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Interaction of oxidative-bleach containing detergents with dyes. Part 3: preparation and resistance of mixed azo/hydrazo dyes derived from 1-aminonaphthalene-8-hydroxynaphthalene-3,6-disulphonic acid (H-acid) to oxidative-bleach containing detergents

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Abstract

The world's largest selling reactive dye, CI Reactive Black 5, provides a universally recognized economic route to heavy navy and black shades in the dyeing of cellulosic substrates with reactive dyes. However, the introduction of ever more powerful domestic detergents has highlighted the instability of this, and many other dyes, to modern activated-bleach containing detergents: these cause a loss of colour on dyed textile substrates by chemical destruction of the chromophore. In this communication we describe approaches to the design, synthesis and evaluation of analogues of CI Reactive Black 5 with superior resistance to oxidative-bleach fading.

Keywords: Reactive dyes; Azo; Hydrazo; Peracid; Peroxide; Oxidative bleach fading

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1. Introduction

In Parts 1 and 2 [1,2] we described two series of dyes, (Figs. 1 and 2), prepared by coupling substituted aryldiazonium chlorides onto 1-aminonapthalene-4-sulphonic acid and 1-hydroxy naphthalene-4-sulphonic acid respectively. We also reported on the degradation, in solution, of these chromophores when subjected to treatment by hydrogen peroxide and *m*-chloroperbenzoic acid. These oxidants were used in one hundred-fold molar excess over dye in order to obtain *pseudo*-first order rate constants for the oxidation reactions. *m*-Chloroperbenzoic acid is a relatively stable peracid and a convenient model for the peracetic acid generated in domestic detergents and in the ISO 105—CO9:2001/BS 1006: [UK-TO] "Oxidative Bleach Response" test [3–5].

Results suggested that the peracid, not the deprotonated anion, was the species responsible for the colour degradation observed in the

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UK-TO test, despite the anion being present in large excess.

We also described the effect of the substituent(s) 'X' (Figs. 1 and 2) on the sensitivity of dyes to oxidation by *m*-chloroperbenzoic acid. In particular, the usefulness of *ortho* halogen substituents in reducing the propensity of a dye to undergo degradation by peracid was especially significant for two reasons. As well as allowing the production of dyes with improved technical properties, particularly enhanced resistance to degradation by oxidative bleaches, the incorporation of halogen substituents in this manner is generally facile and commercially viable.

2. Experimental

Elemental microanalyses for carbon, hydrogen, nitrogen and sulphur were carried out on a Carlo Erba 1108 elemental analyzer, at the Department of Chemistry, UMIST. Mass spectra were recorded by two techniques, FAB (fast atom bombardment) and MALDI (matrix assisted laser desorption/ionization). Ultraviolet–visible spectra were recorded using a Phillips PU 8700 spectrophotometer and aqueous solutions of dyes. Reflectance spectra on dyed fabrics were made on a Datacolor Spectraflash 600 spectrophotometer under a D65 lamp. Thin layer chromatography (TLC) was conducted using aluminum plates coated with silicagel 60 F_{254} (Merck), eluant *iso*-butanol:*n*-propanol:ethyl acetate:water (2:4:1:3). High performance liquid chromatography (HPLC) was performed using a Hewlett-Packard 1100 instrument with Purospher RP—18 (5 μm) packing and a LiChroCART 125—4 column cartridge. The mobile phases were an aqueous (0.25%) solution of cyclohexylammonium phosphate (solvent A) and acetonitrile (solvent B). All dyes were essentially pure as judged by TLC and HPLC but contained inorganic salt (usually sodium chloride) and water. The effective agent content of each was determined by titration against a standard solution of titanium^{III} chloride.

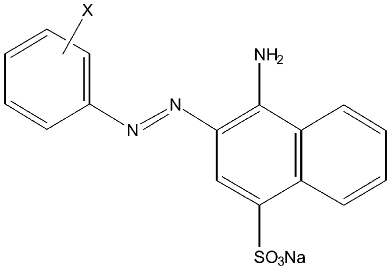


Fig. 1.

2.1. Preparation of dyes

Nine mixed azo/hydrazo navy dyes were prepared according to Fig. 3. In the first stage (Fig. 3) commercial 4-(β-sulphatoethanesulphonyl-)aniline (Intermediate 1) was separately brominated, with *N*-bromosucccinimide to give 2-bromo-(β-sulphatoethanesulphonyl-)aniline (Intermediate 2), and chlorinated, with *N*-chlorosuccinimide, to yield 2-chloro - (β - sulphatoethanesulphonyl -)aniline

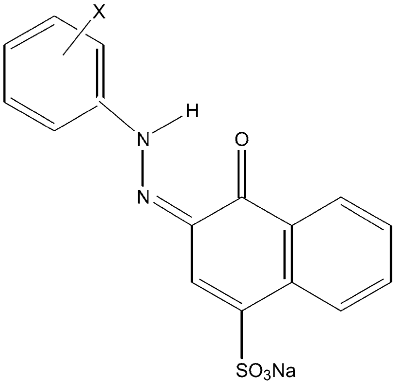


Fig. 2.

Table 1
CI Reactive Black 5 analogues (see Table 3)

Reactive dye number	X Substituent	Y Substituent
7	H	H
8	H	Br
9	H	Cl
10	Br	H
11	Br	Br
12	Br	Cl
13	Cl	H
14	Cl	Br
15	Cl	Cl

(Intermediate 3). In the next stage (Fig. 3) each of the intermediate diazo components (1), (2) or (3) was diazotised and the resulting diazonium salt coupled separately (Fig. 3) at pH 1.5, onto H-acid, 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, to yield red 1-amino-2-arylazo-8-hydroxynaphthalene-3,6-disulphonic acid dyes (4), (5) and (6). Each of these monoazo derivatives was then reacted separately, at higher pH, generally 5 to 5.5, with each of the diazo components utilized above to yield a total of nine "twice coupled H-acid" dyes, 7 to 15 (Fig. 3 and Table 1). The chlorination and bromination stages were carried out without isolation of the resulting 2-bromo and

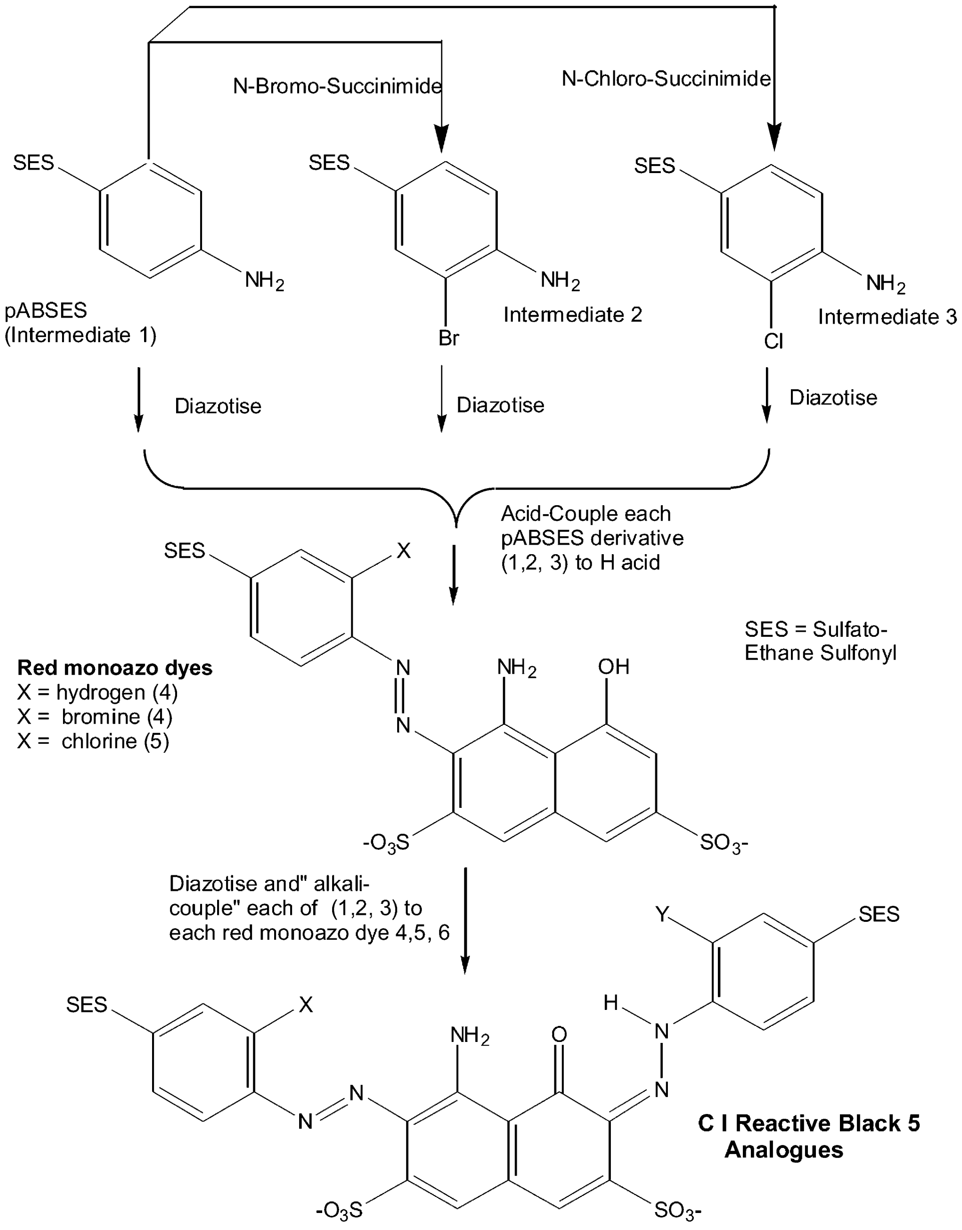


Fig. 3. Synthetic route for the preparation of dyes.

2-chloro derivatives (2) and (3) and the resulting products diazotised immediately after preparation. The preparation of 1-amino-2-[4-(2-sulphatoethylsulphonyl)-phenylazo-]-7-[4-(2-sulphatoethylsulphonyl)-2-bromophenylazo-]-8-hydroxynapthalene-3,6-disulphonic acid, Dye 8, is typical.

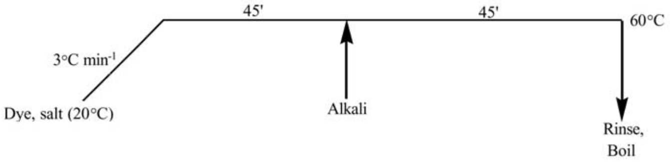
2.2. Synthesis of 1-amino-8-hydroxy-2-[4-(2-sulphatoethylsulphonyl)-phenylazo]-napthalene-3,6-disulphonic acid (intermediate) (Red Dye 4, X = H—Fig. 3)

4-(β-Sulphatoethanesulphonyl-)aniline (Intermediate 1—Fig. 3, 53 g, 0.18 mols, 95.5%) was slurried with vigorous agitation in water (600 ml). The resulting suspension was cooled to 5 °C and hydrochloric acid (45 ml, 0.46 mols, 32% w/w aqueous solution) was added slowly. The temperature was maintained below 5 °C. Sodium nitrite (13 g, 0.188 mols, +98%), dissolved in the minimum volume of water, was added dropwise below 5 °C. Completion of diazotisation was confirmed by a negative reaction with Ehrlich's reagent. Sulphamic acid was then added in small amounts to destroy a small excess of nitrous acid. A yellow diazonium salt solution was obtained. H-acid (70 g, 0.18 mols, 82%) was slurried with efficient stirring in water (500 ml) at 0–5°C. Sodium bicarbonate was added to give a solution of the sodium salt of H-acid at pH 5.5 before adding hydrochloric acid solution (2M) to form a finely divided suspension at pH 1.5. The diazonium salt solution was added slowly to this suspension to effect coupling at < 5 °C. After all the diazonium salt solution had been added the cold mixture was stirred for a further 16 h at pH 1.5, with control by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC). Methylated spirit (1000 ml.) was added slowly, with stirring, to precipitate the acid coupled monoazo product, which was filtered, re-slurried in acetone, re-filtered and dried (overnight under vacuum).

Yield: 119 g (80%; Mol In 823; Effective agent [EA] content 82%). The product was essentially pure as judged by TLC ($R_f = 0.34$) and hplc ($R_t = 1.52$min). Mass (MALDI) m/z: 613 (M + 2H).

2.3. Synthesis of 1-amino-8-hydroxy-2-[4-(2-sulphatoethylsulphonyl)-phenylazo]-7-[2-bromo-4-(2-sulphatoethylsulphonyl)-phenylazo]-naphthalene-3,6-disulphonic acid (Navy Dye 8—Fig. 3 and Table 1, X = H; Y = Br)

(i). 4-(β-Sulphatoethanesulphonyl-)aniline (8.82 g, 0.03 mols) was dissolved with strong agitation in water (80 ml) by adding sodium bicarbonate (2.5 g, 0.03 mols) at pH 4.5 and 20 °C. *N*-Bromosuccinimide (5.61 g, 0.032 mols) was added dropwise to the solution over a period of 2 h at pH 3–4 and 18–20 °C. The formation of 2-bromo-4-(β-



Depth of Shade	Liquor Ratio	Concentration / gl^{-1}		
		Glauber's Salt	Alkali	
		Na_2SO_4	Na_2CO_3	NaOH
0.5%	10:1	50.0	5.0	0.9
1.0%	10:1	50.0	5.0	0.9
2.0%	10:1	50.0	5.0	1.3
4.0%	10:1	50.0	5.0	1.3
6.0%	10:1	80.0	5.0	1.3

Fig. 4. Dyeing conditions.

sulphatoethanesulphonyl-)aniline, was followed by HPLC(R_t = 1.13 min vs. 2,6-dibromo- derivative R_t = 1.65min) and T.L.C. (R_f = 0.54 vs. dibromo-, R_f = 0.63) and was used direct without isolation.

(ii). Sodium nitrite (2.2 g, 0.032 mols) was added, the mixture was cooled to 5 °C and poured slowly into dilute hydrochloric acid (9 ml 12N acid in 50 ml water) at <5 °C. Sulphamic acid was added to destroy excess nitrous acid. The intermediate red monoazo dye (4) prepared above (15 g, 0.018 mols, 74.2%) was dissolved, at 5 °C, in aqueous sodium bicarbonate to give a solution of pH 4. The resulting solution of 4-(β-sulphatoethanesulphonyl-)-2-bromomphenyl diazonium chloride was added dropwise to the stirred solution of monoazo dye (4) and coupling effected at pH 5–6 and at 4–5 °C. After completion of coupling, control by HPLC, methylated spirit was added (1500 ml) to precipitate the product (8) which was collected by filtration and dried under reduced pressure.

Yield: 13.11g., Mol In by titanous estimation = 1295; EA = 82.6%; Mass (MALDI) m/z: 1026 (M-2H + 2Na). Found: C, 26.1%; H, 2.4%: N, 5.8%; Br, 6.4%; S,17.1%. Calc. for $C_{26}H_{20}N_5O_{19}S_6BrNa_4.7H_2O$: C, 26.1%; H, 2.8%: N, 5.85%; Br, 6.7%; S,16.1%.

Other dyes prepared by the same general procedure are listed in Table 1. All were essentially pure as judged by HPLC and TLC and were characterised by mass spectrometry.

2.4. Determination of dye strength and optical properties

As isolated, the dyes were essentially pure organically but invariably contained some inorganic electrolyte and water. The effective agent content of each dye was assessed by titration against titanous chloride [6] and expressed in terms of Mole In, where Mole In represents the weight in grammes of dye which contains one mole of dye.

For each dye the wavelength of maximum absorbance, λ_{max}, the molar extiction coefficient, ϵ_{max}, and the half band width, $\Delta\lambda$, were recorded as described previously [1].

2.5. Application of dyes to cotton

All dyes were applied at five depths of shade, viz. 0.5, 1, 2, 4, 6% dye o.m.f., to 5 g pieces of mercerized woven cotton using the process described in Fig. 4. Following this, each sample was rinsed in cold water, acidified to pH 5 with dilute acetic acid and then washed in boiling water (liquor ratio 40:1) for 20 min to remove any unfixed or hydrolysed dye before being air-dried.

2.6. Build-up characteristics of dyes

The colour strength of each dyeing, expressed in units of k/s, was assessed using a Datacolor Spectraflash 600 and build up graphs (k/s versus amount of dye applied) plotted. From these it was possible to select appropriate concentrations of dye in order to allow the fastness properties of each dye to be studied at two pre-selected depths of shade, viz $k/s = 13$ and $k/s = 26$.

2.7. Assessment of bleach resistance

2.7.1. (a) Using the ISO 105—CO9:2001 [BS 1006: UK-TO] test method

The ISO 105—CO9:2001 test is employed to predict the loss of colour of a fabric due to multicycle domestic laundering using an activated oxygen-bleach detergent [3–5]. Specimens are laundered under appropriate conditions of temperature, time and bleach concentration such that a fading result, which correlates with multicycle machine washing, is obtained in a conveniently short time. The detergent composition used in the test is given in Table 2. Freshly prepared detergent solution was stirred vigorously at 20 ± 2 °C for 10 ± 1 min before running the test.

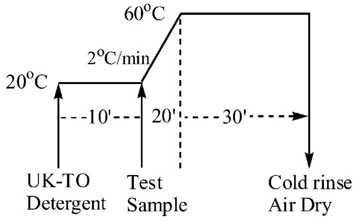


Fig. 5. Application conditions for dyeing cellulose using Everzol Black B dyeing method.

Dyed fabric, 5 × 10 cm, was placed in a stainless steel container of the laundering device and the appropriate amount of detergent solution added to provide a liquor: fabric ratio of 100:1. The container was closed, placed in the laundering device and the test initiated. The procedure followed is illustrated in Fig. 5.

The temperature was raised from 20 ± 2 °C to 60 °C, at rate of 2 °C/min and the test was run for a further 30 ± 1 minutes at this temperature, after

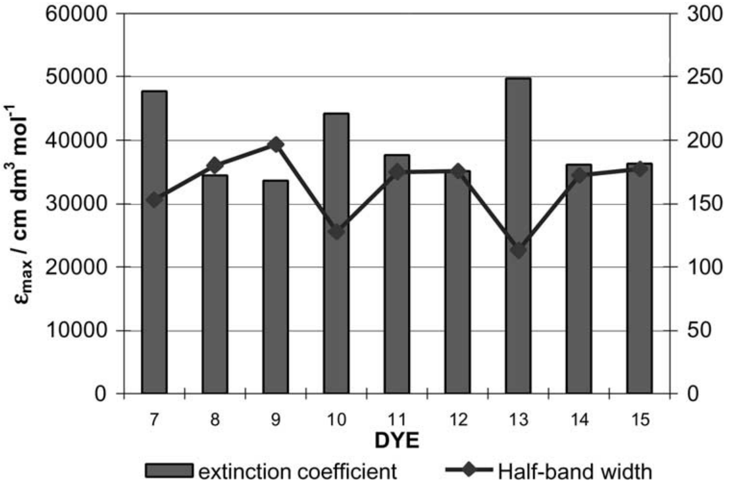


Fig. 6. Extinction coefficient and half-band width of Dyes 7 to 15.

Table 2
Detergent composition

Reference detergent for the ISO 105—CO9:2001 test

1.1.1.1 Reagent	Amount (g/l)
ECE non-phosphate reference detergent	10
Sodium perborate tetrahydrate	12
TAED (tetraacetylethylenediamine) (100% activity)	1.8

The composition of the ECE non-phosphate reference detergent is given below

ECE non-phosphate reference detergent without optical brighter

1.1.1.1.1 Component	Amount (%)
Base powder	
Linear sodium alkyl benzene sulphonate	9.7
Ethoxylated fatty alcohol	5.2
Sodium soap	3.6
SIK (foam inhibitor concentrate, 8% silicon or inorganic carrier)	6.5
Sodium aluminium silicate zeolite 4A	32.5
1.1.2 Sodium carbonate	11.8
Sodium salt of acrylic/maleic acid copolymer	5.2
Sodium silicate (SiO_2:Na_2O = 3.3:1)	3.4
Carboxymethylcellulose (CMC)	1.3
Diethylenetriamine penta (methylene phosphonic acid)	0.8
Sodium sulphate (as accompanying substance or added)	7.8
Water	12.2

which the fabric was removed, rinsed under cold water, squeezed and dried at room temperature. The change of colour of the specimen was assessed, either with grey scales or instrumentally with reference to the original, using the CIELab equation for visual colour differences ($\Delta\mathring{A}^*$) [7]

2.7.2. (b) By multiple machine washing

In order to validate the results obtained using the ISO 105—CO9:2001 test to predict fading during repeated domestic laundering, a sample of each dyed fabric was put through a series of multiple machine washes. Undyed cotton fabric was added as ballast up to 5 kg to give a liquor to good ratio of 5. The washes were carried out using the 60 °C cotton main wash programme, spin speed 1100 rpm, in a Miele W698 washing machine. The detergent composition is shown in Table 3. Fading measurements were taken after 5, 10, 15 and 20 washes.

3. Results and discussion

3.1. Preparation and optical properties of dyes

All dyes were readily prepared according to the route depicted in Fig. 3. The effective agent (EA) contents/percentage strengths, of the dyes are listed in Table 4.

Fig. 6 shows the tinctoral strength of the disazo dyes 7–15, in terms of both molar extinction coefficient, $\epsilon_{\max}$, and half band width, $\Delta\lambda$. The three dyes in which Y = H, viz (7), (10) and (13), all exhibit a substantially higher extinction coefficient than those in which Y is a bromine or chlorine atom: these higher extinction coefficients are however offset by narrower half band widths: thus all were of comparable colour value when applied to fabric, though build up properties varied marginally. In each sub series (Y = H, Y = Br and Y = Cl) the value of $\lambda_{\max}$ increases with increasing electronegativity of X (Table 5). Thus in the case where Y = H the wavelength of maximum absorbance, $\lambda_{\max}$, increases from 587.2nm (X = H) to 599.2nm (X = Br) to 609.2 nm (X = Cl). Conversely, when X was constant, changes in Y had a less noticeable effect.

Table 3
Detergent composition for use in multiple machine washing

Component	Mass/g
ECE reference detergent	116.0
Sodium perborate (PB4)	30.0
TAED	4.5

3.2. Resistance to oxidative-bleach fading

The resistance of dyes to oxidative bleaching was assessed using the accelerated "CO9" test and also by multiple machine washing.

In the former protocol dyeings which exhibited a fading/shade change (ΔE CIELab) of greater than 4 were deemed bleach sensitive. Without exception, all of the dyes were found to be 'insensitive' to oxidative-bleach fading when applied at a heavy depth, $k/s = 26$; that is, they exhibited a low

Table 4
Mol In and EA strength of 'CI Reactive Black 5′ analogue dye

Dye	Mol In/g mol^{-1}	Molecular Mass/g mol^{-1}	EA strength/%
Everzol Black B	1731	991.8	57.3
7	1469	1070.7	67.6
8	1249	1026.3	85.7
9	1722	1070.7	59.6
10	1195	1149.6	89.6
11	1435	1105.2	80.1
12	1282	1026.3	86.2
13	1187	1187.4	86.4
14	1267	1263.8	87.5
15	1229	1228.7	86.3

Table 5
Absorption characteristics of dyes

Dye	$\epsilon_{\max}$	$\lambda_{\max}$/nm
7	47,700	587.2
8	34,500	595.5
9	33,600	588.1
10	44,200	599.2
11	37,700	597.8
12	35,200	595.7
13	49,800	608.9
14	36,100	600.9
15	36,400	599.2

level of fading, ΔE CIELab <4 (see Fig. 7). At the paler depth of shade, $k/s=13$, Dye 7, a laboratory prepared sample of CI Reactive Black 5 ($X=Y=H$) gave the expected fail result ($\Delta E=7.3$). A further two dyes (10 and 13) were also judged to be sensitive. Each of the three bleach sensitive dyes has the common feature of an 'unprotected' aryl ring attached to the hydrazone bond. Hence the incorporation of a halogen *ortho* to the hydrazone bond was beneficial in reducing the oxidative-bleach sensitivity of CI Reactive Black 5 probably to a commercially acceptable level.

The performance of dyes on multiple machine washing mirrored very closely their behaviour in the ISO CO9 test (Fig. 8). In this case a ΔE CIELab change in shade of greater than 10 indicates unacceptable sensitivity to oxidative bleaching.

In previous communications [1,2] we described and quantified the efficiency of halogen substituents in conferring increased peracid resistance to 1-amino-2-arylazonaphthalene derivatives and the corresponding hydrazo dyes derived from 1-hydroxynaphthalene-4-sulphonic acid. This beneficial effect was attributed to the ability of an electronegative halogen atom to withdraw electron density from the conjugated π-bond system and hence reduce the nucleophilic character of the dye. In addition, by placing halogen substituents in close proximity, i.e. *ortho* to the hydrazo group, attack by the oxidant molecule was sterically inhibited. These observations suggested that attaching a chlorine or bromine atom *ortho* to the azo and hydrazo fucnctions in analogues of CI Reactive Black 5 might provide a useful route to providing navy dyes with superior resistance to oxidative bleaching. Preparation of such derivatives may be effected relatively easily by chlorinating/brominating 4-(2 - sulfatoethylsulfonyl -) aniline (pABSES) and synthesizing the derived disazo dyes as shown in Fig. 3.

It can be seen, from Figs. 7 and 8, that introduction, ortho to the azo function, of a chlorine or bromine substituent into the aromatic ring of the "acid coupled" component (Dyes 10 and 13) has little effect, either beneficial or detrimental, on the bleach resistance both in the ISO 105—CO9:2001 test and on multiple machine washing. This is surprising in view of earlier results [1] indicating that introduction of a halogen atom *ortho*- to the azo bond of an arylazo-naphthylamine system is effective in reducing the sensitivity of such chromophores to degradation by peracid. However, the introduction of such substituents *ortho* to the hydrazo group confers increased resistance to oxidative bleaching, as evidenced by much improved performance in the ISO 105—CO9:2001 test and multiple machine washing. Thus the instability of the mixed azo-hydrazo "twice coupled H-acids" appears to be associated with attack at, or near, the hydrazo function. Again this is unexpected since it had been demonstrated that, in isolation,

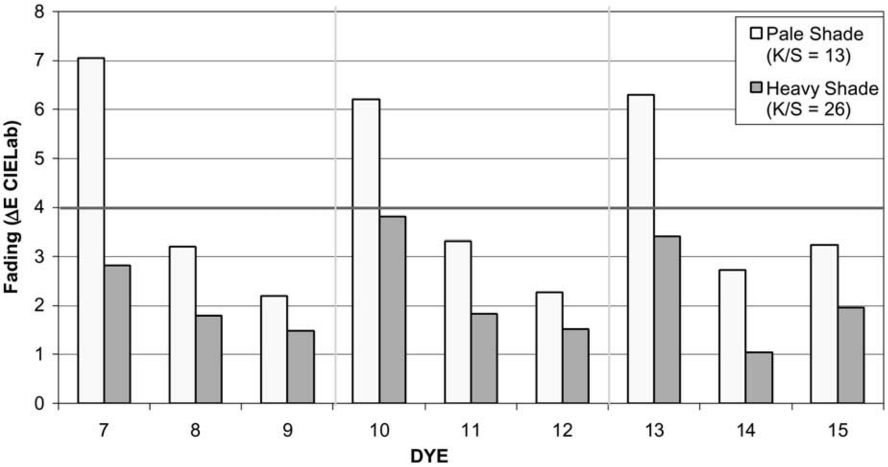


Fig. 7. Fading of cotton dyed with Dyes 7 to 15 in the UK-TO test.

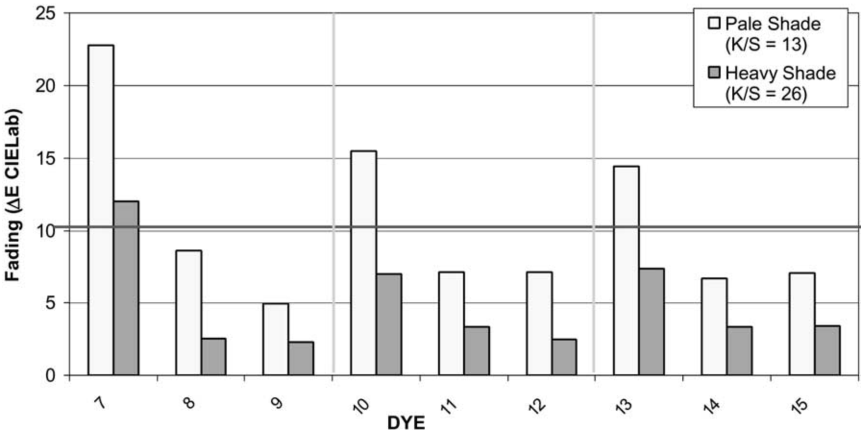


Fig. 8. Fading caused by 20 machine washes.

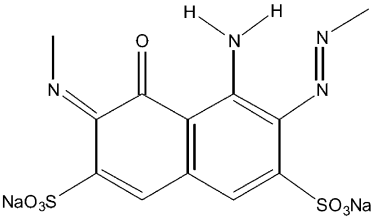


Fig. 9. Interaction of peri carbonyl group with amino group.

the aminoazo dyes, Fig. 1, are, per se, less stable to peracid, the major bleaching species in the ISO 105—CO9:2001 test, than the corresponding hydrazo derivatives, Fig. 2 [2], and that both are much less susceptible to attack by peroxide than peracid. This suggests that the aminoazo function of such dyes is unexpectedly resistant to attack by peracid, which is produced in the ISO 105—CO9:2001. This might well be associated with the carbonyl group present in the peri position, Fig. 9. The presence of an electron withdrawing group, such as carbonyl, would be expected to render the amino group less nucleophilic, that is, less readily attacked by electrophilic agents such as peracids.

Although peracid appears to be much more effective than peroxide in destroying colour, some chromophore destruction by oxidative-bleach containing detergents might be attributable to the latter reagent: Katayama et al. had already demonstrated [8] that arylazo dyes are more resistant to degradation by peroxide, an electrophilic reagent, than similar hydroxyaryl azo dyes and the above observation that the hydrazo, rather than azo, unit is undergoing attack is consistent with this. Dye degradation by peroxide has been attributed by some workers [9,10] to the perhydroxyl anion and by others to the perhydroxyl radical anion [11,12]. Results of this and other studies are consistent with the free peracid, not the dissociated anion, being the active species in dye degradation [1,2,13].

4. Conclusions

The introduction of a halogen atom, chlorine or bromine, *ortho* to the azo group, has minimal effect upon the resistance to oxidative-bleach of monohalogenated derivatives of CI Reactive Black 5. Thus Dyes 7, 10 and 13 all fail the UK-TO test at pale depths of shade: this sensitivity to oxidative-bleach containing detergents is confirmed on multiple machine washing. Conversely, the introduction of a chlorine or bromine atom, *ortho* to the hydrazo function, has a pronounced beneficial effect: thus Dyes 8, 9,11, 12, 14 and 15 all pass both tests at pale and heavy depths of shade. It is therefore probable that dye destruction proceeds predominantly in the vicinity of the hydrazo function.

Peracid had earlier been shown to be more aggressive than peroxide in causing chromophore destruction. The results of the present study are consistent with attack by peracid, a highly electrophilic reagent: introduction of an electron withdrawing chlorine atom *ortho* to the hydrazo leading to reduced rate of dye destruction.

The introduction of a single halogen substituent into the CI Reactive Black structure, such as in Dye 9, represents a potentially economic and feasible route to analogues with greatly improved resistance to oxidative bleach containing detergents [14].

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