Dyes and Pigments 1 (1980) 121–137

THE HYDROLYSIS OF THE BONDS BETWEEN FIBRE REACTIVE DYES AND CELLULOSE BY SODIUM PERBORATE AND HYDROGEN PEROXIDE SOLUTIONS

IAN D RATTEE and K F. SO

Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, Great Britain

SUMMARY

The hydrolysis of the bonds formed between a 2,4-difluoro-5-chloropyrimidin-6-yl and a 2,4-dichloro-1,3,5-triazin-6-yl fibre reactive dye and cellulose by treatment in sodium perborate and hydrogen peroxide solutions has been studied. The evidence points to the formation of reactive products between the fixed dye and hydrogen peroxide, with the main part of the hydrolysis promoted by heat rather than light as was believed to be the main factor. Residual leaving groups on the reactive system of the dye provide one of the centres for the formation of reactive products.

1. INTRODUCTION

The fibre reactive dyes for cellulose achieve their fastness to wet processes such as washing by virtue of the formation of a covalent bond between a reactive group in the dye molecule and hydroxyl groups in the cellulose. In general the available reactive dyes fall into two categories,

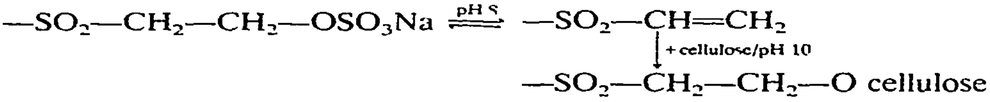
(a) dyes reacting by nucleophilic addition, and
(b) dyes reacting by nucleophilic substitution.

The majority of exploited reactive dye systems fall into the second category although important dyes are to be found in the first. In both cases the nucleophilic reagent is the so-called cellulosate ion formed by the ionisation of hydroxyl groups under alkaline conditions. The presence of alkali inevitably results in a competing hydrolysis reaction in which the nucleophilic reagent is the hydroxyl ion.

Dyes and Pigments 0143-7208/80/0001-0121/$02·25—
Printed in Northern Ireland

The reactivity of the cellulosate ion as a nucleophilic reagent is not sufficient to achieve sufficiently ready reaction without the assistance of electrophilic substituents in the reactive group creating an electron deficient centre for the nucleophilic reaction. These substituents remain after the reaction has occurred so that the dye–fibre reaction product remains subject to attack by nucleophilic reagents, albeit rather less so than the original reactive dye. In designing a reactive dye system it is necessary to maximise the different levels of reactivity to achieve the best results. These features are emphasised by examples

The sulphate ethyl sulphonyl reactive system reacts by nucleophilic addition,



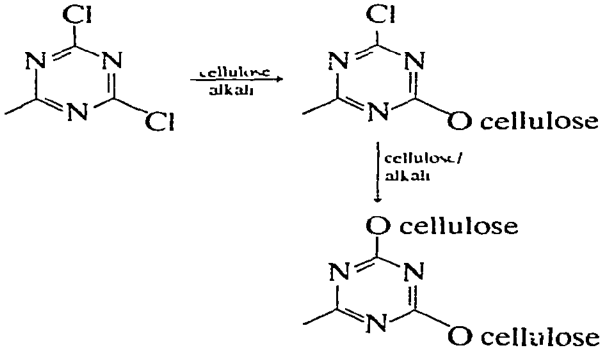
$$-SO_2-CH_2-CH_2-OSO_3Na \xrightleftharpoons{pH\ 8} -SO_2-CH{=}CH_2 \xrightarrow{+\text{cellulose}/pH\ 10} -SO_2-CH_2-CH_2-O\ \text{cellulose}$$

The sulphonyl group is essential for the sufficient development of a centre for nucleophilic attack. Its influence remains in the dye–fibre product so that if the concentration of a nucleophilic reagent, e g OH⁻, is high then a further reaction can occur.

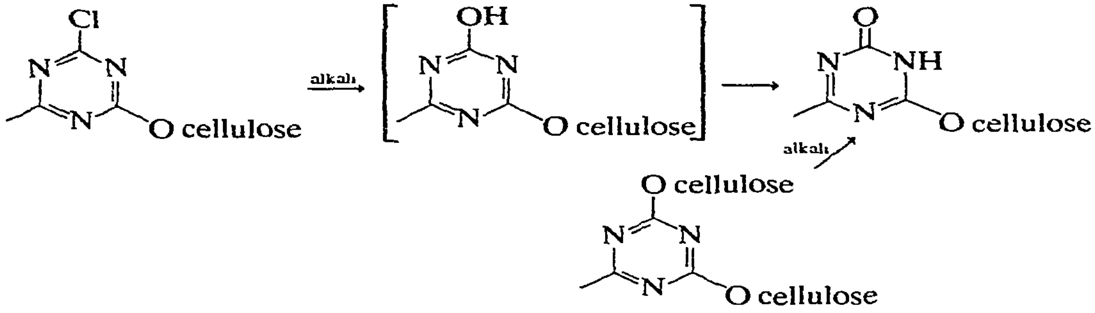
$$-SO_2\ CH_2.CH_2\ O\ \text{cellulose} \xrightarrow{pH\ 12} -SO_2.CH_2CH_2OH + \text{cellulose}\ O^-$$

which leads to the rupture of the dye–fibre bond

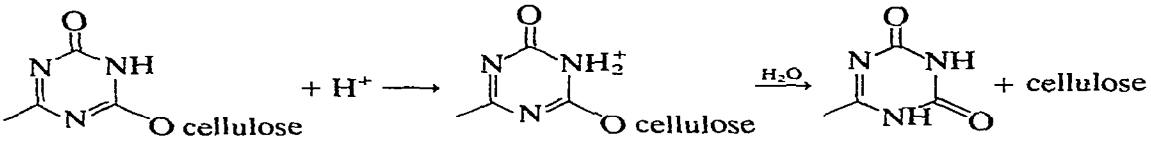
A similar situation arises with a halogeno heterocyclic reactive system reacting by nucleophilic substitution, e g



The two dye–cellulose products here possess residual reactivity by virtue of the effect of the heterocyclic ring so that they can undergo further reactions,

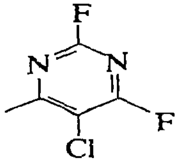


In this case the effect of alkali is not to break the dye–fibre bond as in the case of the vinyl sulphonyl dye, but to form a dye–fibre compound in which the heterocyclic ring is changed This has important repercussions since this form undergoes its own reactions under acid conditions.

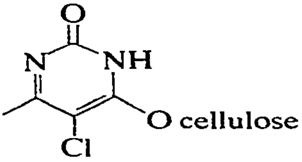


leading to a rupture of the dye–fibre bond.

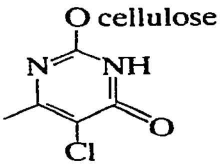
Recent reports have pointed to an unexpected manifestation of this post-fixation reactivity by a range of dyes marketed by Bayer under the name Levafix EA dyes These contain the 2,4-difluoro-5-chloropyrimidin-6-yl reactive system,



and exhibit a fairly high level of reactivity towards cellulose under alkaline conditions. The most probable centre for dye–fibre reaction is the 4-position on the pyrimidinyl ring but there is a distinct possibility that reaction could occur to a lesser extent at the 2-position leading to a mixture of products. In either case the dye–fibre reaction product would bear a labile fluorine substituent of significant but not high reactivity. Treatment with alkali could lead as a consequence to the formation of



and

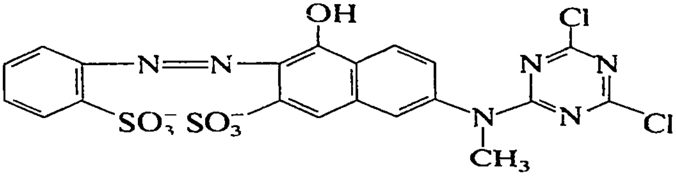


together with some cross-linked product formed by reaction with two cellulose residues. Unusual fastness effects were observed with these dyes soon after their introduction. Dyeings which had been fast to washing, it was found, suddenly became not so. The cause was traced to the combined effects of washing in sodium perborate containing detergent followed by exposure to sunlight No apparent change was produced by these combined agencies but on subsequent washing or even simple immersion in warm water, the dye–fibre bonds in the exposed regions were found to be extensively ruptured, resulting in extensive colour loss. The reasons for this unexpected effect which, it was claimed, did not appear with any other dyes, were not explained and there has been no publication relating to the topic, despite its widespread technical and scientific interest and the enforced withdrawal of dyes containing the 2,4-difluoro-5-chloropyrimidin-2-yl reactive system.

The present investigation has been concerned primarily to explore the processing variables in relation to the effect and to examine at least one aspect of the claim that other fibre reactive systems do not suffer from this deficiency. Only one dye from the Levafix EA range was examined, Levafix Orange E3GA. The structure of the chromophoric system in this dye has not been disclosed and consequently no investigation of the role of the colour system was carried out

2 MATERIALS AND METHODS

The dyes used in the investigation were Levafix Orange E3GA (Bayer), the structure of which has not been disclosed but which contains the 2,4-difluoro-5-chloropyrimidin-6-yl reactive system and the dichlorotriazinylamino dye of the structure,



The Levafix dye was applied to bleached scoured woven cotton material at a 3% (on weight of fibre) shade depth at 45°C using 80 g litre^{-1} sodium sulphate decahydrate crystals and 20 g litre^{-1} anhydrous sodium carbonate for 120 min. After dyeing was completed the fabric was removed, rinsed thoroughly in cold water and unfixed dye removed by boiling in a dilute non-ionic detergent solution for 20 min. The fabric was finally rinsed and dried. The dyeings were checked periodically to ensure that no readily removable dye had developed due to hydrolysis during storage.

The dichlorotriazinyl dye was applied to the same cotton fabric by padding to 80% wet pick up using a solution containing 30 g litre^{-1} dye, 200 g litre^{-1} urea, 30 g litre^{-1} sodium bicarbonate and 2 g litre^{-1} ethylene oxide condensate wetting agent. The padded fabric was rolled up and stored for 24 h at 18–20°C. It was then well rinsed and cleared as in the case of the Levafix dye. The dyeing was designated Type 1. Part of the dyeing was then boiled in 1 g litre^{-1} sodium carbonate for 30 min. The treated dyeing was well rinsed with water to remove all residual alkali and dried. The dyeing was designated Type 3.

2.1. *The measurement of fixed dye on the fibre*

Dyed fabric (0·2 g) was chopped into small pieces and dissolved in 25 ml of concentrated (98%) sulphuric acid in a stoppered tube kept at 0°C in an ice bath. The low temperature avoided the formation of brown colouration due to carbonisation. The tube was regularly shaken to assist the dissolving process which took 4–5 h. The solution was then poured into 60–65 ml of a 1 g litre^{-1} aqueous solution of a stearol–ethylene oxide condensate. The mixing was done slowly in an ice bath to prevent heating-up. The solution was made up at room temperature to 100 ml with water. A reference blank was made up at the same time using undyed cotton. The concentration of dye on the fibre was estimated by optical density measurement carried out using a Unicam SP600 spectrophotometer and calibration curves from measurements carried out on dye solutions in 25% sulphuric acid containing 1 g litre^{-1} of the same surfactant. Several repeat estimations were carried out on each dyeing to give the average values for dye content shown in Table 1.

TABLE 1
THE CONCENTRATION OF DYE FIXED TO THE COTTON PRIOR TO SODIUM PERBORATE OR HYDROGEN PEROXIDE TREATMENT

Dye	*Normal shade depth* (% o.w.f.)	*Dye on fibre* (g kg^{-1})
Levafix Orange E3GA	2	15·63
	3	21·00
	4	25·75
Dichlorotriazinyl dye (Type 1)	3	10·25
Dichlorotriazinyl dye (Type 3)	3	9·00

2.2 *Extraction of hydrolysed dye*

The weighed, treated patterns were extracted at 120°C with 50/50 dimethyl formamide/water in a continuous extractor. The patterns were first rinsed with cold solvent mixture three or four times to remove residual perborate or peroxide before the apparatus was warmed. After all removable dye had been extracted the solutions were made up to 50 ml and the dye content estimated spectrophotometrically.

2.3 *Sodium perborate solutions*

Sodium perborate (A.R.) was weighed out as required and dissolved in water at 50°C. The available oxygen content was determined by the method of Kolthoff and Belcher.[1] The titration result agreed well with the calculated result based on a formula for sodium perborate, $NaBO_2.H_2O_2.3H_{20}$. This was used to calculate the strength of equivalent peroxide solutions

2 4 *Detergent solutions*

The detergent used was the ECE standard detergent believed to have the following composition,

Linear alkyl benzene sulphonate (Na salt)	20·5
Soap	2·5
Sodium tri polyphosphate	42·5
Sodium silicate	10·0
Sodium sulphate	11·5
Moisture etc	13·0
	100·0

Aliquots of detergent were weighed out, dissolved in water at 50°C and cooled to 20°C as required

2 5 *Drying of samples*

Preliminary experiments showed the need for standardised drying procedures Accordingly, after impregnation the patterns were squeezed in a mangle to 85% pick up and dried in a Benz forced air dryer at 90°C for 60 s. Drying after treatments was varied as specified

2 6 *Light exposure*

Patterns were exposed to light in a Microscal fadeometer using a mercury–tungsten fluorescent lamp MBTF (240–250 V, 300 W). This lamp has a phosphor coating as well as a tungsten filament to add yellow and red light to the mercury vapour spectrum. The energy simulation of this lamp is reasonably characteristic of daylight.[2] The temperature of exposure was found to be 40°C When a u v. filter was used, it was a Kodak Wratten filter No. 2B mounted so as to avoid contact with the pattern

2.7. *Rinsing*

Preliminary tests based on colourimetric analysis showed that four washes in 1 litre of cold water removed all normally retained sodium perborate from cotton and this rinsing procedure was used whenever rinsing was needed.

3. RESULTS AND DISCUSSION

The results of a preliminary investigation of the effects of a number of perborate pretreatment conditions followed by exposure to light are shown in Table 2. The results, all of which are based on the use of 5 g litre^{-1} sodium perborate pretreatment, show that some hydrolysis occurs during the pretreatment alone, i.e., without subsequent exposure to light, and that the effect increases with time, temperature of the treatment and the temperature of drying after the treatment. If the % hydrolysis figures for the exposed patterns are corrected for this initial hydrolysis an interesting picture emerges as shown in Table 3.

From these data it is clear that very short-term pretreatments, while causing significant dye–fibre bond hydrolysis, leave a real but small photochemical destabilisation effect. Using longer pretreatment times, greater photochemical

TABLE 2

THE HYDROLYSIS OF DYE-FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS THE EFFECT OF TREATMENT VARIABLES

(3% o w f Levafix Orange E3GA 5 g litre^{-1} sodium perborate all drying for 60 s)

Length of pretreatment (*min*)	*Temperature of pretreatment* (°C)	*Temperature of drying* (°C)	*% Hydrolysis*		
			Time of exposure to light (*min*)		
			0	30	60
0·03	20	90	0·70	0·85	0·98
10			0·76	1·64	1·89
20			1·35	1·76	1·85
0·03	20	120	0·61	0·68	0·75
10			1·12	1·31	1·56
20			1·37	1·57	1·88
0·03	50	90	0·62	0·85	0·95
10			1·19	1·86	2·74
20			1·56	2·29	2·56
0·03	50	120	0·64	0·67	0·75
10			1·57	1·74	2·06
20			1·50	1·69	1·97

TABLE 3

THE HYDROLYSIS OF DYE–FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS. THE EFFECT OF TREATMENT VARIABLES CORRECTED FOR LIGHT EXPOSURE ALONE

(3% o w f Levafix Orange E3GA· 5 g litre^{-1} sodium perborate· all drying for 60 s)

			% Hydrolysis (corrected for exposure effect alone)	
			Time of exposure to light (min)	
Length of pretreatment (min)	*Temperature of pretreatment* (°C)	*Temperature of drying* (°C)	30	60
0·03			0·15	0·28
10	20	90	0·88	1·13
20			0·41	0·50
0·03			0·07	0·14
10	20	120	0·19	0·44
20			0·20	0·51
0·03			0·23	0·33
10	50	90	0·67	1·55
20			0·63	1·00
0·03			0·03	0·11
10	50	120	0·17	0·49
20			0·19	0·47

effects are to be seen but the temperature factor is clearly important. First, drying at 120°C leaves a much smaller residual photochemical effect than does drying at 90°C Secondly, in all cases more hydrolysis is caused by the stages of the treatment prior to exposure to light than by those applied subsequently.

The importance of defining the stages prior to exposure to light in evaluating the photochemical effect is emphasised by the data in Table 4, which indicates the relative dye–fibre bond hydrolysis caused by different heating programmes. The selection of an oven heating temperature of 40°C was based on the observation that the temperature in the fadeometer was also 40°C so that light exposure tests were also, in effect, heat treatments. It can be seen that rapid drying (treatment 2) causes some increased hydrolysis but prolonged drying at a low temperature is much more severe Heating at 40°C for 30 min after drying has a more severe effect and the figures suggest that the separate effects are additive. Light exposure has a definite effect but it is small compared with the effect of heating alone.

In a further series of experiments, the pretreated dyeings were thoroughly rinsed with water after soaking in sodium perborate and prior to drying. The results are shown in Table 5. It can be seen that the photochemical effect has been reduced to a very small factor by rinsing except when the pretreatment is prolonged. It is also clear that rinsing has not eliminated the sodium perborate

TABLE 4
THE HYDROLYSIS OF DYE–FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS· THE RELATIVE EFFECTS OF DIFFERENT HEATING AND EXPOSURE PROGRAMMES
(3% o w f. Levafix Orange E3GA· 5 g litre^{-1} sodium perborate.)

Conditions of treatment	*Relative hydrolysis*
1 Soaking in 5 g litre^{-1} sodium perborate 20°C for 20 min. Squeeze to 70% expression	100
2. As for 1 followed by drying for 60 s at 120°C	117
3 As for 1 followed by oven drying for 30 min at 40°C	141
4 As for 1 followed by drying for 60 s at 120°C and 30 min at 40°C	157
5. As for 1 followed by drying for 60 s at 120°C and 30 min light exposure	170
6 As for 1 followed by 30 min light exposure	162

effect on heating (i.e. drying) especially when the pretreatment is of 10–20 min duration.

That sodium perborate causes direct hydrolysis of dye–fibre bonds is clearly shown by Fig. 1. which illustrates the very much greater effect of sodium perborate as compared with sodium carbonate. Although the very significant effect of heat treatment is well demonstrated by the data presented in Fig. 1, the photochemical factor is not so clearly to be seen. However, experiments carried out on rapidly dried patterns exposed in the fadeometer with and

TABLE 5
THE HYDROLYSIS OF DYE–FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS
THE EFFECT OF RINSING AFTER SOAKING AND PRIOR TO DRYING
(3% o w f Levafix Orange E3GA, 5 g litre^{-1} sodium perborate, all drying at 90°C for 60 s)

Length of pretreatment (min)	*Temperature of pretreatment (°C)*	*% Hydrolysis*		
		Time of exposure to light (min)		
		0	30	60
0·03		0·17	0·15	0·17
10	20	0·41	0·43	0·46
20		0·53	0·66	0·89
0·03		0·30	0·29	0·29
10	50	0·78	1·17	1·22
20		0·72	1·36	1·41

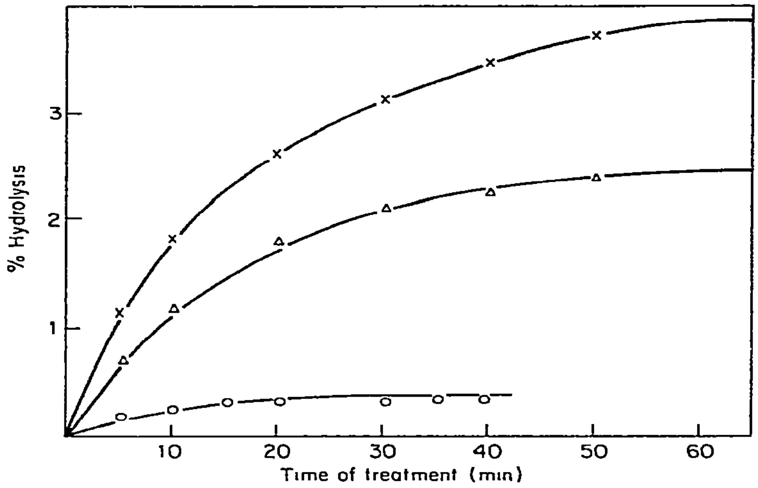


Fig 1 Hydrolysis of dye–fibre bonds in solutions of sodium perborate and sodium carbonate Levafix Orange E3GA 3% o w f × 5 g litre^{-1} sodium perborate, 70°C, pH 10 26, △ 5 g litre^{-1} sodium perborate 50°C, pH 10 26, ○ 1 g litre^{-1} sodium carbonate 50°C, pH 10 47

without a u v. filter clearly showed that light had a real effect. The results are shown in Table 6. Clearly, elimination of the u.v. light from the total energy falling on the pattern reduced the extent of hydrolysis to a significant degree.

A comparison was made of the relative effects of sodium perborate and hydrogen peroxide using equivalent concentrations, i.e , 5 g litre^{-1} sodium perborate and 0·4 V hydrogen peroxide. Patterns dyed with a 3% shade of Levafix Orange E3GA were immersed in the treatment solutions at 20°C for various periods of time, removed and squeezed to 70% expression, dried at 90°C for 60 s and exposed in the fadeometer for 30 min. The sodium perborate

TABLE 6

THE HYDROLYSIS OF DYE–FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS THE EFFECT OF ULTRA VIOLET FILTRATION DURING LIGHT EXPOSURE

(3% o w f Levafix Orange E3GA, Pretreatment in 5 g litre^{-1} sodium perborate for 20 min at 20°C squeezed to 70% expression and dried at 120°C for 60 min)

Exposure conditions	*Exposure time (min)*	*Relative hydrolysis*
Without u v filter	30	100
With u v filter		87
Without u v filter	90	100
With u v filter		88

solution was pH 10·26 and the hydrogen peroxide treatment was carried out at the same pH and also at pH 10·41. The results are shown in Fig. 2. It can be seen that the hydrogen peroxide and sodium perborate are virtually equivalent at the same pH. The reaction with hydrogen peroxide is clearly very sensitive to pH as increasing from pH 10·26 to 10·41 produces a very large increase in hydrolysis resulting in over 6% of hydrolysis during the short exposure time.

In a further series of experiments the effect of the sodium perborate concentration and the effect of the presence of a detergent was examined. The results are shown in Fig. 3. The effect of sodium perborate can be seen to bear a linear relation to its concentration. This fact taken together with the slow development of the effect with soaking time and the results of Table 4 points strongly to the formation of a reaction product between the dye and the perborate which is sensitive to heat and light. Figure 3 also shows that the presence of detergent has a marked effect on the hydrolysis. It seems unlikely that the detergent enters directly into whatever sequence of reactions is involved. However the pH of the detergent is about 10·5 and its effect may be

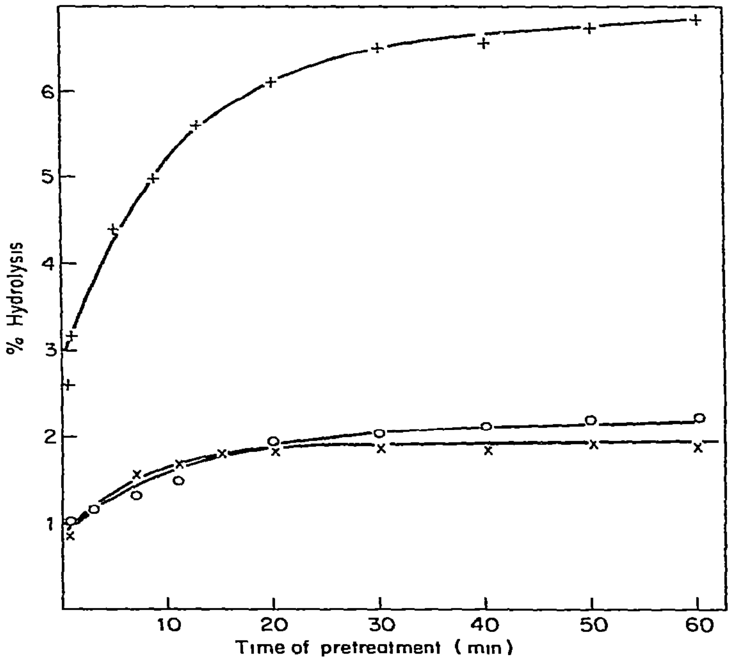


Fig 2 Hydrolysis of dye–fibre bonds caused by pretreatment in sodium perborate or hydrogen peroxide Levafix Orange E3GA 3% o w f · treatment at 20°C for 20 min, dried 60 s at 90°C, exposure for 30 min + 0·4 V hydrogen peroxide, pH 10·41 ○ 0·4 V hydrogen peroxide, pH 10·24, × 5 g litre^{-1} sodium perborate, pH 10·26

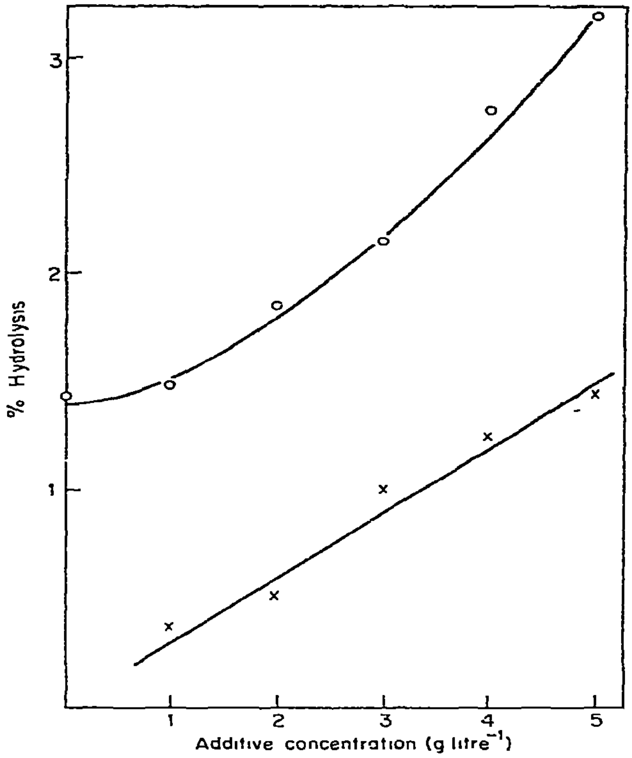


Fig 3 The effect of sodium perborate concentration and ECE detergent addition on the hydrolysis of dye–fibre bonds Levafix Orange E3GA 3% o w f treatment at 20°C for 20 min dried 60 s at 90°C, exposure for 30 min ○ 5 g litre^{-1} sodium perborate with added ECE detergent, × varying concentrations of sodium perborate

simply an enhancement due to alkalinity as observed with hydrogen peroxide. The formation of a reaction product between sodium perborate and the fixed dye pointed to a likely technical effect whereby successive treatments in sodium perborate might lead to the build up of the effect of heat and light even when the dyeings were thoroughly rinsed. This was checked by conducting a sequence of pretreatments as follows:

(a) soak—squeeze—dry—expose to light
(b) soak—rinse—soak—squeeze—dry—expose to light
(c) soak—rinse—soak—rinse—soak—squeeze—dry—expose to light.

All soaking treatments were at 20°C for 20 min in 5 g litre^{-1} sodium perborate. Squeezing was such as to give 70% expression. Rinsing was in cold water sufficient to remove all free sodium perborate. Drying was carried out for

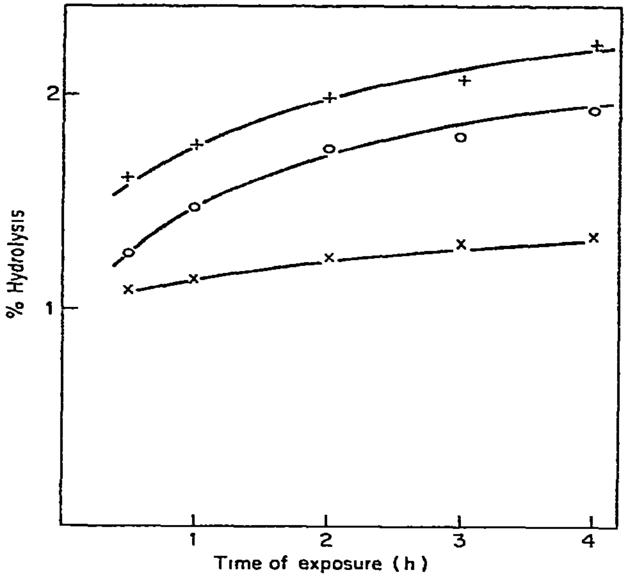


Fig. 4 The effect of rinsing after pretreatment of dyeings with sodium perborate on the hydrolysis of dye–fibre bonds during exposure to heat and light Levafix Orange E3GA 3% o w f. all perborate treatment at 20°C for 20 min with 5 g litre^{-1} sodium perborate, all drying 60 s at 90°C, all exposures 30 min (+ soak—rinse—soak—rinse—soak—squeeze—dry—expose, O soak—rinse—soak—squeeze—dry—expose, × soak—squeeze—dry—expose)

60 s at 90°C and all patterns were exposed to light for 30 min. The results are shown in Fig. 4. The cumulative effects of perborate treatments can be clearly seen. The relationship between depth of shade, sodium perborate concentration and degree of hydrolysis is shown in Table 7.

All treatments were carried out at 20°C for 20 min followed by squeezing to give 70% expression and drying for 60 s at 90°C. The patterns were then

TABLE 7

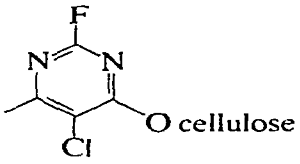
THE HYDROLYSIS OF DYE–FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS THE EFFECT OF SHADE DEPTH AND SODIUM PERBORATE CONCENTRATION

(Levafix Orange E3GA, all pretreatments at 20°C for 20 min, all drying at 90°C for 60 s)

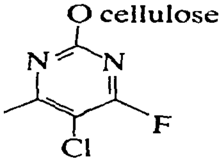
Normal depth of shade (% o w f)	*Sodium perborate concentration* (g litre^{-1})		
	5	3	1
2	0.62	0.46	0.20
3	0.63	0.54	0.19
4	0.57	0.50	0.19

exposed to light for 30 min. It can be seen that at any given sodium perborate concentration the proportional hydrolysis is not significantly affected by the depth of shade. The concentration of sodium perborate is, on the other hand, highly significant. This result is also symptomatic of the formation of a reactive product with the kinetics driven by the dye and perborate concentrations equally. Due to the ambiguity surrounding the actual concentration of sodium perborate (or hydrogen peroxide) inside the fibre, no meaningful reaction constant can be calculated

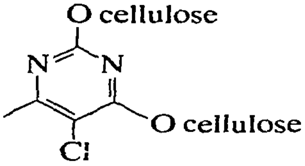
The bifunctionality of the reactive system in the Levafix EA dyes has already been discussed. Five different modes of attachment to the fibre are possible.



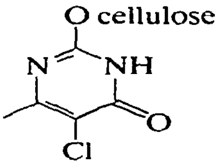
Tvpe la



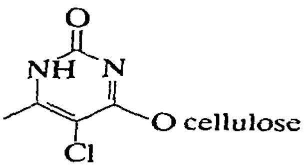
Type 1b



Type 2



Type 3a



Type 3b

Treatment of dyeings with hot sodium hydroxide solutions will convert Type 1a and 1b dyeings together with Type 2 dyeings into Type 3a or 3b dyeings. The effect of this on the sodium perborate effect was examined. Dyeings were boiled in 1 g litre^{-1} sodium hydroxide for 5 min and 60 min. The dyeings were then rinsed thoroughly and sodium perborate treatments given as follows·

(a) soak (20 min, 20°C)—squeeze (70% expression)—dry (60 s, 90°C)—expose to light,

and

(b) soak (20 min, 20°C)—rinse—squeeze (70% expression)—dry (60 s, 90°C)—expose to light.

Both treatments were carried out on dyeings boiled for 60 min in sodium hydroxide. Only the first treatment was carried out on dyeings boiled for 5 min. The dye–fibre bond hydrolysis is shown in Table 8 for the pretreatment patterns relative to patterns given no caustic soda treatment. The results show that pretreatment with caustic soda has a marked effect. The short (5 min)

TABLE 8

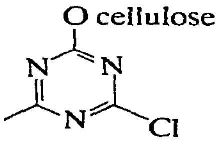
THE HYDROLYSIS OF DYE–FIBRE BONDS BY SODIUM PERBORATE SOLUTIONS THE EFFECT OF TREATMENT WITH SODIUM HYDROXIDE BEFORE PERBORATE TREATMENT

(3% Levafix Orange E3GA- sodium perborate 5 g litre^{-1}: all pretreatment at 20°C for 20 min. all drying at 90°C for 60 s)

	% Hydrolysis		
		Boiled 60 min in 1% NaOH	
Period of exposure to light (min)	*Boiled 5 min in 1% NaOH*	*Rinsed after perborate treatment*	*Not rinsed after perborate treatment*
0	0 386	0 287	0 469
5	0 395	0 342	0 522
15	0·442	0·419	—
30	0 488	0 455	0 544
60	0 562	0·493	0 663
120	0 649	0 612	0 803
180	0 654	0 616	0 773
240	0 677	0 653	0 746

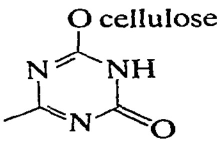
pretreatment is only slightly less effective than the longer treatment (60 min) and the effect of both pretreatments becomes less with increasing exposure time. The effect is consistent with a generally unchanged mechanism but the formation of a less readily hydrolysed reaction product with the sodium perborate is a result of the sodium hydroxide pretreatment. The effectiveness of rinsing after perborate pretreatment is increased by caustic soda preboiling Rinsed patterns or patterns not treated with sodium hydroxide give about 69% of the hydrolysis given by unrinsed patterns. However, when the dyeings are pretreated with sodium hydroxide this falls to about 42%. Thus a less readily formed product with sodium perborate is indicated also.

On the basis of the idea that caustic soda pretreatment would remove residual leaving groups from the reactive system, two dyeings based on corresponding dye–fibre bonding systems using triazine rings were prepared.



Type 1

and



Type 3

These were prepared using the dichlorotriazinyl dye, by the methods described. The dyeings were given the same treatment as the sodium hydroxide treated Levafix EA dyeings. The Type 1 dyeing was given both treatments, while the

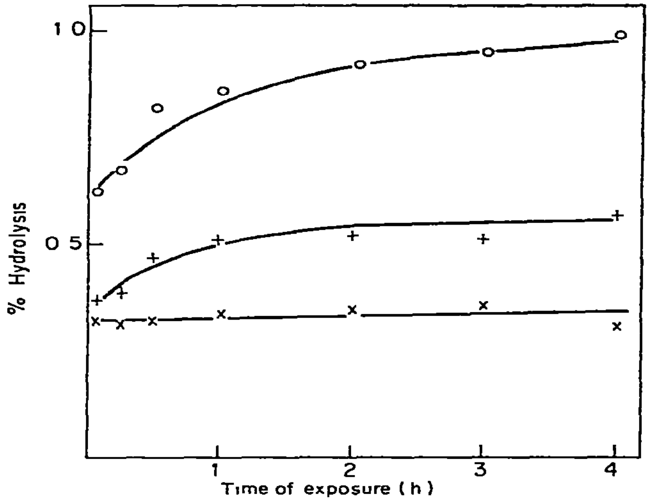


Fig 5 The effect of sodium perborate on the stability to heat and light exposure of Type 1 and Type 3 dye–fibre bonds between cotton and a dichlorotriazinylamino dye All treatments at 20°C for 20 min all dryings 60 s at 90°C (O Type 1 dyeing soak—squeeze—dry—expose, + Type 1 dyeing soak—rinse—soak—squeeze—dry—expose, × Type 3 dyeing soak—squeeze—dry—expose)

Type 3 dyeing was given the first. The results are shown in Fig. 5. It can be seen that with the Type 3 dyeing, while the pretreatment had caused some dye–fibre bond hydrolysis during pre-soaking and drying, no further hydrolysis occurred during light exposure whether from light or the inevitable associated heating. The Type 1 dyeing on the other hand showed the familiar pattern, i.e., dye–fibre bond hydrolysis during the pretreatment and drying with a further increase during exposure, with evidence for the formation of a reaction product resistant to break-down during rinsing. The stability of the product to rinsing moreover appears to be comparable with that given by the 2,4-difluoro-5-chloropyrimidin-6-yl compound.

4. CONCLUSIONS

The evidence points to the fact that sodium perborate causes both thermal and photochemical instabilisation of the dye–fibre bonds between cellulose and a 2,4-difluoro-5-chloropyrimidin-6-yl fibre reactive dye and that the thermal effect is the greater The perborate appears to act as a provider of hydrogen peroxide so that its behaviour is equivalent to that of hydrogen peroxide present in equivalent amounts. The instabilisation reaction appears to involve the formation of a reaction product or adduct between the fixed dye and the peroxide, that formation being markedly sensitive to pH. The reaction product between hydrogen peroxide and the fixed dye is stable to rinsing processes which will remove free perborate or peroxide from the fabric so that successive treatments have a cumulative effect.

The formation of a reaction product or adduct depends upon the chemical nature of the group involved in the fixation of the reactive dye. The presence of a residual leaving group appears to enhance the reaction so that the effect of perborate or peroxide treatment is lessened (but not eliminated) by treatments eliminating such groups. In the case of the Type 3 dichlorotriazinyl dye–cellulose product, the photochemical reaction is virtually absent although the thermal reaction is still evident. The same trend is shown with the 2,4-difluoro-5-chloropyrimidin-6-yl dye–cellulose product but the greater difficulty in forming the Type 3 equivalent makes the indications less definite. Examination of the physical and organic chemical features of the reactions involved will require the study of reactions with soluble model compounds in view of the evidence for more than one reaction and the intrusion of surface potential effects causing an abnormal distribution of ions when studying reactions in water swollen fibres.

The association of the effect with light rather than with heat in common experience is difficult to explain It may be due to the fact that the consumer's encounter with light involves intense sunshine, with which heat is inevitably associated.

REFERENCES

1 I. M Kolthoff and R Belcher, *Volumetric Analysis* Vol 3 New York, Wiley Interscience (1957)

2 C H Giles C D Shah and D Baillie, *J Soc Dyers and Colourists*, **85**, 410 (1969).