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The wash-off of dyeings using interstitial water. Part 4: Disperse and reactive dyes on polyester/cotton fabric

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ABSTRACT

Polyester/cotton fabric which had been dyed with disperse and reactive dyes can be washed-off using two, novel processes that employ nylon beads. The bead wash-off processes furnished dyeings that were of similar colour strength and colour to those which had been reduction cleared in the case of disperse dyeings and washed-off using a conventional process for reactive dyeings. Fastness to washing at 60 °C of dyeings which had been bead washed-off was at least as good as that of dyeings which had been reduction cleared and conventionally washed-off. The bead wash-off processes enabled reductions of ~70% in both the amounts of energy and water consumed during wash-off. Whereas the conventional wash-off of polyester/cotton fabric generated large volumes of effluent that contained various chemicals, the comparatively small amount of wastewater generated by bead wash-off contained no such chemicals. In addition, bead wash-off avoided the environmentally unacceptable generation of aromatic amines in the case of the reduction clearing of azo dyes. The beads absorbed vagrant dye molecules, potentially enabling a major reduction to be achieved in terms of the BOD, COD and TOC which can be generated during conventional wash-off procedures for dyed polyester/cotton.

1. Introduction

Of the different types of textile fibre available, polyester is the most popular synthetic fibre and cotton the most popular natural fibre; indeed, polyester fibres accounted for ~50% (38.7×10^6 T) and cotton fibres ~35% (27.1×10^6 T) of the 77.5×10^6 T world textile fibre demand in 2011, with other man-made and synthetic fibres comprising ~13% (10.4×10^6 T) and wool, silk and other natural fibres making up the remaining small proportion (~2%; 1.3×10^6 T) [1]. Forecasts of global textile fibre demand predict that the marked popularity of cotton and polyester fibres, which has enjoyed steady growth since the 1970's, is likely to continue for the foreseeable future. Global dye production is ~10^6 T per year [2] of which reactive dyes and disperse dyes are two of the most important classes; dye production can be assumed to increase in-line with expected increases in textile fibre production.

Polycotton is the acronym used to describe a blend comprising polyester fibres and cotton fibres; in such, commonly, fabric blends, the polyester component imparts strength and resilience as well as both stain- and wrinkle-resistance whilst the cotton provides absorbency and comfort. Such blends are available in various ratios (e.g. 35:65; 'cotton rich', etc.) depending on end-use requirements. Whilst polyester fibres are produced in both filament yarn and staple fibre forms, it is the latter variant, in assorted guises (e.g. ~0.4 dtex; 30–150 mm long; round/modified cross section; crimped/flat, etc.), that is blended with cotton to produce polycotton; around 1/3rd of global polyester production is in the form of staple fibre. Of the different types of polyester fibre available, those made from poly(ethylene terephthalate) (PET) predominate [3].

Not all of the dye that is applied to a textile during dyeing is 'fixed' insofar as a proportion of the applied dye will not be physically and/or chemically reserved within the textile substrate at the end of dyeing (with the possible exception of dye applied by mass coloration). Such 'unfixed' or surplus dye presents major problems from technical, economic and environmental viewpoints, as vagrant dye molecules can desorb from the dyed material during processing and use. The extent of 'dye fixation' varies for different dye application methods (exhaust, continuous, etc.) and different dye/fibre combinations (Table 1) [4]; the exhaust (immersion) application of reactive dyes to cotton and sulphur dyes to cotton tend to display the lowest levels of dye fixation. 'Wash-off' is the generic term employed to describe the aqueous treatment by which surplus dye (and dyeing auxiliaries) is removed from dyeings at the end of dyeing [5]. Unless such a treatment is carried out, unfixed dye molecules will desorb during subsequent laundering (and other wet processing) and the ensuing vagrant dye molecules

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Table 1
Unfixed dye for different dye types and applications [4].

Fibre	Dye	Unfixed dye/%
Wool & nylon	Non-metallised acid	7–20
	Reactive	7–20
	Metal complex	2–7
	Mordant	1–2
Cotton/rayon	Azoic colorants	5–10
	Direct	5–20
	Reactive	20–50
	Sulphur	30–40
	Vat	5–20
Polyester	Disperse	8–20
PAN	Cationic	2–3

will stain adjacent materials, resulting in the dyeings displaying poor wet/wash fastness. Wash-off invariably takes the form of multi-stage aqueous rinses that use combinations of cold/warm/hot water and which also commonly include chemicals (e.g. acids, alkalis) and/or specific auxiliary agents (e.g. surfactants, oxidants) to expedite dye and dyeing auxiliary removal and also ensure that the optimum colour, depth of shade, fastness, etc. is achieved. An example of such a multi-stage wash-off process is given in Fig. 1, which shows a five-stage wash-off process recommended for monochlorotriazine reactive dyes in deep shades on cotton [6]. Different conditions are employed for the wash-off of different dye/fibre combinations, the particular conditions depending on various factors such as type of dye used, depth of shade, fibre type, substrate construction, etc. Nevertheless, all wash-off methods routinely consume large amounts of water.

The amount of water that is used in textile wet processing (e.g. dyeing, wash-off) is commonly described by the 'liquor ratio' (L:R), this being the ratio of the amount of water used to the amount of fibre used. Wash-off processes typically employ liquor ratios of 10–20:1 per stage. In the case of the wash-off process shown in Fig. 1, if each of the five wash-off stages used a 10:1 L:R, then the wash-off of 1 tonne of dyed cotton would consume 50 tonnes of water (50:1 total L:R). Should overflow rinsing be used (Fig. 1), in which clean water is fed into the rinse vessel and drained through an overflow weir, water consumption will be greatly increased. A corollary of this large water usage is that wash-off processes habitually generate very large volumes of wastewater that typically contains residual dyes, surfactants, electrolytes, etc. and which, characteristically, displays marked resistance to biodegradation [5], thereby posing both environmental and economic challenges; an example of the size and nature of wastewater typically generated during exhaust dyeing is given in Table 2 [7]. Invariably, dye wastewaters are admixed and treatment processes often are focussed on removing the coloured compounds present in the dye wastewater (e.g. by adsorption), which adds to the complexities and cost of wastewater treatment. Sadly, whilst the treatment and disposal of dye wastewater has been the focus of an exceptionally high number of research papers in recent years [8], no single wastewater treatment method is universally applicable to all dye/fibre systems nor does one appear to enjoy widespread commercial success.

Of the several methods that have been devised over many years to dye polycotton fabrics, the simplest and most popular is a 'two-bath, two-stage' process in which the polyester component is firstly dyed using disperse dyes at ~130 °C under acidic conditions and the cotton component is then dyed using reactive dyes at ~60 °C under alkaline conditions. However, surplus dye must be removed at the end of each dyeing stage, not only to ensure optimum fastness to laundering and other wet processes, but also to avoid cross-staining during dyeing, of the disperse dyes on cotton and the reactive dyes on polyester.

Rinse
70°C; 10 min
(if required, with overflow)
↓
Soap
95-98°C; 15 min
1-3 gL^{-1} *Cyclanon XC-W New*
↓
Soap
95-98°C; 15 min
1-3 gL^{-1} *Cyclanon XC-W New*
↓
Rinse
70°C; 10 min
↓
Rinse
40°C; 10 min

Fig. 1. Wash-off process recommended for monochlorotriazine reactive dyes in deep shades (6).

In the case of PET fibres dyed with disperse dyes, a specific wash-off process, commonly referred to as 'reduction clearing' is used (Fig. 2), in which the dyed material is treated in an aqueous, alkaline solution of sodium dithionite ($Na_2S_2O_4$; sodium hydrosulfite). The reduction clearing process, which is widely used in the case of medium/heavy depths of shade and, in some cases regardless of dye depth of shade to remove surface deposited polyester oligomers [3], breaks the azo bond in azo dyes, liberating colourless amino compounds and converts anthraquininoid disperse dyes to the virtually colourless, water-soluble, low substantivity, ionised form of the dye (Fig. 3). Unfortunately, in addition to the reduction clearing process consuming large amounts of water, energy and chemicals, the highly alkaline wastewater produced contains the robust reducing agent sodium dithionite as well as aromatic amines in the case of azo disperse dyes. Despite many attempts, over several decades, to reduce the environmental impact and the cost of reduction clearing, including the environmentally unacceptable generation of aromatic amines in the case of azo dyes, the traditional, aq. alkaline, $Na_2S_2O_4$ reduction clearing process continues to enjoy widespread use [9].

Reactive dyes are so-called because, unlike other types of dye, they 'react' with the textile substrate (wool, nylon, cotton, etc.), forming covalent bonds between appropriate electrophilic groups in the dye (e.g. –N=C–R–**X**) and nucleophilic groups (e.g. $-\mathbf{O}^-$; $-\mathbf{NH_2}$) in the fibre. In the case of cotton, reactive dyes are by far the

Table 2
Sequence of discharge baths from exhaust dyeing of cotton with sulphur dyes in dark shades [7].

Bath	COD/mg O_2 L^{-1}	AOX/ mg Cl L^{-1}	pH	Conductivity/ mS cm^{-1}
Exhausted dyebath	4800	3.3	11.5	63
Hot rinse bath	600	0.4	10	3.2
Rinse bath	36	0.03	8.2	0.62
Rinse bath	25	0.04	8	0.34
Hot rinse bath	580	0.3	8.3	1.3
Rinse bath	30	0.04	7.4	0.52
Rinse bath	25	0.04	7.4	0.5
Hot rinse bath	390	0.25	8.2	1.5
Rinse bath	24	0.03	7.6	0.52
Rinse bath	12	0.04	7.7	0.5
Softening bath	2200	1.6	7.7	1.1