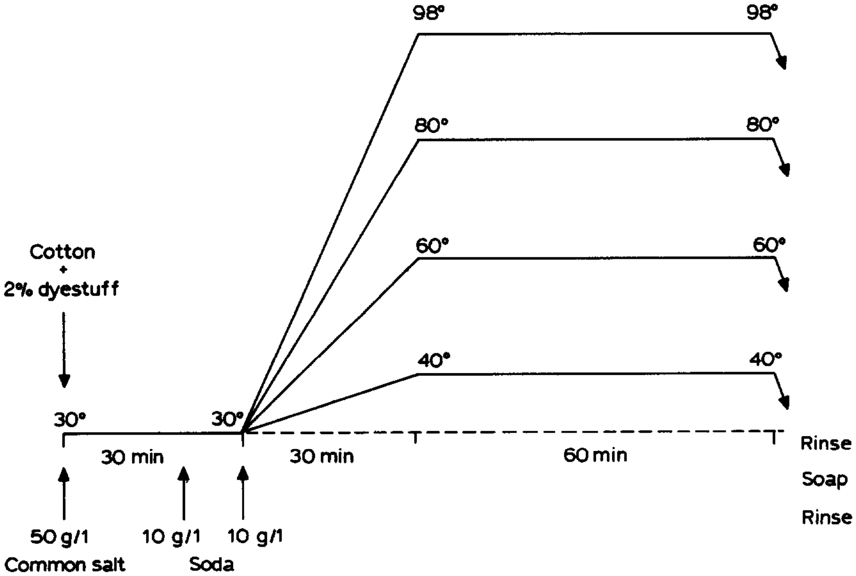


Chart 1.

A general visual comparison of the dyeings readily shows at which temperature the highest dye fixation takes place. In this case the optimum dyeing temperature is 40°C. This sample, dyed at the most favourable temperature, was colourimetrically measured to determine the amount of dye required for dyeings of 1/1 standard depth.[46] The cotton fabric was again dyed with this dye concentration at the optimum dyeing temperature and extinction measurements are carried out in the dye liquor to determine the exhaust values (*EV*) and the fixation value (*FV*).[10-14] The exhaustion value *EV* indicates that portion of dye which is adsorbed on the fibre during the dyeing process, and the fixation value *FV* indicates that portion of dye which forms a covalent bond with the fibre.

Two fastness tests[47,48] were also carried out with the dyeing in 1/1 standard depth, viz.,

1. A contact fastness called acid hydrolysis: in this case there was a partial cleavage of the dye–fibre bond and distinct staining of the adjacent cotton and wool fabric by the hydrolysed dye.
2. A washfastness called alkaline hydrolysis: after this treatment, distinct fading, i.e. destruction of the original dyeing was observed.

Such a fastness level is always considered poor.

The blue reactive dye **48d** consists of a disazo chromophore and a difluoropyrimidine reactive system. It exhibits a nearly uniform dyeing behaviour in the temperature range of 40–98°C. The fastness level can be described as generally good, as the dyeings exhibit no fading or staining of the adjacent fabrics.

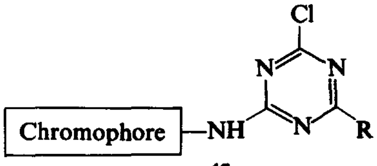
3.2 Structure–property relationships: triazine dyes

Tables 1–7 present the application test results of the different reactive dyestuff classes. Each table shows the individual chromophore, the substituent R in the general formula, the optimium dyeing temperature, the exhaust and fixation values and a brief comment on the hydrolysis fastness properties (— = poor, ○ = moderate, + = good). The last column indicates the shade on cotton.

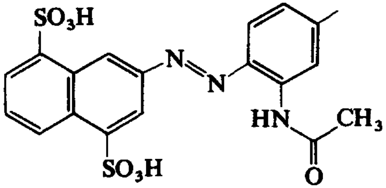
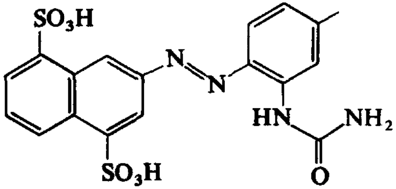
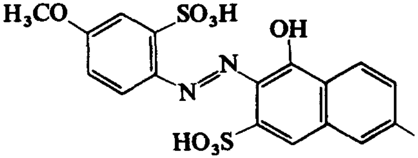
All the methyl- and ethylsubstituted chlorotriazine dyes **43** exhibit an optimum dyeing temperature of 40°C. The exhaustion values (*EV*) lie within the acceptable range of 77–90% but the fixation values (*FV*) are scattered between 30 and 50%, which are at a rather low level (an acceptable *FV* range would be from 70–90%).

The relative fixation value was defined as the number obtained by dividing the fixation value by the exhaustion value × 100. This describes the portion of fixed dye as compared to that which is adsorbed on the fibre, and is a

TABLE 1
Application Test Results for **43a–e**



43

No.	Chromophore	R	Optimium dyeing temp. (°C)	EV (%)	FV (%)	Rel. FV (%)	Hydrolysis		Shade on cotton
							H^+	OH^-	
43a		$—CH_3$	40	84	30	36	—	—	Yellow
43b		$—C_2H_5$	40	83	50	60	—	—	Yellow
43c		$—C_2H_5$	40	87	51	59	—	—	Golden-yellow
43d		$—CH_3$	40	90	35	39	—	—	Scarlet
43e		$—C_2H_5$	40	77	34	44	—	—	Scarlet

rough measure of the selectivity with which a reactive dye reacts with cotton. If the relative fixation value is rather low, as in the present case, this indicates that considerable hydrolysis has occurred during the course of the dyeing process.

Whereas the exhaustion and fixation values can be influenced, e.g. by the type of chromophore or the amount of salt used in the dye liquor, this is not so easily effected with the relative fixation value since this is a proportional measure. The hydrolysis fastness properties of the dyeings on cotton produced with this class of dyes are poor in all cases, permitting the conclusion that the dye–fibre bonds are relatively unstable under both acid and alkaline conditions.

The 2-aryl-4-chlorotriazine dyes **44** exhibit optimum dyeing temperatures between 40 and 80°C, depending on the substituent in the aryl residue. The exhaustion values (*EV*) are in the range of 70–95%, the fixation values (*FV*) are between 42 and 73% and the relative fixation values are between 47 and 88%. This indicates that the aryl substituted triazine dyes show a higher selectivity than the alkyl substituted derivatives. The hydrolysis fastness properties under acid and alkaline conditions are generally poor.

A picture similar to that for the aryl substituted chlorotriazine dyes **44** is shown by the heteroaryl substituted chlorotriazine dyes **45** (R = furyl, thienyl or N-methylpyrrolyl). The most favourable dyeing temperatures vary between 40 and 80°C; the relative fixation values range from 61 to 74% and the hydrolysis fastness properties are again poor in most cases.

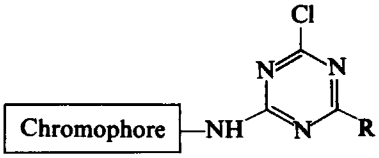
Table 4 describes the O-methyl-, O-phenyl- and S-carboxyalkyltriazine dyes. The optimum dyeing temperature is nearly always 40°C. The hydrolysis fastness properties are medium to good in the case of the yellow chromophore, but are poor in the case of the red chromophore.

3.3 Structure–property relationships: pyrimidine based dyes

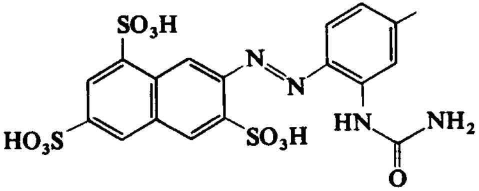
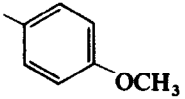
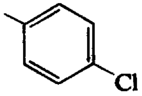
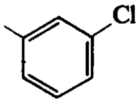
Following the reactive dyes based on triazine, Table 5 shows examples analogous to pyrimidine reactive systems, viz. the 5-formyl- and the 5-cyanochloropyrimidines. The 5-formyl-2,4-dichloropyrimidine dyes **47b** and **47d** exhibit maximum dyeing power at 40°C in each case, with relative fixation values of 66% and 55% respectively. With the 5-cyano-2,4-dichloropyrimidine derivatives **47a**, **47c** and **47e** the most favourable dyeing temperature varies from 40 to 80°C. The relative fixation values range from 69 to 78%, i.e. the cyano derivatives exhibit greater selectivity than the formyl derivatives with respect to reaction with cellulose. The hydrolysis fastness level here can be considered generally as moderate.

The 2,4-difluoropyrimidine dyes **48** all show optimum dyeing temperatures of 60°C. The representatives with R = H exhibit relative fixation values

TABLE 2
Application Test Results for **44a–h**



44

No.	*Chromophore*	*R*	*Optimium dyeing temp. (°C)*	*EV (%)*	*FV (%)*	*Rel. FV (%)*	*Hydrolysis*		*Shade on cotton*
							H^+	OH^-	
44a			60	95	73	77	○	○	Golden-yellow
44b			80	89	52	58	○	+	Golden-yellow
44c			60	90	42	47	○	–	Golden-yellow

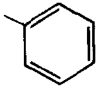
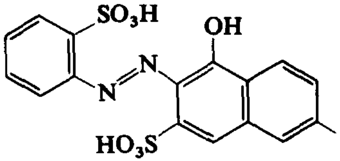
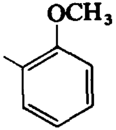
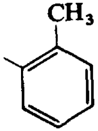
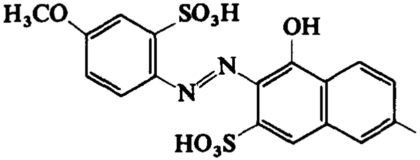
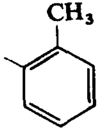
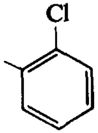
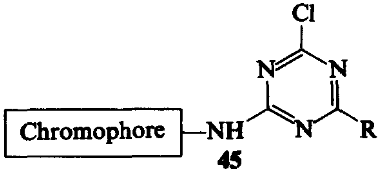
44d			60	91	64	70	–	–	Orange
44e			40–60	82	71	88	–	–	Orange
44f			60	71	50	70	–	–	Orange
44g			60	82	57	70	–	–	Scarlet
44h			40	97	71	73	–	–	Scarlet

TABLE 3
Application Test Results for **45a–g**



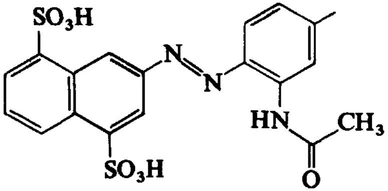
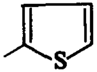
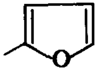
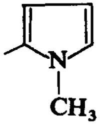
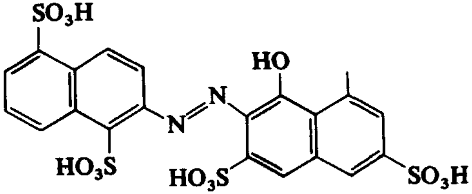
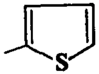
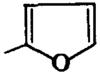
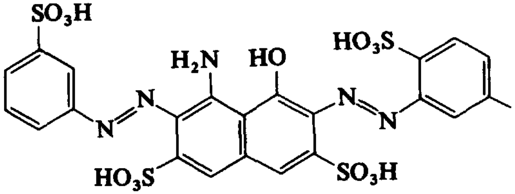
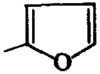
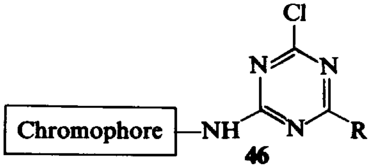
No.	*Chromophore*	*R*	*Optimium dyeing temp. (°C)*	*EV (%)*	*FV (%)*	*Rel. FV (%)*	*Hydrolysis*		*Shade on cotton*
							H⁺	*OH⁻*	
45a			60	97	72	74	○	–	Yellow
45b			60	96	59	61	○	–	Yellow
45c			80	87	63	72	○	+	Yellow
45d			40	87	60	69	–	–	Red
45e			40	63	43	68	–	–	Red
45f			40–60	88	62	70	–	–	Navy-blue
45g			60–80	92	58	63	○	–	Navy-blue

TABLE 4
Application Test Results for **46a–g**



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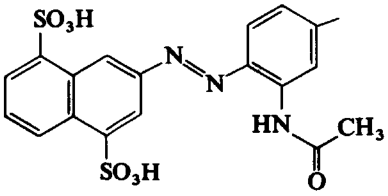
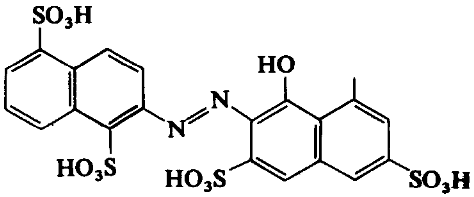
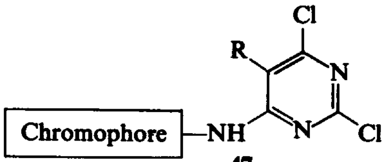
No.	*Chromophore*	*R*	*Optimium dyeing temp. (°C)*	*EV (%)*	*FV (%)*	*Rel. FV (%)*	*Hydrolysis*		*Shade on cotton*
							H^+	*OH^-*	
46a		—O—CH_3	40	73	38	52	○	○	Yellow
46b		—O—C_6H_5	40	86	41	48	–	+	Yellow
46c		—S—C_2H_4COOH	40	84	45	54	○	○	Yellow
46d		—S—CH_2COOH	60	88	57	65	+	○	Yellow
46e		—O—CH_3	40	55	35	64	–	–	Red
46f		—O—C_6H_5	40	55	36	65	–	–	Red
46g		—S—CH_2COOH	40	51	31	61	–	–	Red

TABLE 5
Application Test Results for **47a–e**



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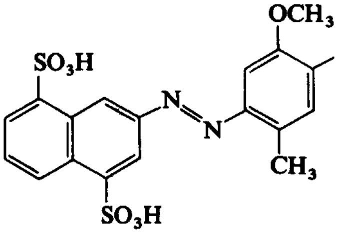
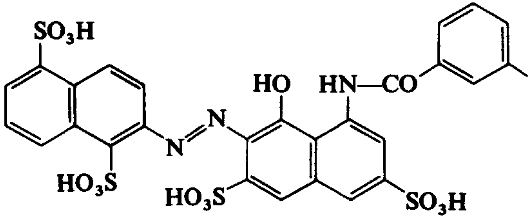
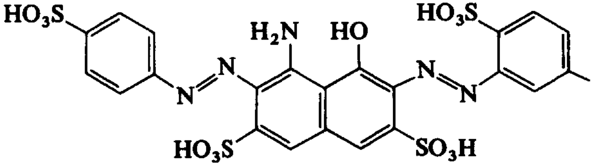
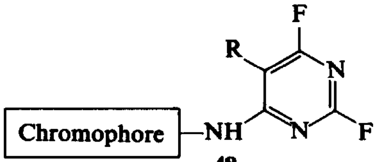
No.	*Chromophore*	*R*	*Optimium dyeing temp. (°C)*	*EV (%)*	*FV (%)*	*Rel. FV (%)*	*Hydrolysis*		*Shade on cotton*
							H⁺	*OH⁻*	
47a		—CN	80	87	68	78	–	+	Yellow
47b		—CHO	40	98	65	66	○	+	Yellow
47c		—CN	60	65	47	72	○	○	Red
47d		—CHO	40	64	35	55	○	○	Red
47e		—CN	40	75	52	69	+	○	Navy-blue

TABLE 6
Application Test Results for **48a–e**



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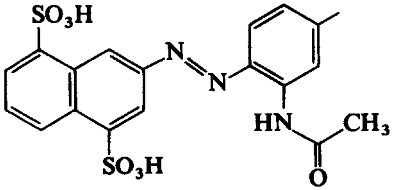
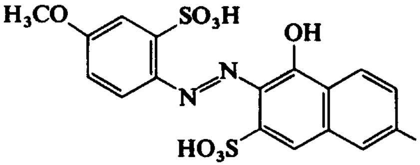
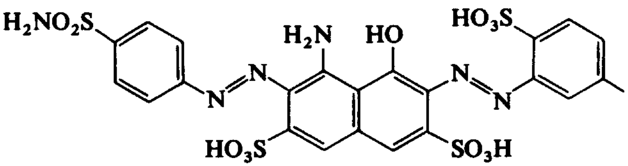
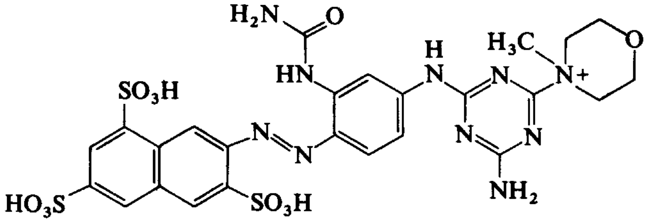
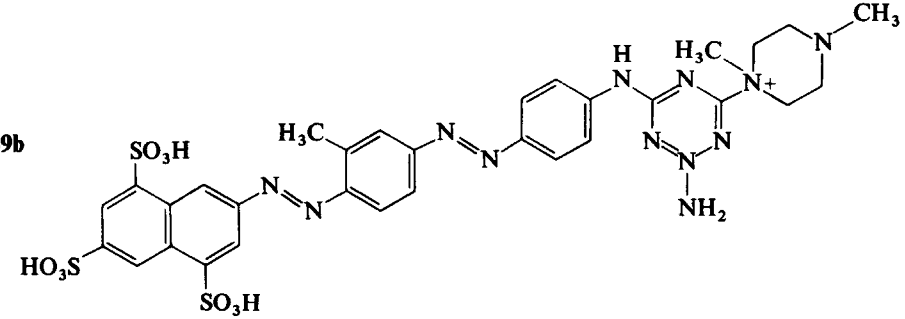
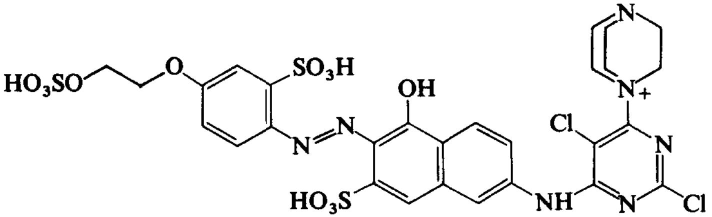
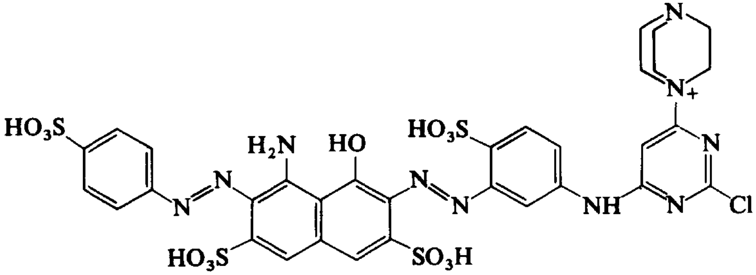
No.	*Chromophore*	*R*	*Optimium dyeing temp.* (°C)	*EV* (%)	*FV* (%)	*Rel. FV* (%)	*Hydrolysis*		*Shade on cotton*
							H^+	OH^-	
48a		—H	60	92	77	84	+	+	Yellow
48b		—H	60	93	77	83	+	+	Scarlet
48c		—CH_3	60	73	24	34	○	○	Scarlet
48d		—H	60	81	69	85	+	+	Navy-blue
48e		—CH_3	60	78	54	69	○	+	Navy-blue

TABLE 7
Application Test Results for **49a–d**

No.	*Dyestuff*	*Optimium dyeing temp.* (°C)	*EV* (%)	*FV* (%)	*Rel. FV* (%)	*Hydrolysis*		*Shade on cotton*
						H^+	OH^-	
49a		40	83	48	58	○	+	Golden-yellow
49b		60	88	29	31	+	+	Orange

49c		60	89	33	37	+	—	Scarlet
49d		40	56	16	29	+	+	Navy-blue

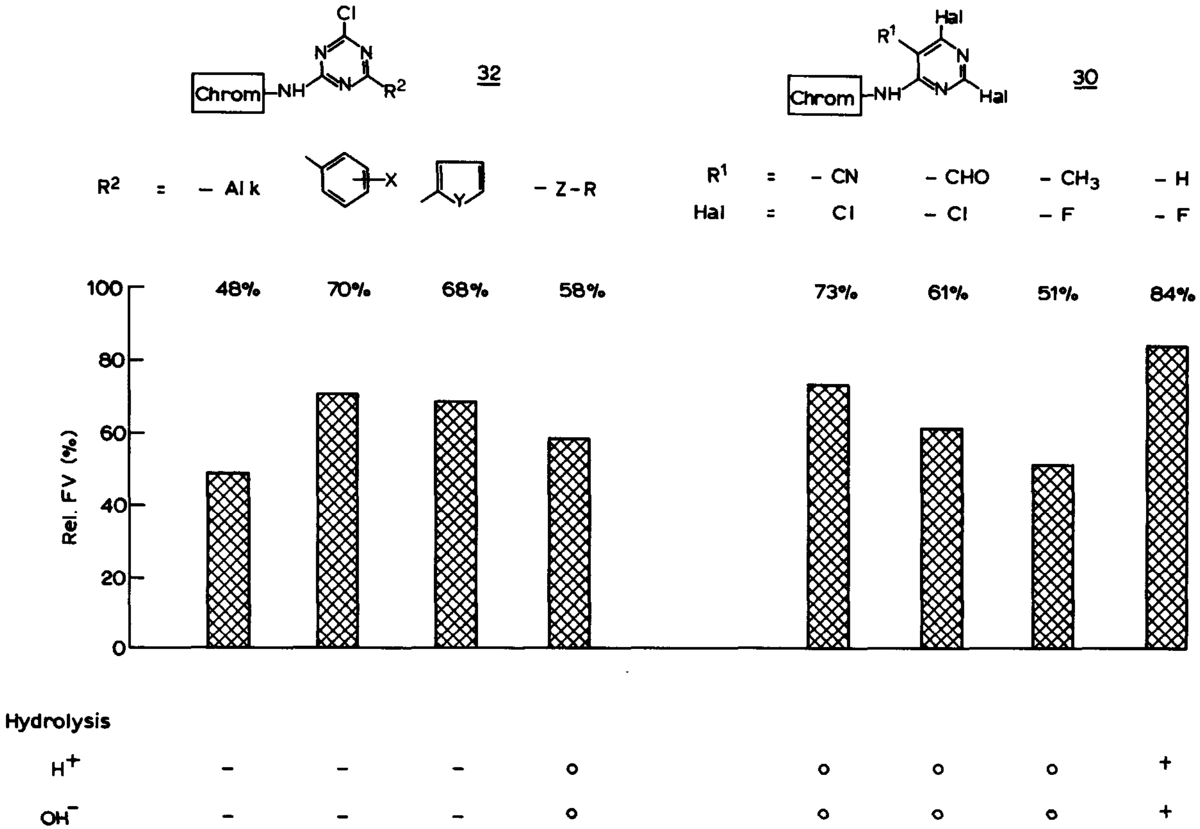


Chart 4. Summary of relative mean fixation values and hydrolysis tests on dyestuffs **32** and **30**.

of 83–85%, and the hydrolysis fastness properties are good in each case. The derivatives with $R = CH_3$ produce significantly lower relative fixation values and a fastness level that is only moderate. Table 7 shows a selection of reactive dyes **49a–d** with quaternary ammonium substituents. The leaving groups of the triazine dyes **49a** and **49b** are respectively N-methylmorpholine and N,N-dimethylpiperazine. The leaving group of the dichloropyrimidine dye **49c** and that of the chloropyrimidine dye **49d** is DABCO.

All the dyestuffs **49** exhibit optimum dyeing temperatures of 40–60°C. The relative fixation values, which are low in all cases indicate that in the dyeing process, dye hydrolysis instead of fixation mainly takes place. The fastness level of the dyes **49** ranges from good to poor.

4 SUMMARY

Chart 4 is an attempt to summarize the performances of the different reactive systems described thus far. The general formula **32** represents our reactive dyes based on chlorotriazine with alkyl-, aryl, heteroaryl-, –OR and –S–R substituents. Formula **30** covers the cyano- and formylsubstituted chloro-pyrimidines as well as the difluoropyrimidine derivatives. In every case, mean values were computed for the relative fixation values of the individual reactive dye classes. These are shown in the form of a bar graph.

Among the triazine dyes **32** the highest average relative fixation values are exhibited by the 2-aryl and 2-heteroaryl derivatives, viz. about 70% in each case. Among the reactive dyes **30** based on pyrimidine, the 5-cyano-2,4-dichloro derivatives show a higher level with 73% while the 2,4-difluoropyrimidines show the highest level with 84%, i.e. they exhibit the highest selectivity in their reaction with cellulose.

The 2,4-difluoropyrimidine dyes also show the best overall picture with respect to the hydrolysis fastness properties, permitting the conclusion, that the dye–fibre bonds are stable under both acid and alkaline conditions. The other pyrimidine dyes can be generally regarded as moderate, while the reactive dyes **32** based on triazine showed poor results in this respect.

ACKNOWLEDGEMENT

I thank my coworkers, Mr R. Iseli and Mr G. Voegtlin, who synthesized most of the reactive components and reactive dyestuffs. I also thank my colleagues Dr M. Greve and Dr P. Matzinger for additional synthetic work in their laboratories and Mr H. Ulshoefer and his team, who did all the application tests. Last but not least I thank Professor E. J. Moriconi, Dr M. Gisler and Ms M. Altoka for their help in preparing this paper.

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