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The wash-off of dyeings using interstitial water part 1: Initial studies

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ABSTRACT

The extent to which a novel wash-off process using polyamide beads removed five different types of dye from three different types of fibre was similar to that achieved using conventional aftertreatments. Whilst bead wash-off and the conventional aftertreatments were of similar duration and temperature, conventional aftertreatment employed a 10:1 or 20:1 liquor ratio whereas bead wash-off used $a < 1:1$ liquor ratio. As vagrant dye was adsorbed onto the bead material during wash-off, the low amount of wastewater generated contained little residual dye, thereby offering the potential of reduced environmental and cost benefits. Bead wash-off did not impair the fastness of two non-metallised acid dyes on nylon 6,6 to washing at 60 °C.

1. Introduction

Invariably, dyeings and prints are subjected to an aqueous treatment at the end of dyeing/printing that is designed to remove surplus dye and dyeing/printing auxiliaries (levelling agents, electrolytes, etc.). In its simplest form, this aqueous treatment, which is inconsistently and variously referred to as, *washing* or *rinsing*, comprises a single rinse with water; however, as such a treatment is rarely stringent enough to remove all surplus dye and dyeing auxiliaries, multi-stage rinsing using combinations of cold/warm/hot water constitute the simplest forms of the aqueous treatment. Such multi-stage aqueous processes also commonly include the use of chemicals (e.g., acids, alkalis) as well as specific auxiliary agents (e.g., surfactants, oxidants) not only to expedite dye and dyeing auxiliaries removal, but also to ensure that optimum colour, depth of shade, fastness, etc. are achieved. This is exemplified by the processes shown in Fig. 1 for the treatment of sulphur dyeings on cotton [1] and in Fig. 2, for arguably the two most commercially important classes of dye in use today, namely disperse [2] and reactive dyes [3]. The use of chemicals/auxiliary agents in the multi-stage aqueous treatment of dyeings/prints has lead to the proposal [4] that, irrespective of the class of dye and type of textile fibre used, the generic term ‘wash-off’ can be applied to an aqueous treatment carried out at the end of dyeing/printing, that is intended to remove surplus dye and dyeing/printing auxiliaries and which enables the desired colour, depth of shade, level of fastness, etc. to be achieved.

In many cases, such as the application of sulphur dyes, the stages of a wash-off process that employ chemicals and/or auxiliary agents (e.g., the oxidation stage in Fig. 1) are not only components of the multi-stage wash-off process, but also are an essential stage of modern dyeing processes. In the case of the sulphur dyeing of cotton, whilst oxidation of a dyeing can be achieved using air, as the results obtained can be variable, recourse to a separate treatment with an oxidant is preferred. For other dye–fibre systems, a wash-off process can also entail the application of proprietary auxiliaries which are specifically designed to enable enhanced levels of fastness to be achieved, as illustrated by the application of *syntans* to acid dyes [5] and *fixing agents* to direct dyes on cellulosic fibres (Fig. 3 [6]). Although such treatments, which are commonly referred to as *aftertreatments* [7], are, in essence, optional, since they usually constitute an integral component of a multi-stage wash-off process, nowadays they are considered to be an intrinsic stage of the overall dyeing process, as exemplified by the Du Pont/DyStar recommended process for the application of the *Stanalan* range of reactive dyes to *Coloursafe* polyamide fibre (Fig. 4 [8]).

In the context of the work described herein, the term ‘wash-off’ is used to describe two, distinct, but conjoined processes namely

- surplus dye and dyeing/printing auxiliaries removal (aka *rinsing*/*washing*) and;

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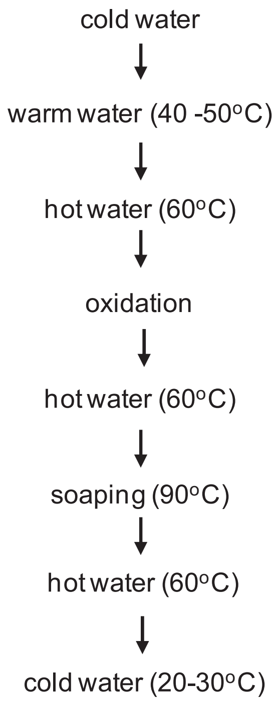


Fig. 1. Wash-off process for sulphur dyes on cellulosic fibres.

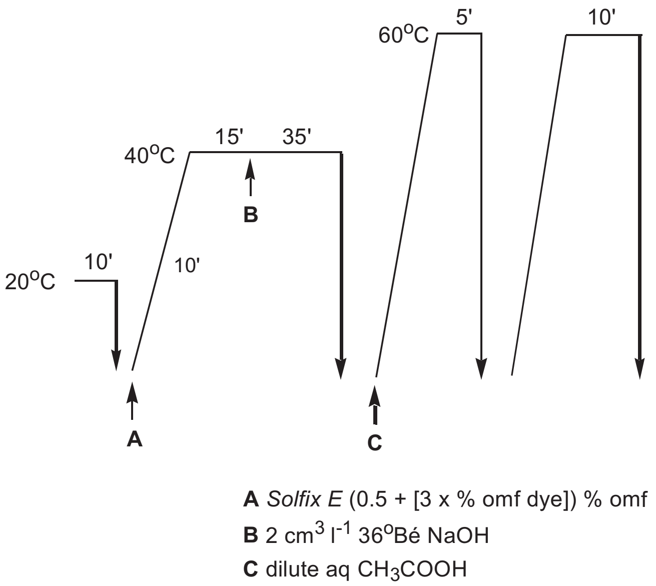


Fig. 3. Wash-off process for direct dyes on lyocell.

- the application of specific auxiliaries (eg syntans, fixing agents, etc.) aka *aftertreatment*; which are used to enable the desired hue, depth of shade, fastness, etc. to be achieved.

From the foregoing, it is apparent that wash-off processes consume very large amounts of water, as illustrated by the water usage shown in Table 1 for the wash-off stages employed in a typical reactive dyeing process [9]. By way of example, if a (commonly used) 10:1 liquor ratio was employed for each of the stages in the three, wash-off processes depicted in Figs. 1 and 2 then the amount of water consumed in the wash-off of 1 tonne of fibre dyed with sulphur, disperse and reactive dyes, would be 80, 40 and 50 tonnes, respectively. Although the particular conditions employed for wash-off depend on various factors such as type of dye used, depth of shade, fibre type, substrate construction, etc., wash-off also generates large volumes of wastewater that typically contains residual dyes, surfactants, electrolytes, etc. and which, characteristically, displays marked recalcitrance towards biodegradation [4], thereby presenting both environmental and economic challenges. Indeed, the treatment and disposal of dye wastewater, which continues to be the subject of plenteous research papers, includes traditional wastewater treatment methods such as adsorption, electrochemistry, oxidation [10–13] as well as emerging technologies, as exemplified by nanofiltration [14], photocatalysis [15], low-cost alternative adsorbents [16], bacterial cells [17], irradiation [18], biosorption [19], advanced oxidation processes (AOP's) [20,21] and hybrid treatments [22]. An indication of the potential magnitude of the problems associated with wastewater treatment is provided by the estimation [23] that, in 2000, some 4 × 10^6 tonnes of cotton was dyed using 80,000 tonnes of reactive dye by immersion (exhaust) methods, which, because only an average dye fixation level of 70% was achieved, generated 24,000 tonnes of hydrolysed and/or reactive dye that was

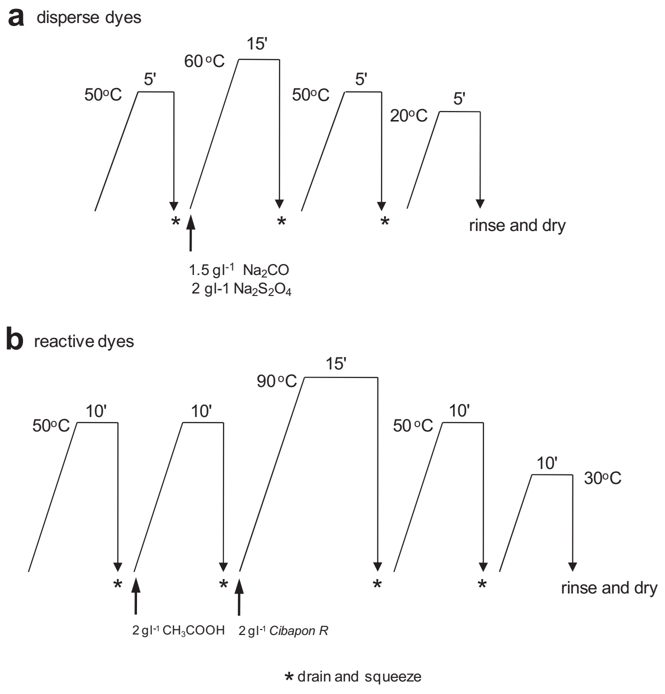


Fig. 2. Wash-off process for disperse dyes on polyester and reactive dyes on cotton.

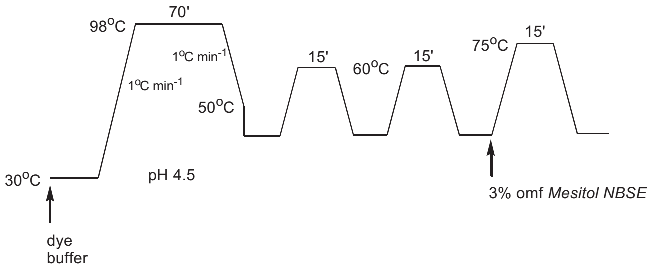


Fig. 4. Dyeing and wash-off process for >3% omf *Stanalan* dyes on polyamide.

Table 1
Water use in wash-off stages of a typical reactive dyeing process for cotton [9].

Process	Wastewater/l	Temperature/°C
hot soap	700	95
warm rinse	700	60
overflow rinse	4300	10
hot soap	700	95
warm rinse	700	60
overflow rinse	4300	10
neutralise & soften	700	40

ultimately discarded in aqueous effluent. Furthermore, the wastewater generated during dyeing processes is characterised by high BOD, COD, total dissolved solids and total suspended solids [3,4,24–26] that stem from the presence of various organic residues in addition to dyes. Wash-off also invariably consumes large amounts of energy as many of the multiple stages involve treatment with warm/hot water/detergent/alkali, etc., as can be deduced from the processes shown in Figs. 1–4. Thus, the high amounts of water, chemicals and energy consumed mean that wash-off is a costly process, this being accentuated by the significant wastewater treatment costs involved.

Clearly, from both economic and environmental perspectives, wash-off needs to use the minimum amounts of water, chemicals and energy so as to generate the minimum amount of wastewater. In this context, this paper describes the use of a wash-off process for dyeings and prints that employs a novel, re-usable and re-cyclable polyamide bead material to replace the vast majority of the water and chemicals that are traditionally used in wash-off. The patented novel process [27], which is currently being commercialised by Xeros Ltd [28] does not use a large reservoir of water to immerse the dyeing/print but, instead, utilises only the relatively small amount of water that is present within the interstices of both the damp fabric and the bead material. This part of the paper comprises an introduction to the wash-off process, describing the theoretical and empirical considerations behind the selection of the nylon bead material as well as the ability of the bead material to remove surplus dye from various dye/fibre combinations. Subsequent parts of the paper will concentrate on the wash-off of reactive dyes on cellulosic fibres and disperse dyes on hydrophobic fibres.

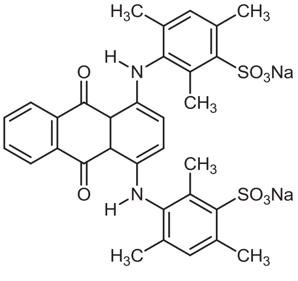
2. Experimental

2.1. Materials

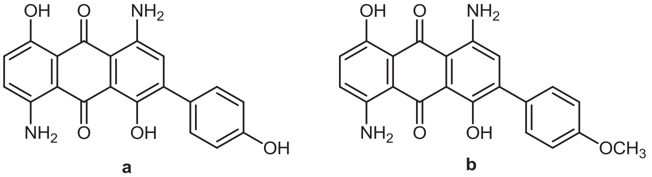
Scoured, knitted polyamide (167 gm^{-2}) and polyester (142 gm^{-2}) fabrics were kindly supplied by Invista, UK; scoured and bleached woven cotton fabric (140 g m^{-2}) was obtained from Whaleys, Bradford. The dyes listed in Table 2 were generously provided by the respective manufacturer and were used without purification. The seven dyes used were chosen arbitrarily, the structures of only two of the dyes having been published in the Colour Index [29], namely C.I. Acid Blue 80 (**1**) and C.I. Disperse Blue 73 (**2**).

Table 2
Dyes used.

Commercial name	C.I. Generic name	Maker
Diresul Black Liq. RL 200%	Leuco Sulphur Black 1	Clariant
Indosol Navy SF-BL	Direct Blue 251	
Nylosan Blue F-L	Acid Blue 80	
Drimarene Blue X-3LR	Reactive Blue 52	
Dianix Blue BG-FS 200	Disperse Blue 73	DyStar
Nylanthrene Red C-RA	none ascribed	Yorkshire
Nylanthrene Blue C-GLF	Acid Blue 281	



1



a b

2 (mixture of a and b)

The dyeing auxiliaries *Diresul Oxidation* Liq BRI (oxidising agent) and *Formusol GR* (reducing agent) were generously provided by Clariant; *Matexil DAN* (dispersing agent) was kindly supplied by Uniqema. All other chemicals used were of general laboratory grade. The various wash-off auxiliaries and surfactants listed in Table 3 were kindly donated by the respective manufacturer.

Owing to commercial confidentiality, details of the polyamide bead material used cannot be disclosed.

2.2. Dyeing

All dyeings were carried out in sealed stainless steel dyepots of 300 cm^3 capacity, housed in a Roaches *Pyrotec* '*S*' laboratory dyeing machine using a liquor ratio of 20:1; the methods used are shown in Figs. 5–10. For all of dyes used, at the end of dyeing, the dyed samples were removed, rinsed in water and either subjected to aftertreatment/bead wash-off or were allowed to dry in the open air.

McIlvaine buffer solutions [30] were used to control the pH of some of the dye and aftertreatment baths. For pH values 4.5, 5, 7 to 8, the quantities of Na_2HPO_4 and citric acid shown in Table 4 were dissolved in 1 l of distilled water. For pH 10, a solution was made by dissolving Na_2HPO_4 (5 g) and KH_2PO_4 (1 g) in 1 l of distilled water; the pH of the ensuing solution was 7.6, this being adjusted to pH 10

Table 3
Wash-off auxiliaries used.

Trade name	Type	Manufacturer
Diresul EW	fatty amine polyglycol ether	Clariant
Nylofixan PSA Liq.	anionic fixing agent, arylsulphonate in aqueous solution	
Nylofixan MFN	anionic fixing agent	
Indosol E-50 Liq.	cationic fixing agent, aliphatic polyamine derivative	
Sandozin NIE	non ionic surfactant	
Sandopur RSK liq.	wash-off agent	
Lanapex R	anionic surfactant	Uniqema

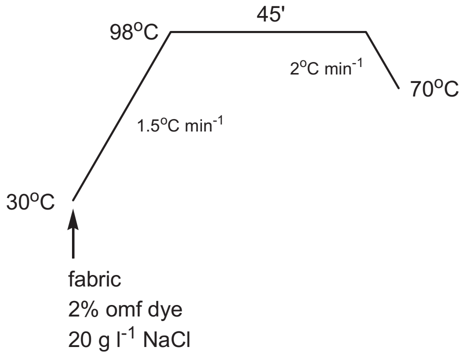


Fig. 5. Dyeing method for direct dye.

by the addition of an appropriate volume of 0.1 M aq NaOH solution.

2.3. *Conventional aftertreatment*

Dyeings were subjected to the respective conventional aftertreatment described below, in sealed, stainless steel dyepots of 300 cm^3 capacity, housed in a Roaches *Pyrotec* ‘S’ laboratory dyeing machine. At the end of each process, the aftertreated sample was removed, rinsed thoroughly in tap water and allowed to dry in the open air.

2.3.1. *Fixing agent*

Cotton which had been dyed using C.I. Direct Blue 251 was aftertreated using the method shown in Fig. 11.

2.3.2. *Reduction clearing*

Polyester fabric which had been dyed with C.I. Disperse Blue 73 was reduction cleared using the method shown in Fig. 12.

2.3.3. *Sulphur dye oxidation*

Cotton which had been dyed with C.I. Leuco Sulphur Black 1 was oxidised using the method shown in Fig. 13.

2.3.4. *Reactive dye wash-off*

Cotton which had been dyed using C.I. Reactive Blue 52 was washed-off using the method shown in Fig. 14.

2.3.5. *Syntan treatment*

Dyeings of nylon produced using the unsulfonated 2:1 metal complex dye, C.I. Acid Blue 80 were aftertreated according to the procedure shown in Fig. 15 whilst those achieved using the two, non-metallised acid *Nylanthrene* dyes, were aftertreated using the method depicted in Fig. 16.

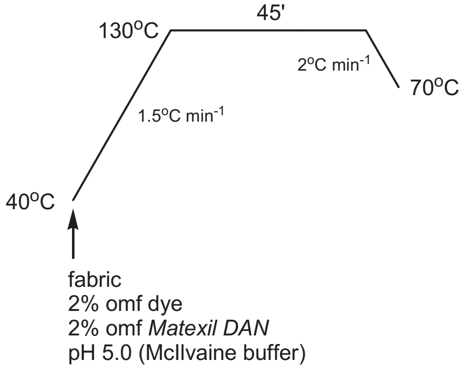


Fig. 6. Dyeing method for disperse dye.

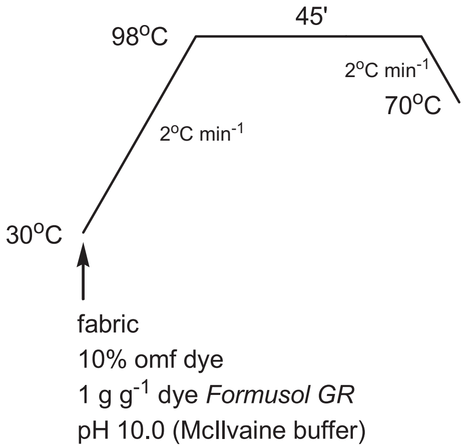


Fig. 7. Dyeing method for sulphur dye.

2.4. *Wash-off using nylon beads*

Dyeings which had been wetted-out using tap water and excess liquid removed by squeezing, were placed in stainless steel dyepots of 300 cm^3 capacity together with nylon beads to provide a bead: fabric ratio of 5:1. The sealed dyepots were housed in a Roaches *Pyrotec* ‘S’ laboratory dyeing machine and wash-off carried out using the method depicted in Fig. 17. At the end of wash-off, the dyeing was removed, rinsed in tap water and allowed to dry in the open air.

2.5. *Colour measurement*

The CIE colorimetric co-ordinates and fk values were calculated from the reflectance values at the appropriate λ_{max} for each dyeing, measured using a *Datacolor Spectroflash 600* spectrophotometer under illuminant D_{65}, employing a 10° standard observer with UV component included and specular component excluded. The samples were folded so as to realise two thicknesses and the average of four measurements was taken for each sample.

2.6. *Photography*

Beads were placed in a light cabinet under illuminant D_{65} and photographs obtained using an *Olympus* [*μju*] *300* (3.2 megapixels) camera at 2048 × 1536 resolution.

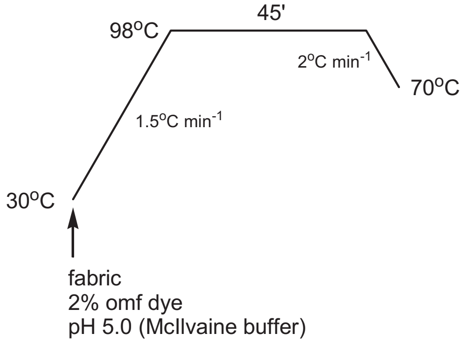


Fig. 8. Dyeing method for C.I. Acid Blue 80.

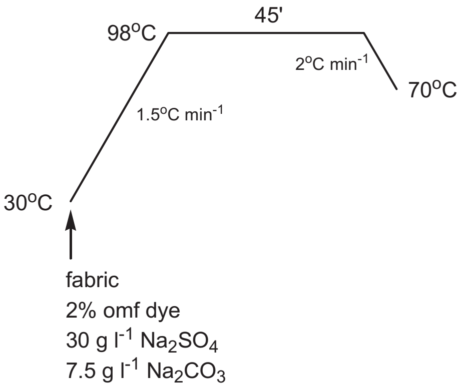


Fig. 9. Dyeing method for reactive dye.

Table 4
McIlvaine buffer composition.

pH	0.2 M Na_2HPO_4	0.1 M Citric acid
4.5	42.3	52.3
5	51.5	48.5
7	82.4	17.6
8	97.3	2.7

3. Results & discussion

3.1. Background

As mentioned, the conditions employed for the wash-off of dyeings and prints depend on various factors such as type of dye used, fibre type, substrate construction, fastness requirements, etc. No ‘universal’ process has yet been devised for use with all dye/fibre systems but, rather, dye and auxiliary makers have developed specific wash-off processes for different dye–fibre combinations, as illustrated by the fact, that, in this work, six different, recommended wash-off processes were used for the six types of dye employed (Figs. 11–16). Such a situation can be attributed to different dye types requiring quite different conditions for their removal from dyeings and prints, as exemplified by considering two, diametrically opposed, wash-off methods that are used for two popular dye classes namely *disperse dyes* (when used on, say polyester), for which treatment with an aqueous, alkaline, solution of detergent and reducing agent are used for wash-off and *sulphur dyes* (on cotton, for example), for which, aqueous, acidic, oxidative conditions are employed. As discussed earlier, in the case of many dye–fibre systems, wash-off also entails the application of specific auxiliaries that are intended to enhance/expedite the fastness of dyeings/prints, as illustrated in this work by the use of a *fixing agent* in the case of C.I. Direct Blue 251 (Fig. 11) and the use of two different *syntans* for the two types of non-metallised acid dye employed (Figs. 15 and 16).

In each of the processes described above, wash-off comprises a multi-stage process that involves the use of specific auxiliaries and which consumes large amounts of water. From the perspective of the work described herein, it was the, typically very large, water consumption of conventional dye/print wash-off, that prompted an investigation into whether it was possible to replace either some or all of the water employed with an alternative medium. In addition, it was also decided to investigate whether a ‘universal’ wash-off process could be developed for use with several dye–fibre systems. Whilst details of the novel wash-off technology are not disclosed, owing to commercial confidentiality, the background considerations that lead to its development are discussed below.

3.2. The nature of wash-off

Despite the importance of the wash-off process for all dye/fibre systems and the availability of tailor-made, wash-off auxiliaries and aftertreatment agents, the fundamental parameters of the process which are applicable, generically, to dye/fibre systems, have received surprisingly scant attention, which is all the more remarkable in the context of the current, seemingly insatiable appetite of researchers working in the area of the consequences of wash-off, namely dye and auxiliary removal from wastewater.

In essence, the wash-off of dyeings/prints is analogous to domestic laundering in that both processes are multi-stage systems that involve submersion of the dyed or soiled fibre in an agitated, aqueous medium with the intention of abstracting and suspending dyes/soils which are subsequently removed by water rinsing. In addition, both dye wash-off and domestic laundering rely upon the combination of mechanical action, time and temperature to expedite ‘cleaning’ and, in both systems, auxiliaries (e.g., detergents, alkali, etc.) are routinely employed. In this context, the ‘Sinner’s Circle’ [31] (Fig. 18a) is commonly used to represent the four main factors that determine domestic laundering performance namely *mechanical action*, *time*, *temperature* and *detergency*. According to this concept, for a given, say, amount of mechanical action, a particular level of clothes washing will be achieved by varying the time, temperature and/or level of detergency employed in the wash cycle. From the above consideration of the similarities between wash-off and domestic laundering, it seems reasonable to suggest that a modified Sinner’s Circle approach can be applied to dye wash-off, such as that displayed in Fig. 18b insofar as, the four parameters involved are *mechanical action*, *time*, *temperature* and *auxiliary* (e.g., detergent, alkali, etc.). However, as proposed in the case of domestic washing [32], so as to reflect the vitally important contribution that water makes to the four parameters, a fifth factor namely *water*, needs to be added to this ‘circle’ (Fig. 18c). The particular contributions of the five parameters depicted in Fig. 18c

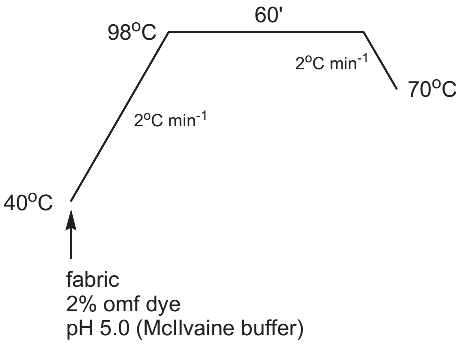


Fig. 10. Dyeing method for *Nylanthrene* dyes.

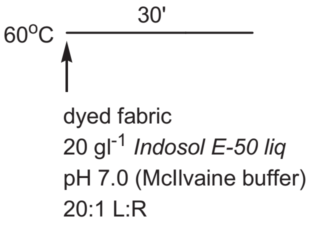


Fig. 11. Aftertreatment with fixing agent.

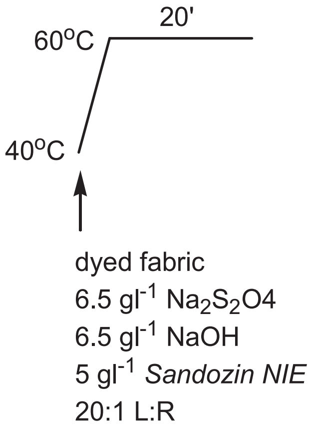


Fig. 12. Reduction clearing method.

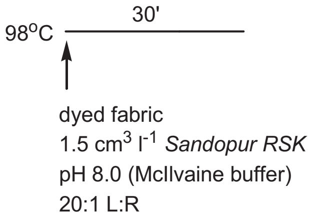


Fig. 14. Reactive dye wash-off.

will vary, from a usage perspective, according to the wash-off process under consideration, as can be anticipated from a consideration of the different wash-off processes shown in Figs. 1–4. In view of the all-encompassing role of water in conventional wash-off, perhaps the representation of the Sinner's Circle displayed in Fig. 18d is appropriate. Clearly, not only will the relative contributions of the five parameters (*mechanical action*, *time*, *temperature*, *auxiliary* and *water*) in Fig. 18d vary, according to the dye type, fibre type, liquor ratio, substrate construction, etc. but, also, a particular depth of shade, colour, level of fastness, etc. will be achieved using different combinations of the five components of the modified Sinner's Circle (Fig. 18d). This latter aspect was recently demonstrated in the case of bis(aminochlorotriazine) dyes on cotton [4]: dyeings of generally the same hue and colour strength and which also displayed similar levels of fastness to repeated washing, were obtained using three, wash-off processes which differed in terms of time, temperature, mechanical action, auxiliary (detergent, alkali) and amount of water used.

3.3. *Role of water*

The crucially important and significant role of water in wash-off can be explained by considering its many and varied functions, such as, for example, provision of mechanical action, fibre wetting, swelling agent, heating and rinse medium, restraining agent for vagrant dyes, etc. From a very much simplified mechanistic viewpoint (Fig. 19), the initial stages in wash-off comprise fibre wetting and fibre swelling, the latter process being crucial for the diffusion of dyes and dyeing auxiliaries out of the dyeing/print as well as the transfer of detergent, alkali, etc. into the fibrous material which aids the removal of dye and dyeing auxiliaries. Vagrant dye which has been removed from the fibre will be dissolved/dispersed in the wash-off water and, ideally, such dye should remain in aqueous dissolution/suspension so as to prevent its re-deposition onto the dyeing; subsequent rinsing of the washed-off textile removes vagrant dyes, auxiliaries, etc. Each of the stages shown in Fig. 19 is both enabled and promoted by water by virtue of its ability to provide the necessary levels of solvation, heating, restraining and mechanical action. In order for a material to replace some or all of the water used in conventional wash-off then that material must be able to perform some or all of the above functions undertaken by water.

All textile wet processing (e.g., dyeing, finishing) involves the highly complex and related operations of water sorption, fibre wetting and fibre swelling, each of which is influenced by both the physical and chemical nature of the fibrous substrate. In this context, fibres vary, markedly, in terms of, for example, the number and type of accessible polar group they contain, glass transition temperature (T_g), degree of orientation, etc. which results in different fibres displaying marked differences in moisture regain and swelling in water (Table 5; [33–46]); indeed, relative hydrophobicity/hydrophilicity is the basis of a method of classification of textile fibres from the perspective of dyeing [47]. In view of the well-known importance of fibre wetting and, especially, fibre swelling in the wet processing of textiles, it is possible to obtain a theoretically approximate measure of the amount of water required to wet-out and saturate a given fibre from values of moisture regain at 100% relative humidity (RH) (Table 5), even though such values are temperature-dependent and their determination is complex [48]. In simple terms, from Table 5 it follows that, as the moisture regain of cotton at 100% RH is 23%, then 1 kg of 100% cotton fabric would absorb ~0.23 kg of water at saturation; the same mass of wool (moisture regain ~34% at 100% RH) would absorb ~0.34 kg water at saturation whilst 1 kg of 100% nylon (moisture regain 8.7% at 100% RH) would absorb some 0.09 kg of water. Thus, theoretically, ~0.23 kg of water is needed to wet-out 1 kg of cotton, ~0.34 kg water to wet-out 1 kg of wool, etc., this being a pre-requisite to enable fibre swelling. In the context of the actual amounts of water which can be consumed in typical wash-off processes, whilst variations arise, according to whether overflow baths and/or fixed volume baths are employed, the liquor:fibre ratio (normally referred to as 'liquor ratio') employed has a major influence on wash-off, as it controls both the rate and extent of the removal of residual dye and electrolyte, alkali, etc. not only in terms of the volume of water in which vagrant dye, alkali, etc. removal

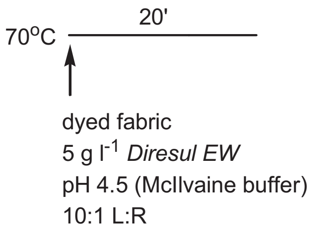


Fig. 13. Sulphur dye oxidation method.

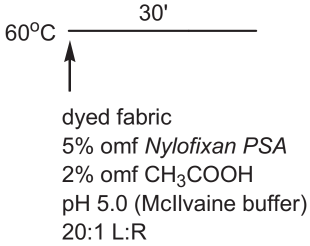


Fig. 15. Syntan aftertreatment for C.I. Acid Blue 80.

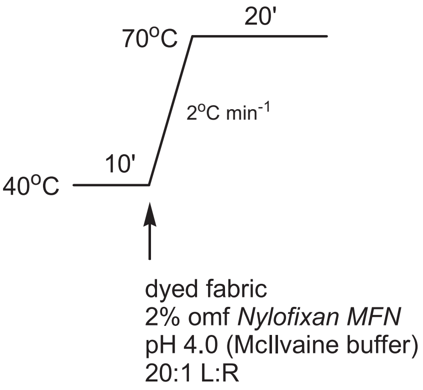


Fig. 16. Syntan aftertreatment for *Nylanthrene* dyes.

occurs but also by virtue of the number of rinse stages required for wash-off. For example, in the case of reactive dyes on cellulosic fibres, it is reported that whilst rinsing at low liquor ratio requires more rinsing steps to achieve a certain level of dye removal for a given depth of shade, this approach may consume less water than that employed using higher liquor ratios and fewer rinse baths [49]. As liquor ratios of between 5:1 and 20:1 are typically used in the wash-off stages employed for reactive dyeings [49,50] then between 5 and 20 kg of water are consumed for each of the various stages of the wash-off process, such as that shown in Fig. 2, in the case of 1 kg of cotton dyed with reactive dyes (although the commonly used unit for liquor ratio is volume [L], for the purposes of this discussion, units of mass [kg] will be used). Whilst this 5–20 kg of water will be used to provide fibre wetting and swelling, heating, rinsing, etc., there is clearly a large difference between the 5–20 kg of water that may used in a conventional wash-off stage for 1 kg of reactive dyed cotton and the ~0.34 kg of water which, theoretically, is required to wet-out the 1 kg of dyed substrate. Hence, only a relatively small fraction of the water used in a conventional wash-off stage is necessary to expedite wetting and swelling, from which it can be concluded that the vast majority of water in conventional wash-off processes is used to provide other functionality, such as mechanical action, heating, dye dissolution/dispersion, rinsing, etc.

In this context, it was decided to describe the minimum amount of water necessary to saturate a given textile substrate and thereby enable wetting and swelling as 'interstitial water' so as to not only recognise water's crucial wetting and swelling functions but also to distinguish these from functions such as heating, mechanical action, etc. of the 'bulk water' which comprises the vast majority of the water in a conventional wash-off stage. In reality, of course, there is little, if any difference between 'interstitial water' (i.e., that which resides within the interstices of the fibrous substrate) and 'bulk water' (i.e., that which surrounds the water-swollen fibre), as the two 'types' of water can be assumed to be in a state of constant interchange and, therefore, each can provide the manifold functions of the water in a wash-off stage namely, heating, rinsing, etc.

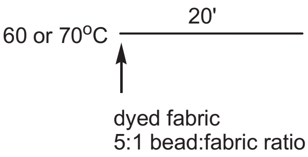


Fig. 17. Polyamide bead wash-off method.

Initial experiments [51] focussed on the selection of a medium that could replace some or all of the 'bulk water' used in wash-off.

3.4. Bulk water replacement

A decision was made to use polyamide as the medium that would replace all/some of the 'bulk water' on the basis of the polymer's unique physical and chemical characteristics which, in combination, impart to the fibre a remarkable susceptibility to absorb vagrant dyes ('grey') during repeated domestic washing, which accrues from:

- the presence of polar groups ($-NH_2$; $-COOH$; $-CONH$; $-COCH_3$);
- an ability to absorb water;
- a 'wet' T_g below the temperatures (30, 40, 60, 95 °C) that are commonly employed in domestic washing;
- substantivity towards all dye classes even under aq alkaline conditions;
- an ability to swell in water.

By way of explanation, since its commercial introduction, almost 70 years ago, polyamide has enjoyed myriad applications, of which its use as a textile fibre, is very well known. Of all textile fibres, nylon can be dyed with the largest number of different types of dye (Table 6 [47]) because of both the chemical and physical characteristics of the polymer. It is well known [7] that the presence of terminal amino end groups in polyamide fibres imparts substantivity towards several types of anionic dye (i.e., *acid* (including *metal complex*) *dyes*, *mordant dyes*, *direct dyes* and *reactive dyes*); the fibre is also dyeable with *disperse dyes*, *azoic colorants*, *vat dyes*, *sulphur dyes* and *cationic dyes* [7] (Table 6). In the case of anionic dyes, the pH-dependence of dye adsorption is attributable to ion–ion interactions operating between the ionic groups (usually sulfonate) in the dyes and protonated terminal amino groups in the substrate; other forces of interaction, such as H-bonding, van der Waals' forces, hydrophobic interactions as well as π–π interactions can be expected to contribute to dye–fibre substantivity. The presence of carboxylic groups in the fibre imparts substantivity towards cationic dyes while the polar and relatively hydrophobic characteristics of nylon also serve to impart substantivity towards disperse dyes as well as sulphur dyes, for which it is considered that dye–fibre substantivity occurs principally through H-bonding, dispersion forces and polar van der Waals' forces of interaction [7].

However, the remarkable dyeability of nylon fibre is also partly attributable to its distinct physical character. Although polyamide is often considered to be a hydrophobic fibre, it nevertheless absorbs water and swells in water (Table 5) owing to the presence of polar groups ($-NH_2$, $-COOH$, $-NHCO-$). The observation that water sorption involves the formation of H-bonds with amide groups in the polymer, which, in turn, disrupt H-bonding between chain $-CONH$ groups and, thereby, constitute *plasticisation*, was recognised in the 1940's [52] and reflected in early water adsorption isotherms [53]. Puffr and Sebenda [54] proposed a two-stage model of water sorption by polyamides in which a first water molecule forms a double H-bond between two neighbouring $-CO$ groups within the accessible (i.e., amorphous) regions of the polymer, this being followed by the absorption of a second and a third water molecule which join the existing H-bonds between the $-NH$ groups and other $-CO$ groups, this disturbing the existing H-bonds within the polyamide structure, resulting in plasticisation. Starkweather [55,56] extended this two-stage model, proposing that water in nylon is essentially unclustered up to a concentration of one water molecule per two amide groups in the amorphous regions but, near saturation, the average cluster size is approximately three water

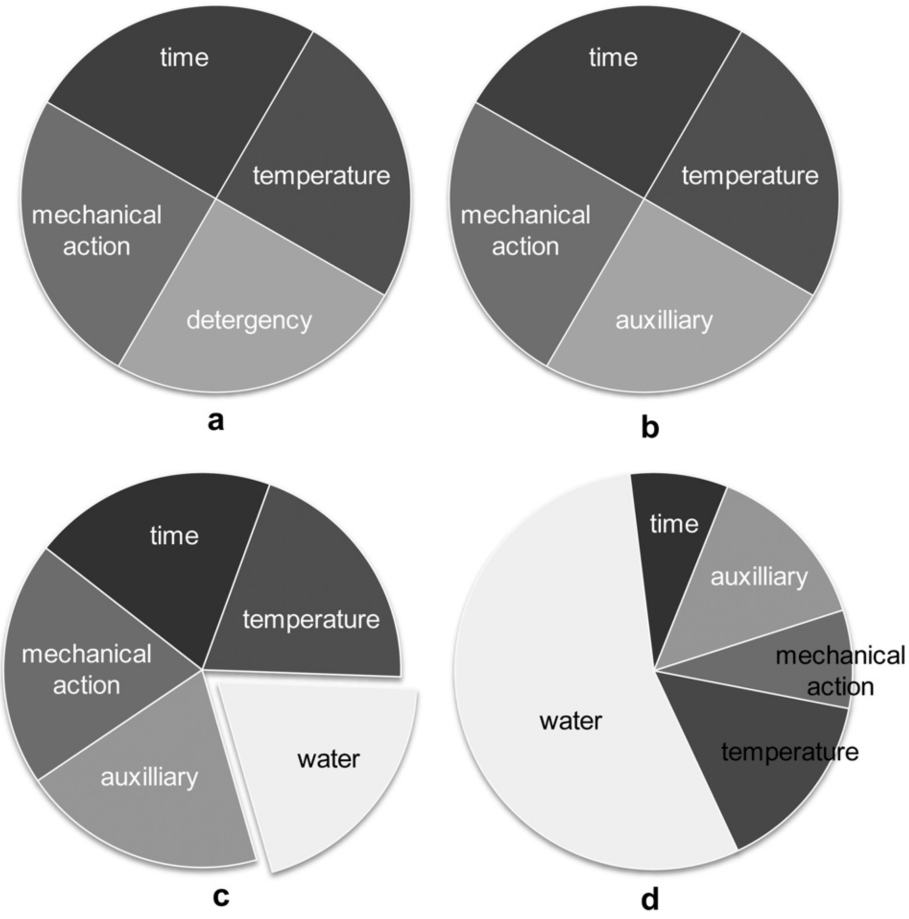


Fig. 18. Variations on the Sinner's Circle.

molecules. The remarkable plasticising effect of water on polyamide fibres is reflected in the dramatic reduction in the T_g of the dry fibre from ~70–80 °C to well below 0 °C for the wet fibre (Table 5). In contrast, the dry T_g of polyester is ~70 °C but is reduced by only some 5–10 °C in water [46] as the highly compact, hydrophobic fibres contain few accessible polar groups, display very low moisture regain and do not swell appreciably in water (Table 5). Consequently, the wet textile processing (e.g., dyeing, finishing) of nylon fibre is always carried out at temperatures well above its wet T_g with the result that, according to *Free Volume Theory* [7], the properties of the amorphous polymer will resemble those of a highly viscous, rubbery liquid, in which both the segmental mobility of the composite macromolecular chains and the constituent free volume will be very high. Hence, during the wet processing of nylon fibre, such as aqueous dyeing, molecules such as dyes, levelling agents, etc. are able to readily diffuse within the fibre, with the result that polyamide can be dyed using a variety of dyes, ranging from small M_r acid dyes through larger M_r direct and reactive dyes to very large M_r, planar, vat dyes without needing to promote the rate of dyeing via the use of elevated temperatures, carriers, etc.

In a related manner, nylon fibre has a marked proclivity to absorb vagrant dyes during domestic washing, which characteristically, results in permanent and unacceptable discolouration or '*greying*' of white garments and pastel shades. Indeed, nylon is the most susceptible of all textile fibres to re-deposition during repeated washing of all textile fibres, as exemplified by the data displayed in Tables 7–9 [5,57,58] which show the extent of staining of adjacent multifibre strip material that occurred as a result of the fastness testing of disperse (Table 7), acid (Table 8) and vat (Table 9) dyes which had been applied to different fibres; the propensity of the adjacent polyamide material to adsorb vagrant dye is evident. Although different types of dye vary in the extent to which they desorb during washing and redeposit on adjacent materials, such is the chemical and physical nature of polyamide that the fibre is substantive to virtually all dye types even under the alkaline conditions of domestic washing, which can range from pH 7.5 to 10.5 [59].

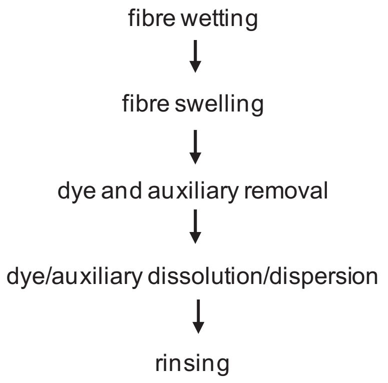


Fig. 19. Simplified wash-off mechanism.

Table 5
Moisture-related characteristics of fibres.

Fibre		Moisture regain/%		Volume swelling in water/%	T_g/°C	
		21 °C; 65% RH	100% RH		dry	wet
wool	hydrophilic	16–18 [32]	33.9 [33]	36, 37.41 [32]	–	–
rayon		12–14 [32]	32–48 [34]	45–82 [35]	–	–
silk		10 [32]	36.6 [36]	30.32 [32]	–	–
diacetate		6, 6.9 [32]	17 [34]	6–30 [35]	–	–
cotton		7–8 [32]	23 [37]	44–49 [35]	–	–
polyamide		4.1 [32]	8.7 [38]	8.1, 10 [32]	6,6:66^{a} 78^{b} [39] 6:80^{c} [40] 72^{d} [41]	−15^{a} −37^{b} [39] −6^{c} [40] −24^{d} [41]
triacetate	hydrophobic	4.5 [32]	12 [42]	very slight [35]	–	–
polyacrylonitrile		1.2 [32]	2.6 [43]	very slight [35]	92 [44]	72 [44]
polyester		0.4 [32]	0.6 [43]	~nil [35]	69 [45]	60 [45]
polypropylene		0.01 [35]	1.3 [43]	nil [35]	–	–

[a] Dynamic.
[b] Static.
[c] Dilatometry.
[d] DMA.

Since the use of polyamide in fibre form was unsuitable as it could not undergo an appropriate level of physical interaction with a dyed substrate, an alternative physical form was required. Nylon bead was selected on the basis that it is a reasonably low-cost, readily available, highly consistent substrate produced under precise conditions. Trials [51] quickly revealed that nylon bead provided an adequate surface area and, most importantly, enabled an appropriate level of physical interaction to be achieved between the dyed fibre and the beads using the different types of agitation that are typically encountered in existing textile processing machinery.

Thus, in essence, the novel bead wash-off process employed in this work essentially comprise two main components namely, the dyed material and the polyamide beads and relies upon the presence of a small amount of water that resides within the interstitial regions of both the dyed material and the absorbing nylon beads.

3.5. Results obtained using conventional wash-off

As mentioned, this part of the paper comprises an introduction to the wash-off process using polyamide beads, describing the theoretical and empirical considerations behind their selection and their ability to remove surplus dyes from various dye/fibre combinations. In the latter context, a total of seven dyes, representing five different dye types (Table 2) together with three different types of textile fibre (cotton, polyester and nylon) were chosen in an attempt to provide a representative selection of typical dyes and substrates. To determine the ability of the beads to remove surplus dye, the effects of three types of wash-off were assessed:

i water rinse → dry
 water rinse followed by drying;
ii conventional aftertreatment → water rinse → dry
 conventional aftertreatment (fixing agent, reduction clear, oxidation, syntan and reactive dye wash-off) followed by water rinse and drying;
iii bead wash-off → water rinse → dry
 bead wash-off followed by water rinse and drying.

3.5.1. *Water rinse → dry*

Table 10 shows the colorimetric data obtained for 2% omf dyeings obtained using C.I. Direct Blue 251 on cotton, C.I. Disperse Blue 73 on polyester, C.I. Sulphur Black 1 on cotton, C.I. Acid Blue 80 on nylon 6,6 as well as C.I. Reactive Blue 52 on cotton (see Figs. 5–9 for the respective application method used), each of which, had been rinsed in tap water at the end of dyeing and allowed to dry in the open air. The corresponding colour strength (fk values) of the dyeings are displayed in Fig. 20 from which it is apparent that the different types of dye displayed different colour strengths on the various substrates employed, which was not surprising and is attributable to differences between both the various dyes (e.g., relative tinctorial strength, extinction coefficient at λ_{max}, etc.) and fibres used (e.g., fibre fineness, fabric construction, fibre lustre, etc.).

3.5.2. *Conventional aftertreatment → water rinse → dry*

Dyeings which had been rinsed in tap water were subjected to the appropriate conventional aftertreatment shown in Figs. 11–15, namely, *fixing agent* (C.I. Direct Blue 251 on cotton), *reduction clear* (C.I. Disperse Blue 73 on polyester), *oxidation* (C.I. Sulphur Black 1 on cotton), *syntan* (C.I. Acid Blue 80 on nylon 6,6) and *wash-off* (C.I.

Table 6
Usage of major dye classes (adapted from [46]).

Fibre	Acid	Azoic	Basic	Direct	Disperse	Mordant	Reactive	Sulphur	Vat
cotton	−	+	−	+	−	−	+	+	+
viscose rayon	−	+	−	+	−	−	+	+	+
wool	+	−	−	−	−	+	+	−	−
diacetate	−	+	−	−	+	−	−	−	−
polyacrylonitrile	−	−	+	−	+^{a}	−	−	−	−
poly(lactic acid)	−	−	−	−	+	−	−	−	−
triacetate	−	+	−	−	+	−	−	−	−
polyester	−	+^{a}	−	−	+	−	−	−	+^{a}
polyamide	+	+^{a}	+^{b}	+^{a}	+	+	+	+	+^{a}

[a] Minor use.
[b] Cationic dyeable nylon.

Table 7
Staining of adjacent multifibre strip materials as a result of repeated washing (ISO CO6/C2) achieved for 2% omf disperse dyes on PLA fabric [56].

Dye	No. of washes	2° acetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Disperse Yellow 42	1	3/4	3/4	1/2	4/5	5	5
	3	5	5	4/5	5	5	5
	5	5	5	5	5	5	5
C.I. Disperse Red 60	1	2/3	5	1/2	4	5	4/5
	3	4/5	5	4/5	5	5	5
	5	5	5	5	5	5	5
Dianix Yellow Brown CC	1	2/3	5	3	4/5	5	4/5
	3	4/5	5	5	5	5	5
	5	4/5	5	5	5	5	5
C.I. Disperse Red 167:1	1	3	4/5	1/2	3	4/5	4/5
	3	5	5	5	5	5	5
	5	5	5	5	5	5	5
Dianix Crimson SF	1	5	5	4/5	5	5	5
	3	5	5	5	5	5	5
	5	5	5	5	5	5	5
C.I. Disperse Blue 56	1	2/3	4/5	1/2	3/4	5	4
	3	4/5	5	4	4/5	5	5
	5	5	5	4/5	5	5	5

Reactive Blue 52 on cotton). The colorimetric data obtained for the aftertreated dyeings which had been subsequently rinsed in tap water and allowed to dry in the open air are shown in Table 10; the corresponding fk values are shown in Fig. 20. Comparison of the colorimetric and colour strength data (Table 10 and Fig. 20) obtained for the dyeings which had received only a water rinse after dyeing with those which had been subjected to conventional aftertreatment reveals that aftertreatment removed surplus dye, as evidenced by the higher L^* value and lower colour strength of the aftertreated dyeings. The colorimetric data in Table 10 clearly show that aftertreatment imparted relatively small changes to both the chroma and hue of each of the five dye–fibre combinations used; the finding (Table 10) that the λ_{max} values of the various dyeings were unchanged as a result of aftertreatment provides further evidence that the changes in colour imparted by each of the five aftertreatments used, were small.

Table 9
Staining of adjacent multifibre strip materials as a result of repeated washing (ISO CO6/C2) achieved for 4% omf vat dyeings on supermicrofibre polyamide [5].

Dye	Dyeing method	No. of washes	Staining of adjacent					
			acetate	cotton	nylon	PET	acrylic	wool
C.I. Vat Violet 1	alkali leuco	1	5	5	4/5	5	5	5
		2	5	5	5	5	5	5
		3	5	5	5	5	5	5
		4	5	5	5	5	5	5
		5	5	5	5	5	5	5
	acid leuco	1	5	5	3/4	5	5	5
		2	5	5	4	5	5	5
		3	5	5	4/5	5	5	5
		4	5	5	4/5	5	5	5
		5	5	5	4/5	5	5	5
C.I. Vat Blue 18	alkali leuco	1	5	5	3	5	5	5
		2	5	5	4	5	5	5
		3	5	5	4	5	5	5
		4	5	5	4/5	5	5	5
		5	5	5	4/5	5	5	5
	acid leuco	1	5	5	4	5	5	5
		2	5	5	4/5	5	5	5
		3	5	5	4/5	5	5	5
		4	5	5	4/5	5	5	5
		5	5	5	5	5	5	5
C.I. Vat Green 3	alkali leuco	1	4	5	5	5	5	5
		2	4	5	5	5	5	5
		3	4	5	5	5	5	5
		4	4	5	5	5	5	5
		5	4	5	5	5	5	5
	acid leuco	1	4	4	4	5	5	5
		2	4/5	5	4/5	5	5	5
		3	4/5	5	4/5	5	5	5
		4	4/5	5	4/5	5	5	5
		5	5	5	5	5	5	5

3.5.3. *Bead wash-off → water rinse → dry*

Dyeings which had been obtained using the direct, disperse, reactive and sulphur dyes as well as C.I. Acid Blue 80 and which had been rinsed in water, were subjected to treatment with the nylon beads at 60 °C using a 5:1 bead: fabric ratio (Fig. 17); at the end of bead treatment, the samples were rinsed in tap water and allowed to dry in the open air. Comparison of the colorimetric and colour strength data (Table 10 and Fig. 20) obtained for dyeings which had been washed-off using the beads with those which had been rinsed in water shows that bead wash-off removed surplus dye, as indicated by the higher L^* values and lower fk values of the bead washed-off dyeings. It is also clear from Table 10 that bead wash-off caused very little change in the colour of each of the five, dye–fibre combinations used, this being reflected in the finding that bead wash-off did not affect the λ_{max} of the various dyeings. Furthermore, it is evident (Table 10) that the extent to which bead wash-off changed the hue and chroma of the dyeings was very similar to that observed for each of the conventional aftertreatments used; Fig. 20 also shows that the colour strength of the bead washed-off dyeings was very similar to that obtained for the conventionally aftertreated dyeings.

Hence, the results obtained demonstrate that wash-off using the polyamide beads at 60 °C removed surplus dye from each of the five different dye/fibre combinations employed and that both the extents of dye removal (as measured by L^* and fk values) and colour change imparted to the dyeings, were very similar to that achieved using the respective, conventional aftertreatment process.

Table 8
Staining of adjacent multifibre strip materials as a result of repeated washing (bold = 40 °C; * = 50 °C; () = 60 °C) achieved for 2% omf acid dyes on nylon 6,6 fabric [57].

dye	No. of washes	2° acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Neutrilan Red K-2G	1	**5** 5* (5)	**5** 5* (5)	**2/3** 1* (1)	**5** 5* (5)	**5** 5* (5)	**5** 5* (3)
	5	**5** 5* (5)	**5** 5* (5)	**3** 2* (1)	5 5* (5)	**5** 5* (5)	**5** 5* (4)
C.I. Acid Orange 67	1	**2/3** 1/2* (1)	**5** 4* (4)	**2/3** 1/2* (1)	**5** 4* (3)	**5** 4* (4)	**5** 2/3* (1/2)
	5	**3** 2/3* (2)	**5** 4/5* (4/5)	**3** 2/3* (2)	**5** 4/5* (4)	**5** 5* (5)	**5** 3/4* (2/3)
Nylanthrene Blue C-GLF	1	**2/3** 1/2* (1)	**3/4** 2/3* (2)	**1/2** 1* (1)	**4/5** 4/5* (3)	**5** 5* (5)	**4** 1/2* (1)
	5	**3** 2/3* (2)	**4** 3* (2/3)	**2** 1/2* (1)	**4/5** 5* (3/4)	**5** 5* (5)	**4/5** 2/3* (1/2)
Nylanthrene Black C-DPL	1	**5** 5* (5)	**5** 5* (4/5)	**1/2** 1/2* (1)	**5** 4/5* (4/5)	**5** 3* (2/3)	**4/5** 3/4* (3)
	5	**5** 5* (5)	**5** 5* (5)	**2** 2/3* (2)	**5** 5* (5)	**5** 4/5* (4)	**5** 4* (4)
Neutrilan Blue S-BGR	1	**5** 5* (5)	**5** 5* (4/5)	**1/2** 1* (1)	**5** 5* (4/5)	**5** 4/5* (4)	**5** 3* (2)
	5	**5** 5* (5)	**5** 5* (5)	**2/3** 2* (1/2)	**5** 5* (5)	**5** 5* (5)	**5** 4* (3)

Table 10
Colorimetric parameters for dyeings.

Treatment	Dye	L^*	a^*	b^*	C^*	h°	λ_{max}
water rinse → dry	C.I. Direct Blue 251	23.5	3.1	−23.1	23.3	278.0	600
	C.I. Disperse Blue 73	14.4	7.5	−28.0	29.0	285.0	640
	C.I. Sulphur Black 1	20.2	−1.6	−0.8	1.8	207.0	620
	C.I. Acid Blue 80	38.2	0.9	−43.7	43.7	271.0	640
	C.I. Reactive Blue 52	47.2	−2.6	−26.5	26.7	264.0	620
conventional → water rinse → dry	C.I. Direct Blue 251	25.3	0.5	−24.4	24.4	271.0	600
	C.I. Disperse Blue 73	15.0	6.2	−27.0	27.7	283.0	640
	C.I. Sulphur Black 1	21.4	−1.1	−0.4	1.2	203.0	620
	C.I. Acid Blue 80	38.2	0.6	−44.0	44.0	271.0	640
	C.I. Reactive Blue 52	49.8	−3.4	−26.3	26.5	262.0	620
polyamide bead → water rinse → dry	C.I. Direct Blue 251	23.9	2.8	−24.2	24.4	277.0	600
	C.I. Disperse Blue 73	14.5	7.4	−27.2	28.2	285.0	640
	C.I. Sulphur Black 1	20.7	−0.9	−0.6	1.1	215.0	620
	C.I. Acid Blue 80	38.3	0.6	−43.9	43.9	271.0	640
	C.I. Reactive Blue 52	48.3	−3.3	−25.9	26.1	263.0	620

As mentioned, the novel wash-off process described in this work comprises two main components, the dyed material and nylon beads and relies upon the presence of a small amount of interstitial liquid within the dyed material. The beads remove surplus dye from the surface of the dyeing as a result of physical contact with the wetted-out material. This is illustrated by the photographs in Fig. 21 of beads both before and after wash-off from which it is apparent that vagrant dye was adsorbed onto the nylon beads. The extent of coloration of the beads varied for the different dyes used which, as discussed in detail in subsequent parts of this paper, is attributable to differences in the amount of residual dye removed during wash-off, the nature of dye–bead interaction, extinction coefficient of the dyes, etc. Studies which will be reported in subsequent parts of the paper, revealed that dye which has been adsorbed onto the surface of the beads diffuses into the interior of the bead and, as a result, the dye is not redeposited on other areas of the dyeing.

The interstitial liquid is vital to the bead wash-off process as it swells both the dyed fibre and the polyamide beads, effects the solubilisation and diffusion of dye within the dyeing, enables the transfer of dye to the bead and facilitates the diffusion of the dye within the bead. Indeed, results [51] suggest that, mechanistically, the novel wash-off process using polyamide beads closely resembles that of a conventional aqueous, wash-off process except that the polyamide beads, rather than water, act as the medium that removes surplus dye from the dyeing and restrains this dye from re-deposition.

3.6. Wash fastness

To determine the effect of the bead wash-off on the wash fastness of dyeings, it was decided to use 2% omf dyeings of two, non-metallised acid *Nylanthrene* dyes on nylon 6,6, as the wash fastness of members of this dye type characteristically leaves much to be desired [60–62] and recourse to an aftertreatment with a syntan is routinely undertaken in order to secure an adequate level of wash fastness. Accordingly, dyeings produced using the method shown in Fig. 10 were subjected to three wash-off treatments:

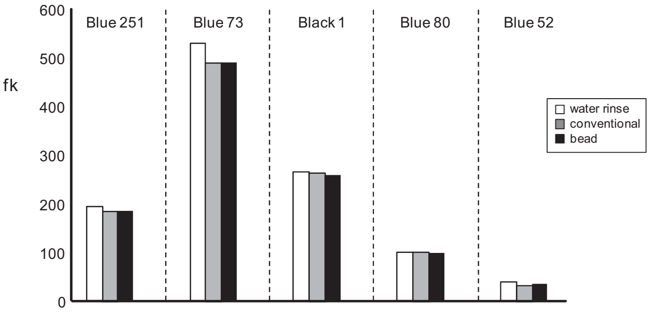


Fig. 20. Colour strength of 2% omf dyeings.

i. water rinse → dry;
ii. conventional aftertreatment (using a syntan at 70 °C; Fig. 16) → water rinse → dry;
iii. bead wash-off at 70 °C (Fig. 17) → water rinse → dry.

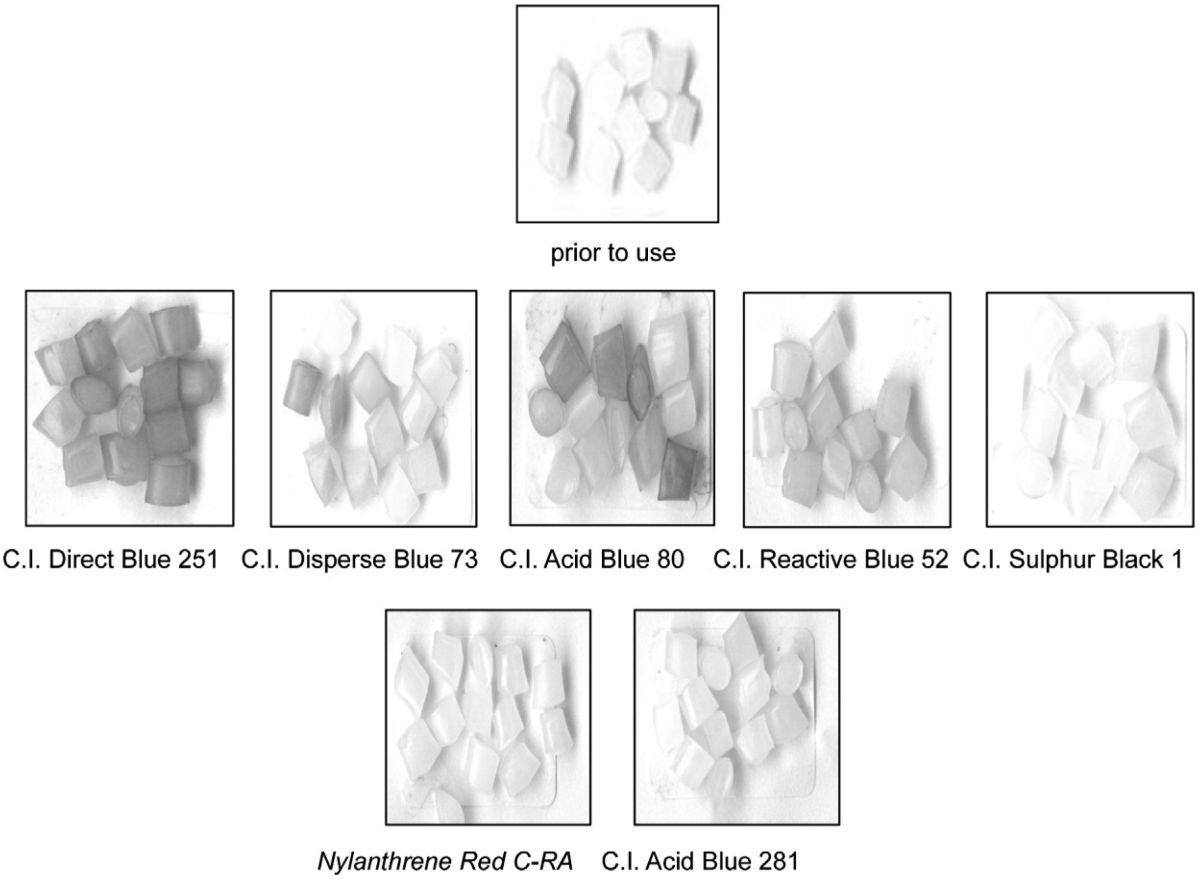
The colorimetric data (Table 11), colour strength (Fig. 22) and change in shade as well as colour difference (Δ*E*) obtained as a result of washing at 60 °C (Table 11) were recorded.

Table 11 shows the colorimetric data obtained for 2% omf dyeings of C.I. Acid Blue 281 and *Nylanthrene Red C-RA*, each of which, had been rinsed in tap water at the end of dyeing and allowed to dry in the open air; the corresponding colour strength (fk values) of the dyeings are displayed in Fig. 22. This data was recorded (and is displayed in Table 11 and Fig. 22) so as to provide a reference against which the effects of both syntan aftertreatment and bead wash-off on colour and depth of shade could be determined.

Table 11 and Fig. 22 also show that prior to wash testing, both conventional aftertreatment with the syntan and wash-off using the beads had very similar effects on the colour and colour strength of the two dyes used. A measure of the extents to which bead wash-off and syntan aftertreatment not only removed surplus dye but also changed the colour of the dyeings is given by the CIEL*a*b* Δ*E* values obtained between the dyeings before and after bead wash-off/syntan aftertreatment (Table 11). The Δ*E* values obtained prior to wash fastness testing were very similar for the two, respective wash-off treatments employed, namely, 0.9 and 0.6 for syntan aftertreatment compared to 0.8 and 1.0 in the case of bead wash-off. Hence, in terms of both surplus dye removal and change in shade, the bead wash-off was very similar to the conventional syntan aftertreatment prior to wash testing. In addition, as each of these particular colour difference values were ≤1.0 Δ*E* units, they can be considered as being not perceivable by the human eye.

The colorimetric data obtained for the dyeings after wash testing (Table 11) reveal that, as expected, the two dyes displayed moderate/poor fastness to washing at 60 °C, this being especially so in the case of C.I. Acid Blue 281. From Table 11 it is evident once again, that the Δ*E* values secured for the dyeings which had been aftertreated with the syntan and also washed-off using the beads were similar in magnitude (i.e., 11.2 and 1.9 for the conventional syntan aftertreatment compared to 11.1 and 2.5 for the bead washed-off dyeings) and identical shade changes were also recorded for the two dyeings (Table 11); Fig. 21 reveals that very similar colour strengths were obtained for both dyeings after washing.

These findings show that the two wash-off processes, namely conventional aftertreatment with syntan and bead wash-off, imparted very similar changes to both the colour and colour strength of the two *Nylanthrene* dyeings. Interestingly, the fastness to washing at 60 °C secured using a wash-off with beads at 70 °C was similar to that achieved using an aftertreatment with syntan at 70 °C. This latter finding was somewhat surprising, bearing in mind that syntan aftertreatment is considered to result in the deposition of a peripheral 'layer' of syntan molecules at the surface of the dyed material that reduces the diffusion of dye out of the dyed, treated fibre during washing [7,63] whereas the bead wash-off simply comprised treatment of the wet dyeing with nylon beads. Of course, these findings relate only to the two non-metallised acid dyes used herein and the results obtained using a larger number of dyes are


prior to use

C.I. Direct Blue 251 C.I. Disperse Blue 73 C.I. Acid Blue 80 C.I. Reactive Blue 52 C.I. Sulphur Black 1

Nylanthrene Red C-RA C.I. Acid Blue 281

Fig. 21. Vagrant dye adsorption onto nylon beads.

required before any meaningful interpretation of the findings can be considered. Nevertheless, the results presented clearly show that bead wash-off did not negatively affect the wash fastness of the two dyes.

3.7. Cost/environmental aspects of bead wash-off

In this work, two temperatures (60 °C and 70 °C) were employed for the bead wash-off process as they were the two most common temperatures employed in the six conventional aftertreatment processes studied (Figs. 11–16). The results obtained indicate that bead wash-off was successful, in terms of the removal of surplus dye from the various dyeings, at each of the two temperatures.

As mentioned, conventional wash-off processes typically consume large amounts of water, as illustrated by the fact that in this work, a 10:1 ratio was employed in the case of the aftertreatment stage for the sulphur dye whereas a 20:1 liquor ratio was used in the cases of the direct, disperse, reactive and acid dyes under consideration. This contrasted markedly to the bead wash-off, for which wetted-out fibre and a 5:1 bead:fabric ratio were employed, resulting in a liquor ratio (ie water:fibre ratio) of $\leq$1:1. Accordingly, the amount of water consumed in the aftertreatment stage of 1 tonne of fibre dyed would, in the cases of the direct, disperse, reactive and acid dyes, be 10 tonnes and, for the sulphur dye, 20 tonnes, respectively compared to $\leq$1 tonne in the case of the bead wash-off. As also discussed, the large amounts of water consumed in conventional wash-off generates large volumes of wastewater that typically contains residual dyes, surfactants, electrolytes, etc. which presents both environmental and economic challenges. Clearly, the much lower volume of water consumed in

Table 11
Colorimetric parameters for *Nylanthrene* dyeings.

Treatment		Dye	Shade change	L^*	a^*	b^*	C^*	h°	λ_{max}	ΔE
water rinse → dry	–	C.I. Acid Blue 281	–	33.1	1.3	−39.4	39.5	271.2	600	–
	–	*Nylanthrene Red C-RA*	–	46.0	57.6	26.8	63.5	24.9	520	–
conventional → water rinse → dry	before washing	C.I. Acid Blue 281	–	32.8	0.8	−38.7	38.7	271.3	600	0.9
		Nylanthrene Red C-RA	–	46.3	57.7	26.3	63.4	24.5	520	0.6
	after washing	C.I. Acid Blue 281	4	43.1	−4.0	−34.9	53.2	263.4	600	11.2
		Nylanthrene Red C-RA	4/5	47.0	56.3	26.2	62.2	24.4	520	1.9
bead → water rinse → dry	before washing	C.I. Acid Blue 281	–	32.8	1.7	−40.0	40.0	272.4	600	0.8
		Nylanthrene Red C-RA	–	45.6	56.6	26.4	62.5	25.0	520	1.0
	after washing	C.I. Acid Blue 281	4	43.7	−3.3	−36.5	36.7	264.7	600	11.1
		Nylanthrene Red C-RA	4/5	47.6	55.5	26.0	60.4	25.5	520	2.5

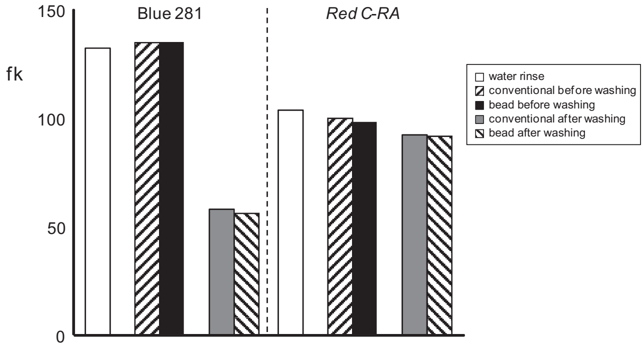


Fig. 22. Colour strength of 2% omf *Nylanthrene* dyeings.

bead wash-off will result in concomitantly lower amounts of wastewater, thereby offering reduced environmental and cost benefits.

In the context of the vagrant dye that is removed from dyeings during conventional wash-off processes and which constitutes coloured effluent, as Fig. 21 shows that during bead wash-off, vagrant dye was adsorbed onto the nylon beads, bead wash-off not only reduced the amount of wastewater generated when compared to the conventional wash-off processes used, but also the smaller amount of wastewater contained less dye, thereby constituting a lower effluent load which offers the potential of reduced environmental and cost benefits. The ability of the beads to adsorb vagrant dye during bead wash-off is discussed in the second part of this paper.

4. Conclusions

Wash-off using polyamide beads removed surplus dye from dyeings obtained using each of the five different types of dye from the three different types of fibre employed. It is apparent that the extents of both dye removal, as evidenced by increased L^* and reduced fk values and colour change imparted by the bead wash-off process were very similar to those achieved using the respective, conventional aftertreatment process, for each of the dye–fibre combinations employed. As such, the bead wash-off method offers potential as a 'universal' wash-off method for different dye–fibre combinations. Bead wash-off also did not impair the fastness of the two non-metallised acid dyes to washing at 60 °C.

Whilst there was little difference between the bead wash-off and the conventional aftertreatments in terms of temperature (60–70 °C) and duration (20 min bead wash-off cf 20–30 min for conventional aftertreatment), there was a significant difference in the amount of water that was used in bead wash-off compared to that consumed in the six conventional aftertreatment methods. Whereas the conventional aftertreatments employed either a 10:1 or 20:1 liquor ratio, bead wash-off used only sufficient water to wet-out the dyeing (<<1:1 liquor ratio), thereby consuming far less water.

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