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DEVELOPMENT OF NOVEL REACTIVE DYES WITH A MIXED BIFUNCTIONAL REACTIVE SYSTEM

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SUMMARY

The advantages of the mixed bifunctional reactive system—vinylsulphone and monochlorotriazine—with respect to dyeing and fastness properties are discussed in detail.

1. INTRODUCTION

In 1956, dichlorotriazine reactive dyes were introduced by ICI as the first reactive dyes for cellulosic fibres. Since that time, many dyestuff manufacturers have made considerable efforts to find new reactive systems and their chromophores. Consequently, the number of reactive dyes registered in the *Colour Index* was more than 600 by 1978. The demand for reactive dyes in Japan has increased dramatically and in 1979 they took the top market share of dyes for cellulosic fibres, displacing direct dyes as shown in Fig. 1.

The reason for such a rapid increase in demand is primarily due to the excellent characteristics of reactive dyes, e.g. their brilliant shades, excellent wet fastness of dyeings and simple dyeing operations which have increasingly been accepted within the industry. However, with the growth in the usage of reactive dyes, additional properties have been demanded by dyeworks and apparel manufacturers,[1–4] in particular high fixation in exhaustion dyeing and high fastness to chlorine, perspiration, light and washing in the presence of peroxides. Considerable progress towards the achievement of these objectives may be made by the use of bifunctional reactive dyes, in particular those with a mixed bifunctional system, the Sumifix Supra dyes.

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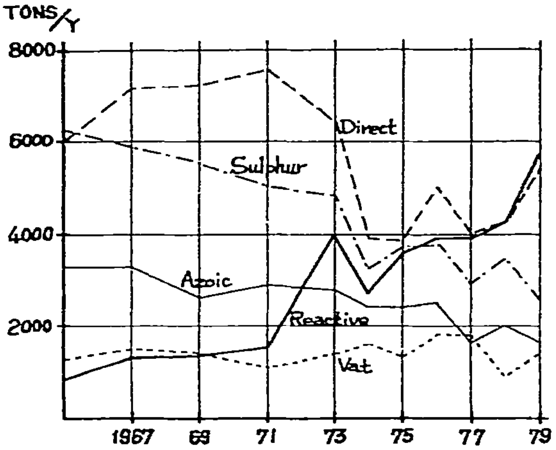
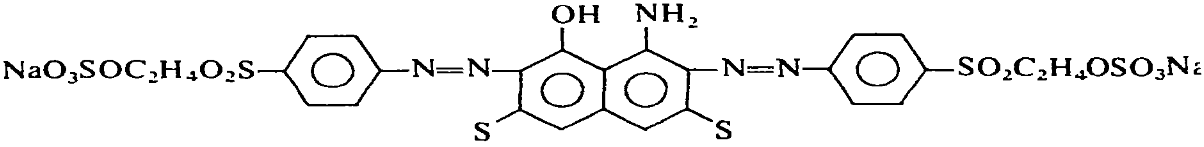


Fig. 1. Recent trends in consumption of various dyes for cellulosic fibres in Japan.

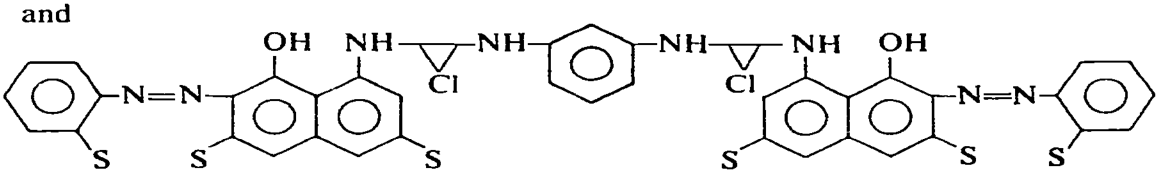
2. DEVELOPMENT OF BIFUNCTIONAL REACTIVE DYES

An inadequate degree of fixation of reactive dyes has been regarded as one of the problems of dyeing and to improve it, an idea of introducing two or more reactive systems into a dye molecule was introduced. There are two types of bifunctional reactive dyes, one having two or more reactive systems of the same kind and the other having two or more reactive systems of different types. Reactive dyes having a dichlorotriazine or difluoromonochloropyrimidine group may be said to be bifunctional in a sense, since they have two or more leaving halogen atoms per reactive system. In this report, however, the term 'bifunctional dye' is defined as a dye molecule having two independent reactive systems. Typical vinylsulphone or monochlorotriazine reactive dyes having two identical reactive systems in the dye molecule are



CI Reactive Black 5 (20505)

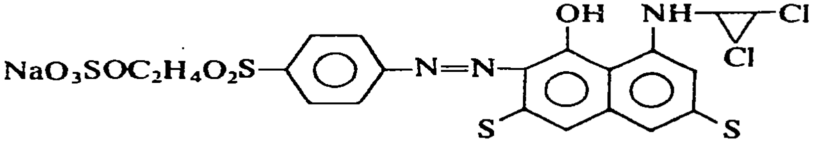
and



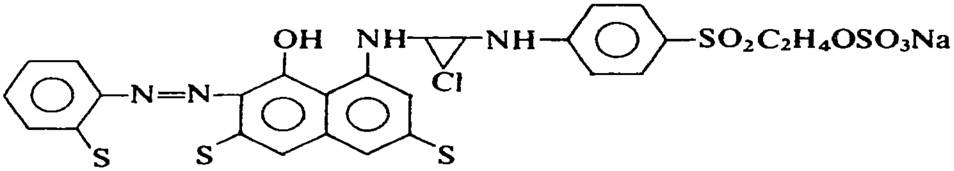
▽ : triazine ring; S: sulphonic acid group (ref. 5)

Patents have been published which describe dichlorotriazine[6] and monofluorotriazine[7] dyes having two reactive systems of the same kind, and also monochlorotriazine dyes having three[8] or four[9] reactive systems. In 1959, ICI applied for a patent[10] relating to the introduction of two or more reactive systems of different kinds into a dye molecule. The characteristic of this patent is that two or more of all the reactive systems of different kinds were combined with one another, and the patent says that the dyes obtained are applicable to all kinds of fibres, but in fact the fibres used in the examples are polyamide in most cases.

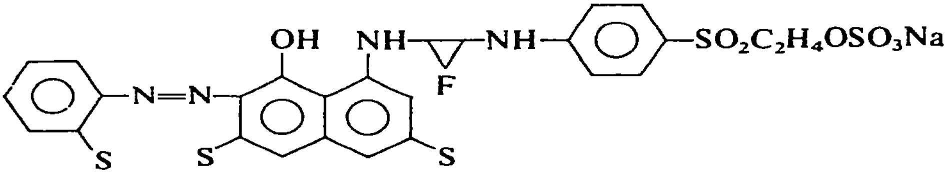
Subsequently many dyestuffs manufacturers applied for patents for producing dyes containing a combination of two different reactive systems. Some dyes having two typical reactive systems are as follows.



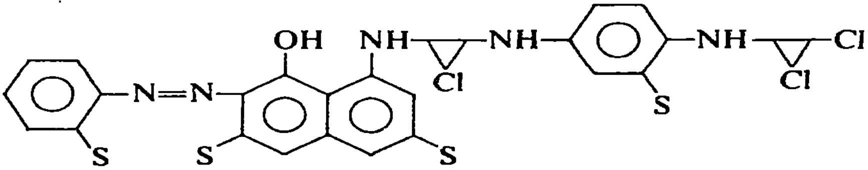
Vinylsulphone/dichlorotriazine[11]



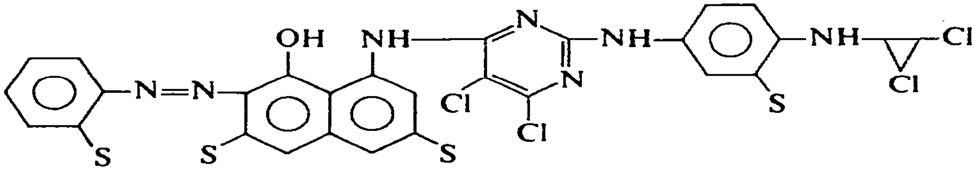
Vinylsulphone/monochlorotriazine (1)[12]



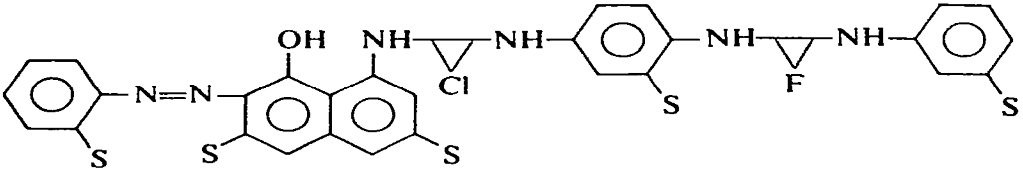
Vinylsulphone/monofluorotriazine[13]



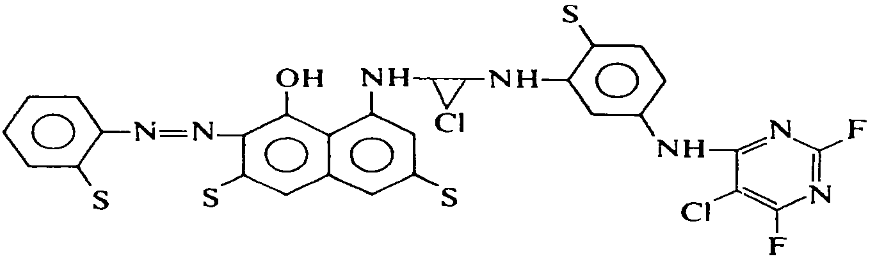
Dichlorotriazine/monochlorotriazine[14]



Dichlorotriazine/dichloropyrimidine[15]



Monochlorotriazine/monofluorotriazine[16]



Monochlorotriazine/difluoromonochloropyrimidine[17]

Further, application was made for patents[18] relating to dyes produced by introducing one vinylsulphone group and two monochlorotriazine groups and also to dyes produced by introducing two vinylsulphone groups and two monochlorotriazine groups.[19]

All the polyfunctional reactive dyes having different reactive systems except monofluorotriazine dyes were researched in the 1950s, but they were not commercially available at that time. However, novel reactive dyes, Sumifix Supra dyes,[20] having a vinylsulphone group and a monochlorotriazine group have been introduced and they are the first mixed bifunctional reactive dyes to become commercially available.

3. VINYLSULPHONE/MONOCHLOROTRIAZINE BIFUNCTIONAL REACTIVE DYES

By combining in the one dye the two different reactive systems it was expected that they would possess the separate advantages of the two groups, namely:

(i) Advantages owing to a vinylsulphone group:
  (a) A chemical bond between a vinylsulphone and cellulosic fibres is very stable to acid hydrolysis, so that these dyes have excellent stability on dyed goods on storage.
  (b) The substantivity of hydrolyzed by-product produced during the dyeing process is very small so that the unfixed hydrolyzed dyes can be easily washed of.
(ii) Advantages owing to a monochlorotriazine group:
  (a) Due to the electrophilic property of the cyanuric group, a wide range of chromophores having good fastness to light, perspiration–light and chlorine can be selected.
  (b) The increase in substantivity resulting from the introduction of a triazine group to the dye molecule improves the degree of exhaustion and fixation of the dyes.

In addition the presence of the two groups was expected to produce a combined advantage since the two reactive systems have different reactivity, so that the range of optimum dyeing temperatures becomes wider, and the shade reproducibility in exhaustion is improved. Similarly, with the improved alkali stability in continuous dyeing and cold pad-batch dyeing, and the improved stability of print pastes in printing, the reliability in these dyeing and printing processes becomes higher.

Increasing consumer standards require reactive dyes to be based on a chromophore resistant to degradation by light, perspiration–light and oxidising agents (e.g. chlorine) and a reactive system giving a dye–fibre bond stable to heat, oxidizing agents (e.g. peroxides) and acid gases.

The reactive dyes **1** to **6** in Table 1 are produced by a typical chromophore (obtained by the coupling of orthanilic acid with H-acid) which is fast to light and perspiration–light and stable to active chlorine in combination with various reactive systems.

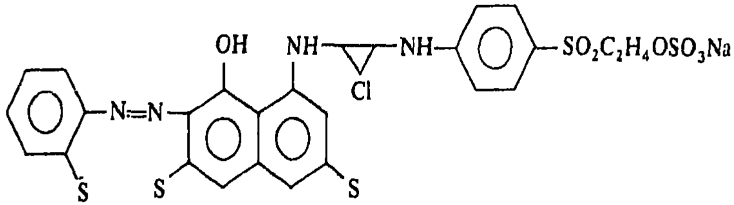
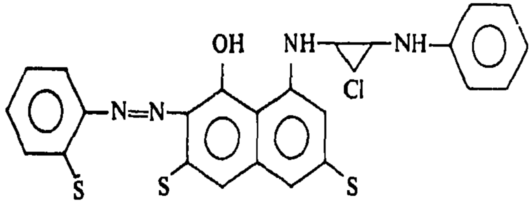
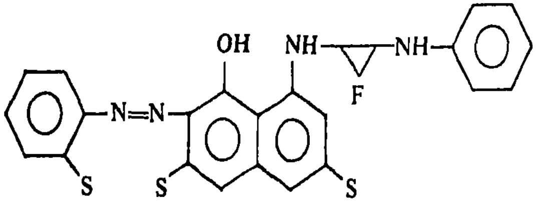
As shown each dye is fast to perspiration–light and chlorine, irrespective of the reactive systems. However, with regard to fastness to acid hydrolysis and peroxide washing, it can be seen that the vinylsulphone/monochlorotriazine reactive dye, **1**, is slightly superior to the monochloro- and monofluoro- triazine dyes, **2** and **3** respectively, and that it is considerably superior to the dichloroquinoxaline and difluoromonochloropyrimidine dyes, **4** and **5** respectively.

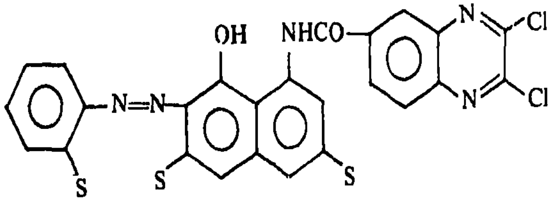
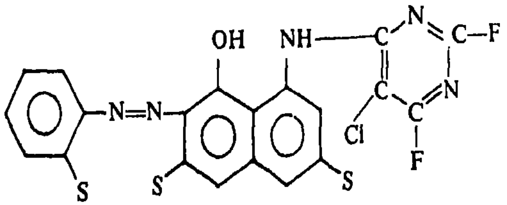
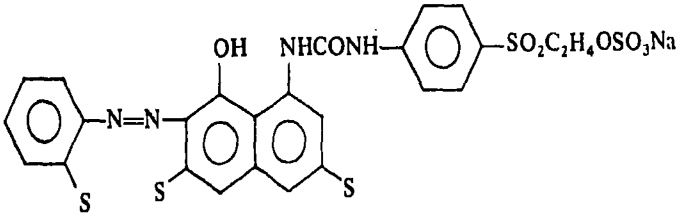
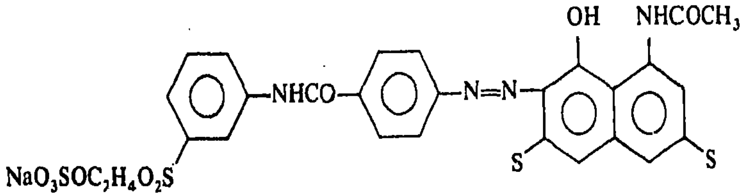
The reactive dye **6** in which a chromophore and a reactive group are linked by a —CO— group in place of the triazine group **1**, is a little more stable than **1** to acid hydrolysis and peroxide washing.

The reactive dye **7**, having a vinylsulphone group on the diazo component, is also stable to acid hydrolysis, but very poor in chlorine fastness for the possible reason that it has no sulphonic acid group in the *ortho* position to the azo group.[21] Thus, by connecting the chromophore through a triazine ring with a vinylsulphone group

TABLE I

RELATIONSHIP BETWEEN CHEMICAL STRUCTURE AND DYE FASTNESS TO VARIOUS TREATMENTS

Dye no.	Chemical structure of dye	Fastness			
		Perspiration-light (JIS method)[a]	*Chlorine (ISO method)*[b]	*Acid hydrolysis (C-Gy method)*[c]	*Peroxide washing (Renown method)*[d]
1		3–4	4	4	4–5
2		3–4	4	3–4	4
3		3–4	4	3–4	4

4		3-4	4	1-2	3
5		3-4	4	3-4	3-4
6		3-4	4	4-5	4-5
7		2	1	4-5	4

The values in the table are those based on:

[a] alkaline perspiration for perspiration-light;

[b] colour change for chlorine;

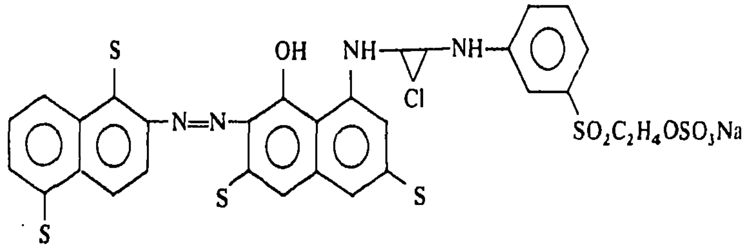
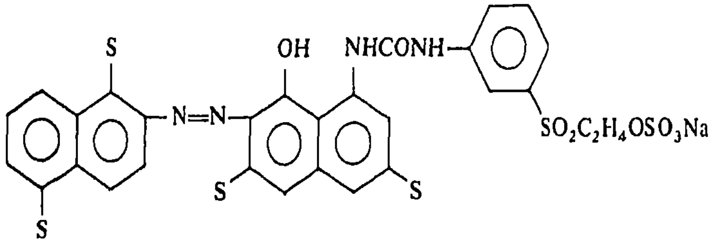
[c] staining on wool for acid hydrolysis; and

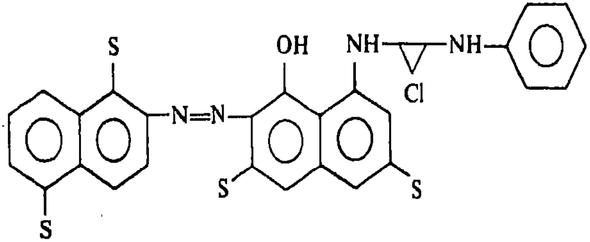
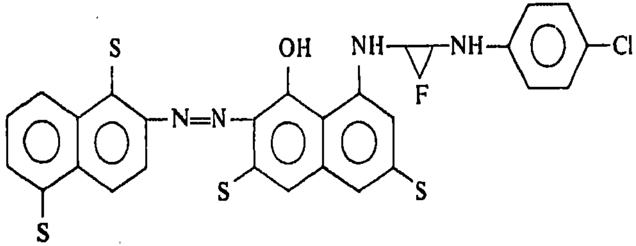
[d] staining on cotton for peroxide washing (dyeing depth 2%).

TABLE 2

REACTIVE SYSTEMS AND DYEING PROPERTIES

(cotton unmercerized 2 % shade; 50 g litre^{-1} Glauber's salt anhydrous; 20 g litre^{-1} sodium carbonate; 20:1 liquor to goods ratio; 60 min)

Dye no.	*Chemical constitution of dye*	*Optimum dyeing temperature (°C)*	*Primary exhaustion*[a] *(%)*	*Secondary exhaustion*[a] *(%)*	*Fixation (%)*	*Washing off (rating)*
8		60	38	78	59	3–4
9		60	26	48	40	3–4

10		80	30	56	43	3
11		40	52	81	55	3

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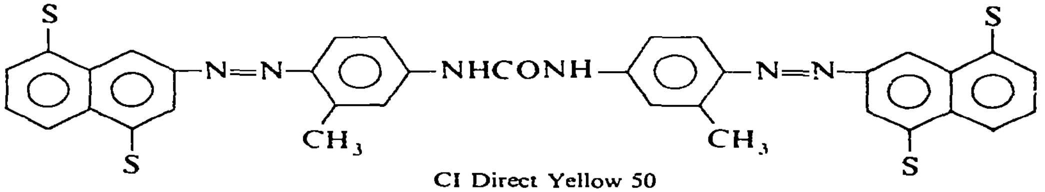
[a] Primary exhaustion indicates the exhaustion of the dye before alkali is added to produce fixation leading ultimately to the secondary exhaustion.

capable of giving bonds stable to acid hydrolysis and peroxide washing, an ideal reactive dye can be obtained from the point of view of fastness. In this case, the monochlorotriazine group effectively acts as bridge link rather than reactive group.

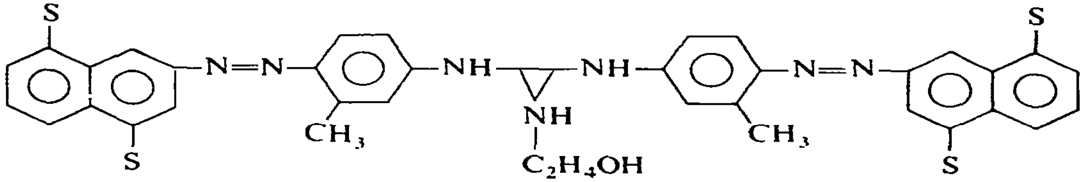
Table 2 shows the comparison of dyeing properties of the vinylsulphone/monochlorotriazine bifunctional reactive dye with those of monofunctional ones having one of the above two reactive groups. Since the reactive dye **8** is bifunctional its fixation is higher than those of the monofunctional dyes **9**–**11**. Referring to the chemical structure of these dyes in detail, dye **8** has a chromophore connected with a vinylsulphone group through a triazine ring, while dye **9** has a —CO— group instead of the triazine ring.

Generally for connecting two amino groups of dye intermediates or a reactive group, a well known method is to form a ureido linkage (—NHCONH—) using phosgene or to form a triazinyl linkage $(\text{—NH}\underset{\text{R}}{\bigtriangledown}\text{NH—})$ using cyanuric chloride.

It is well known with direct dyes, that the dyes with a triazinyl linkage give higher substantivity than those with a ureido linkage and that the former is distinctly superior to the latter with regard to stability in aqueous solutions at high temperatures. Thus C.I. Direct Yellow 86 having a triazinyl linkage is used more widely for dyeing viscose rayon, cotton and their blends with polyester than C.I. Direct Yellow 50 having a ureido linkage.



CI Direct Yellow 50



CI Direct Yellow 86

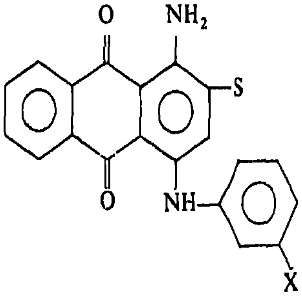
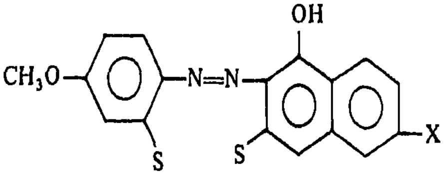
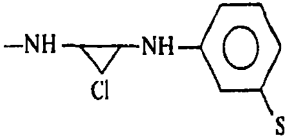
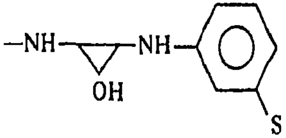
Dyeing with the monofluorotriazinyl dye **11** can be carried out at a lower temperature (40 °C) than that for the monochlorotriazinyl dye **10**, so that it exhibits an effectively higher substantivity and fixation,[22] but it is inferior in fixation to the bifunctional dye **8**.

With dyes of high substantivity, it is often difficult to remove unfixed or hydrolysed dye after dyeing. Dye **8**, although it has a high degree of exhaustion,

TABLE 3

SUBSTANTIVITY OF VINYLSULPHONE AND MONOCHLOROTRIAZINE DYES

(cotton mercerized; 1 % shade; pH 6·8; 20:1 liquor to goods ratio; 60 min dyeing)

Chromophore	*Dyeing temperature (°C)*	*X*	*Substantivity (exhaustion degree) (%)*	
			Na_2SO_4	
			25 g litre^{-1}	*50 g litre^{-1}*
CI Reactive Blue 19(61200) 	40	$—SO_2C_2H_4OSO_3Na$	22	33
		$—SO_2CH{=}CH_2$	81	95
		$—SO_2C_2H_4OH$	25	35
CI Reactive Red 	80		—	75
			—	76

is superior in washing-off to dye **11**. The reason for this is that the substantivity of the vinylsulphone reactive dyes depends to a large extent on the form as shown in Table 3. The substantivity of the sulphatoethylsulphonyl and, particularly of the hydrolyzed hydroxyethylsulphonyl forms of the dyes is much less than that of the reactive vinylsulphonyl form. On the other hand, monochlorotriazinyl dyes vary little in substantivity between the reactive form and the hydrolyzed form. This renders the removal of the latter after dyeing relatively more difficult.

One of the great advantages obtained by having the vinylsulphonyl and monochlorotriazinyl reactive systems in the molecule is that in exhaust dyeing there is little change in yield at dyeing temperatures ranging from 50 to 80 °C, because the reactivities of two reactive systems compensate each other within this temperature range.

Figure 2 shows relative colour yield when unmercerized cotton knits are dyed by the exhaust process between 40 and 80 °C with reactive dyes having the different reactive systems of Table 1. With the monofluorotriazinyl dye **3** and difluoromonochloropyrimidinyl dye **5**, the maximum colour yield is reached at about 40 °C and then the yield rapidly drops with increases in the dyeing temperature. With the vinylsulphonyl dye **6** and monochlorotriazinyl dye **2**, the maximum yield is obtained at 50–60 °C and 80 °C, respectively. On the other hand, the vinylsulphonyl/monochlorotriazinyl reactive dye **1** shows very little change in colour yield between 50 and 80 °C and is expected to give excellent practical performance when the temperature distribution in the dyebath is not completely uniform, e.g. in the dyeing of cotton knitted goods in winch dyeing machines.

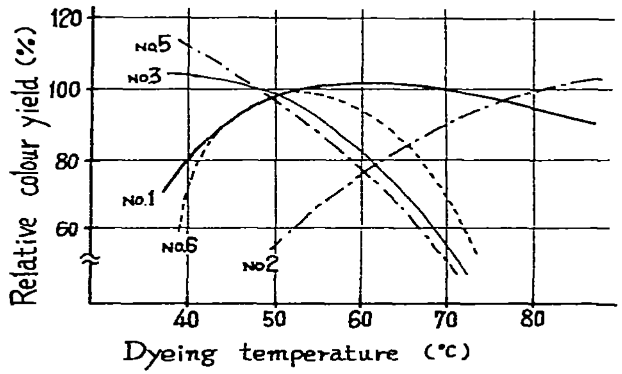
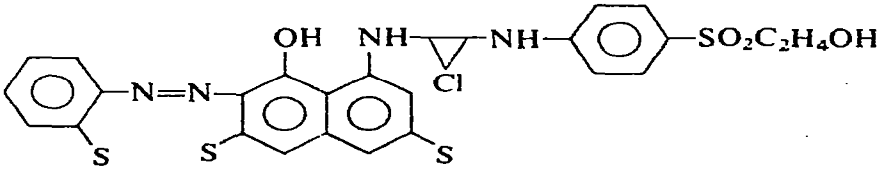
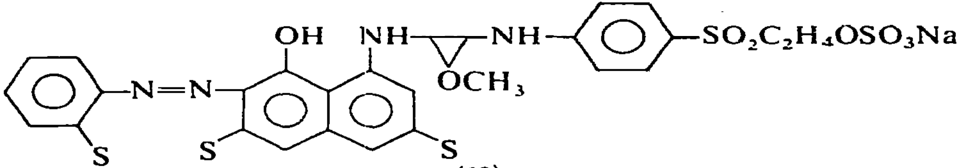


Fig. 2. Temperature sensitivity of reactive dyes.

In order to examine the effect of each individual reactive system of dye **1**, two dyes, **12** and **13**, were synthesized in each of which one of the two 'reactive' systems is



(12)



(13)

inactive. The correlation between the dyeing temperature and colour yield was then examined with these dyes. The results are shown in Fig. 3.

Dye **13**. having an inactivated monochlorotriazinyl group, is a monofunctional vinylsulphone dye, and shows the maximum colour yield at about 60 °C. At temperatures higher than 60 °C it shows a reduction in the colour yield owing to the decrease of substantivity and the alkaline hydrolysis of dye–fibre bonds. Thus it can be seen that the two reactive groups in **1** complement one another to give temperature-insensitive dyeing behaviour.

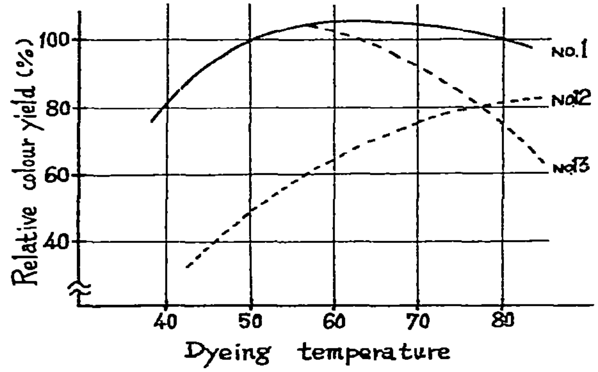


Fig. 3. Comparison of temperature sensitivity between bifunctional dye (**1**) and monofunctional dyes (**12** and **13**). Dyeing conditions are the same as in Fig. 2. Dyeing temperature: °C.

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