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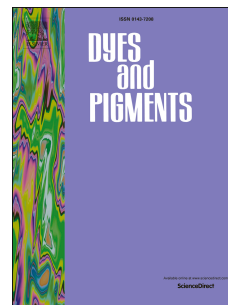
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# Accepted Manuscript

The role of auxiliaries in the immersion dyeing of textile fibres: Part 1 an overview

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# 1 **The role of auxiliaries in the immersion dyeing of textile fibres: Part 1 An** 2 **overview**

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7

## 8 **Abstract**

9 Although auxiliaries have been a key component of immersion dyeing processes for many years the  
10 precise mode of action of many auxiliaries has not been fully resolved. This part of the paper  
11 discusses the various types of auxiliary available and the nature of the assistance they provide in  
12 immersion dyeing processes, together with both environmental and financial aspects associated  
13 with their use, as well as a discussion of the relationship between liquor ratio and the use of  
14 auxiliaries in immersion dyeing.

15

## 16 **Highlights**

- 17 • there are many different types of dyeing auxiliary
- 18 • they are chemically diverse and perform many essential operations
- 19 • the precise mode of action of many auxiliaries is unclear

20

## 21 **keywords**

22 fibres; auxiliaries; dyeing; finishing

23

## 24 **abbreviations**

25 PA: polyamide; PES: poly(ethylene) terephthalate; COD: Chemical Oxygen Demand; BOD<sub>5</sub>

26 Biological Oxygen Demand; TDS: Total Dissolved Solids

## 27 **1 Introduction**

28 By some margin, water is the most commonly used medium for the dyeing of textile materials, with  
29 *air* being employed in the *vapour-phase dyeing* of hydrophobic fibres and both non-aqueous *liquid*  
30 *solvents* and non-aqueous *supercritical fluids* having attracted only small-scale, mostly niche  
31 interest (1). This paper concerns the application of dyes to textile fibres from *aqueous dyebaths*  
32 using *immersion* processes (aka *batchwise* -, *exhaust* -, *long liquor*- processes) and the role of the  
33 many and varied *auxiliaries* which are used in such dyeing processes.

34

35 In this context, an auxiliary can be defined as *a chemical or formulated chemical product which*  
36 *enables a processing operation in preparation, dyeing, printing or finishing to be carried out more*  
37 *effectively or which is essential if a given effect is to be obtained* (2). Such *auxiliaries*, which often  
38 are referred to as *dyeing auxiliaries*, are extensively utilised in immersion dyeing for all dye-fibre  
39 systems (eg disperse dyes/polyester, reactive dyes/cotton, acid dyes/wool, etc.); indeed, auxiliaries  
40 are commonly viewed as essential components of such dyeing process. Auxiliaries are also widely  
41 used in *continuous dyeing* (aka *padding processes*) and, whilst some auxiliaries are specifically  
42 intended for use in either batchwise or continuous dyeing, many auxiliaries can be used in both  
43 types of process.

44

## 45 **2 auxiliaries used in dyeing**

46 Accounts of auxiliaries that are used in dyeing, as well as in other aspects of textile wet processing,  
47 are available [eg (3-14)]. By way of brief introduction, auxiliaries assist the dyeing process, but  
48 usually in a very particular way, insofar as the assistance furnished by a given auxiliary will typically  
49 address a specific aspect of dyeing, such as fibre wetting, dye-fibre substantivity, dye levelling, fibre  
50 protection, etc. As such, a wide variety of different types of dyeing auxiliary is available (eg  
51 dispersants, sequesterants, lubricants, etc.); furthermore, owing to the diverse, and often quite  
52 specialised, nature of the assistance they exert, auxiliaries comprise a heterogeneous group of  
53 chemicals (eg acids, surfactants, reductants, etc.), as illustrated by the data presented in Table 1.  
54 Although many dyeing auxiliaries may have one primary function and comprise an individual

55 compound, others may fulfil more than one role, and many commercial auxiliary products often are  
 56 proprietary mixtures that contain several components. Auxiliaries therefore include simple chemicals  
 57 such as inorganic salts (eg NaCl, etc.), lye (eg NaOH), acids (both organic such as CH<sub>3</sub>COOH and  
 58 inorganic such as HCl, etc.), reducing and oxidising agents (eg Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, etc.), as well as  
 59 oligomers, polymers and a wide variety of surfactants.

60

61 Table 1 overview of auxiliaries employed in dyeing, their effects and chemical composition (15)

62

process	auxiliary	effect	chemical type
dissolving dyes	dye solubilising agents;	promote dissolution of dyes in	alcohols; polyols; fatty alcohol ethoxylates;
	hydrotopes	water	esters naphthalene sulfonic acid formaldehyde
dissolving dyes	dispersing agents;	promote formation and stability	condensates; naphthalene sulfonates;
	protective colloids	of dye dispersions	lignosulfonates; fatty alcohol ethoxylates; alkylsulfonates; alkylaryl sulfonates; polyacrylates
exhaust dyeing	wetting agents;	increase wetting capacity of	alkylsulfates; alkanesulfonates;
	deaeration agents	the dye liquors; increase dye adsorption	alkylarylsulfonates; salts of sulfosuccinic acid; esters; fatty alcohol ethoxylates; alcohols; phosphoric acid esters; hydrocarbons
exhaust dyeing	dye protecting agents;	protect dyes during application	buffers and/or oxidants (nitrobenzene
	boil-down protecting agents		sulfonate); urea; alkylarylsulfonates
exhaust dyeing	oxidising agents	oxidise reduced forms of vat and sulphur dyes; strip dyes and auxiliaries from the fibre	peroxo compounds; sodium perborate; sodium persulfate; sodium chromate; salts of <i>m</i> - nitrobenzene sulfonic acid; bromite; sodium chlorite

		sodium dithionite; sulfonic acid
reducing agents	reduce vat and sulphur dyes; reduction clearing; dye stripping	derivatives; sodium sulphide; glucose and mixtures thereof; thiourea dioxide; sodium or zinc formaldehyde sulfonic acids
brightening agents	partial removal of adsorbed dye	polyvinylpyrrolidone; polyglycol ether; cellulases; alkyl aryl sulfonates; alkyl amine ethoxylates; reducing agents and oxidising agents
fibre-protective agents	prevent or reduce fibre damage during dyeing	protein hydrolysates; polyglycol ether; protein fatty acid condensates; lignosulfonates; formaldehyde eliminating products (urea derivatives); guanidine derivatives; benzophenones; benzotriazoles
mordants	improve dye fastness	Al, Cr, Fe salts
pH-regulators; acids and alkali dispensers	pH adjustment/control	organic acids; esters; buffers
acids and alkalis	pH adjustment	organic acids (mainly acetic acid, formic acid, oxalic acid), inorganic acids (sulfuric acid, hydrochloric acid); sodium hydroxide; ammonium hydroxide; sodium carbonate
salts	increase dye substantivity	sodium chloride; sodium sulfate
complexing agents	complexation of heavy metals	polyphosphates; phosphonates; polycarboxylates, (polyacrylates, polyacrylate- maleinic acid copolymers); sugar copolymers; hydroxycarboxylic acids; amino carboxylic acids

exhaust dyeing: PES; PES/WO	carriers	accelerate dye adsorption, dye diffusion	aromatic hydrocarbons; chlorinated aromatic compounds; benzoic acid esters; phthalic acid esters; alkyl phthalimides; alkylphenoethoxylates
levelling	retarding agents; migration agents; penetrating agents	promote even distribution of dye	alkyl -; alkyl aryl -; alkyl amine -; and alkyl aryl amine ethoxylates; fatty acid esters and amides; fatty acid condensates; polyvinyl pyrrolidone; quaternary ammonium compounds; alkyl sulfates; alkyl aryl sulfonates
aftertreatment	fastness improvement agents	improve rubbing, wet and light fastness	aftertreatment with detergents or polymers; cationic fixing agents; polysulfonates for PA dyed with anionic dyes; organic copper compounds for PA and PES fibres

63

64 A large number of commercial auxiliary products are available, as exemplified by a 2008 publication  
65 (16) that lists >6500 commercial products derived from 400-600 active compounds. Consumption of  
66 dyeing auxiliaries is estimated to be 60-70% of that of dyes (12), which, in 2012, would have  
67 corresponded to  $0.96-1.2 \times 10^6$  T of auxiliary consumed in textile dyeing, according to an estimated  
68 global dye consumption of  $1.6 \times 10^6$  T (1). However, auxiliary usage varies according to several  
69 factors, such as the particular dye-fibre system employed, depth of shade of the dyeing, machine  
70 type, liquor ratio employed (a detailed account of liquor ratio is presented in section 5), etc., as  
71 illustrated by Table 2, which shows some of the types of auxiliary that can be employed in the  
72 immersion dyeing of different types of fibre and, also, by the data displayed in Table 3, which  
73 presents typical types and amounts of auxiliary utilised in the dyeing of knitted cotton fabric with  
74 reactive dyes.

75

76 Table 2 auxiliaries that can be used in the immersion dyeing of different types of fibre

process	auxiliary	effect	chemical type
---------	-----------	--------	---------------

dissolving dyes	dye solubilising agents;	promote dissolution of dyes in	alcohols; polyols; fatty alcohol ethoxylates;
	hydrotopes	water	esters
dissolving dyes	dispersing agents;	promote formation and stability	naphthalene sulfonic acid formaldehyde
	protective colloids	of dye dispersions	condensates; naphthalene sulfonates; lignosulfonates; fatty alcohol ethoxylates; alkylsulfonates; alkylaryl sulfonates; polyacrylates
wetting agents; deaeration agents		increase wetting capacity of the dye liquors; increase dye adsorption	alkylsulfates; alkanesulfonates; alkylarylsulfonates; salts of sulfosuccinic acid; esters; fatty alcohol ethoxylates; alcohols; phosphoric acid esters; hydrocarbons
	dye protecting agents; boil-down protecting agents	protect dyes during application	buffers and/or oxidants (nitrobenzene sulfonate); urea; alkylarylsulfonates
oxidising agents		oxidise reduced forms of vat and sulphur dyes; strip dyes and auxiliaries from the fibre	peroxo compounds; sodium perborate; sodium persulfate; sodium chromate; salts of <i>m</i> - nitrobenzene sulfonic acid; bromite; sodium chlorite
	exhaust dyeing	reduce vat and sulphur dyes;	sodium dithionite; sulfonic acid
reducing agents	reduction clearing; dye stripping		derivatives; sodium sulphide; glucose and mixtures thereof; thiourea dioxide; sodium or zinc formaldehyde sulfonic acids
brightening agents	partial removal of adsorbed dye		polyvinylpyrrolidone; polyglycol ether; cellulases; alkyl aryl sulfonates; alkyl amine ethoxylates; reducing agents and oxidising agents
fibre-protective agents	prevent or reduce fibre damage during dyeing		protein hydrolysates; polyglycol ether; protein fatty acid condensates; lignosulfonates; formaldehyde eliminating products (urea derivatives); guanidine derivatives; benzophenones; benzotriazoles

mordants	improve dye fastness	Al, Cr, Fe salts
pH-regulators; acids and alkali dispensers	pH adjustment/control	organic acids; esters; buffers
acids and alkalis	pH adjustment	organic acids (mainly acetic acid, formic acid, oxalic acid), inorganic acids (sulfuric acid, hydrochloric acid); sodium hydroxide; ammonium hydroxide; sodium carbonate
salts	increase dye substantivity	sodium chloride; sodium sulfate polyphosphates; phosphonates; polycarboxylates, (polyacrylates, polyacrylate-
complexing agents	complexation of heavy metals	maleinic acid copolymers); sugar copolymers; hydroxycarboxylic acids; amino carboxylic acids
exhaust dyeing: PES; PES/Wool	carriers accelerate dye adsorption, dye diffusion	aromatic hydrocarbons; chlorinated aromatic compounds; benzoic acid esters; phthalic acid esters; alkyl phthalimides; alkylphenoethoxylates
levelling	retarding agents; migration agents; penetrating agents promote even distribution of dye	alkyl -; alkyl aryl -; alkyl amine -; and alkyl aryl amine ethoxylates; fatty acid esters and amides; fatty acid condensates; polyvinyl pyrrolidone; quaternary ammonium compounds; alkyl sulfates; alkyl aryl sulfonates
aftertreatment	fastness improvement agents improve rubbing, wet and light fastness	aftertreatment with detergents or polymers; cationic fixing agents; polysulfonates for PA dyed with anionic dyes; organic copper compounds for PA and PES fibres

78

79

80 Table 3 Typical requirements for immersion dyeing of knitted cotton fabric with reactive dyes (15)

81

component /g kg <sup>-1</sup> textile	light shade	medium shade	dark shade
dye	0.5-4	5-30	30-80
organic auxiliary	0-30	0-30	0-35
inorganic auxiliary	50-250	30-150	30-150
salt	90-400	600-700	800-2000

82

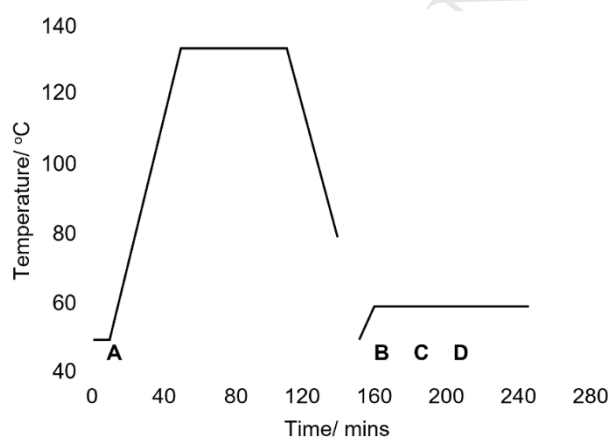
83 *2.1 the nature of the assistance afforded by auxiliaries*

84 The principal aims of all immersion dyeing processes are to produce uniform dyeings of the desired  
85 colour and depth of shade that display the required level of fastness to specified agencies (eg  
86 washing, light, etc.). Of these (and other) characteristics sought in a dyed material, uniformity is  
87 perhaps of greatest importance, because, if a dyeing is unlevel, then regardless of its colour, depth  
88 of shade or fastness properties, it is most likely unsaleable. In this context, dyes vary, considerably,  
89 in their ability to migrate during dyeing and thereby, to furnish level dyeings. Although such  
90 migration ability is an inherent characteristic of a given dye and, often, a particular dye-fibre system,  
91 dye migration during immersion dyeing can be conveniently manipulated by controlling the level of  
92 dye-fibre substantivity within the dyeing process. As dye-fibre substantivity comprises both  
93 mechanical and physico-chemical elements, the level of dye-fibre substantivity within exhaust  
94 dyeing procedures can be adjusted by controlling machine-dependent factors (eg rate and extent of  
95 dye-substrate interchange, heating rate, etc.) and by manipulating both the nature and extent of  
96 dye-dye and dye-substrate interactions within the dyebath via, for example, pH adjustment,  
97 temperature control, selection of liquor ratio, and, of relevance to this paper, the use of auxiliaries.

98

99 In virtually all immersion dyeing processes, a 'base' level of dye-fibre substantivity control is  
100 commonly employed using simple chemicals, such as inorganic acids or buffer systems (eg

101  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  in the case of acid dyes/PA fibres) or inorganic electrolytes in the dyeing of  
 102 cotton using direct dyes. Usually, commercial auxiliary products are additionally employed to  
 103 promote dyebath stability, maintain pH, enhance levelling, etc. Customarily, the use of proprietary  
 104 auxiliaries in immersion dyeing is highly recommended by dye makers, as exemplified by the  
 105 different types of commercial auxiliary product advocated for use in the immersion application of  
 106 *Novacron LS* (Huntsman) reactive dyes to cellulosic fibres, which are intended, for example, to  
 107 improve levelness and appearance (penetrating/de-aerating/defoaming products), to avoid problems  
 108 that arise from impurities in the dyebath (reduction penetrant, dispersing agent, Ca inactivation,  
 109 protective colloid and lubricant) and also to ensure that fastness is optimised (wash-off agents and  
 110 cationic fixing agents) (17). Routinely, commercial dyeing recipes include the use of several  
 111 auxiliary products, as exemplified by the procedures displayed in Figures 1 and 2.



- 119
- 120 **A** *Terasil WWW-EL* dyes    **B** *Novacron FN* dyes    **C** NaCl    **D**  $\text{NaHCO}_3$   
 NaOH  
 121 3-4  $\text{gl}^{-1}$  *Albatex AB-45* or  
 2  $\text{gl}^{-1}$   $(\text{NH}_4)_2\text{SO}_4 + \text{HCOOH}$   
 122 0.5  $\text{gl}^{-1}$  *Albaflow JET*  
 1-2  $\text{gl}^{-1}$  *Albatex AR* (if necessary)  
 123 1  $\text{gl}^{-1}$  *Univadene DPL*

124 Figure 1 dyeing method for PES-cellulose blends (18)

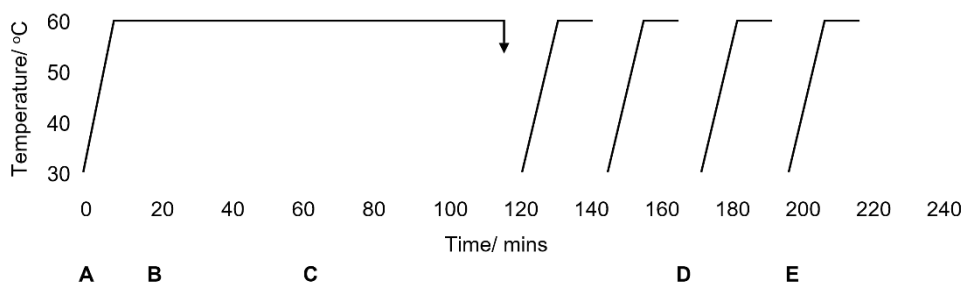
125

126 Auxiliaries differ in terms of their role in the dyeing process and the permanence of the effect sought  
 127 from their deployment. For example, in the application of direct dyes and reactive dyes to cellulosic

128 fibres, inorganic electrolytes such as NaCl or Na<sub>2</sub>SO<sub>4</sub> are used to promote dye exhaustion and, in  
 129 the case of reactive dyes, to promote dye fixation.

130

- 131 A x gl<sup>-1</sup> NaCl or Na<sub>2</sub>SO<sub>4</sub>  
 2 gl<sup>-1</sup> *Ladiquest 1097 liq*  
 132 1 gl<sup>-1</sup> *Imacol C3G liq*  
 1 gl<sup>-1</sup> *Humectol C liq hc*  
 133 B *Drimaren HF dye*  
 C NaHCO<sub>3</sub>  
 134 D 1 gl<sup>-1</sup> *Ladiquest 1097 liq*  
 1 gl<sup>-1</sup> *Ladipur RSK liq*  
 135 E neutralisation (pH 6-7)



136 Figure 2 dyeing and wash-off process for *Drimaren HF* reactive dyes (17)

137

138 In each of these dye-fibre systems, the promotional effects imparted by the added inorganic  
 139 electrolyte during dyeing are non-permanent insofar as, at the end of dyeing, the electrolyte is  
 140 removed, which is of especial importance in the case of the wash-off stages that are employed in  
 141 the immersion dyeing of cellulosic fibres with reactive dyes. In a similar manner, carriers are  
 142 sometimes used to promote the sorption and levelling of disperse dyes on PES fibres but the  
 143 specific promotional effect imparted by the carrier is non-permanent and their complete removal  
 144 from the dyed substrate at the end of dyeing is essential in order for the dyed samples to display  
 145 optimum fastness to various agencies. In contrast, auxiliaries that are specifically employed to  
 146 improve the fastness properties of dyeings, such as fixing agents (aka cationic fixing agents) which  
 147 impart improved wet fastness to direct dyes on cellulosic fibres, or UV absorbers which provide  
 148 improved protection towards fading by light, must remain within the dyed substrate in order for their  
 149 impact to be achieved. In some cases, as exemplified by the use of reducing agents in the  
 150 application of sulphur dyes to cellulosic fibres, the auxiliary is an indispensable, essential  
 151 component of the dyeing process; in this particular case, the reducing agent converts the water-  
 152 insoluble colorant into the fibre-substantive, water-soluble, thiol derivative that is adsorbed by the  
 153 fibre.

154

**155 3 environmental aspects associated with the use of dyeing auxiliaries**

156 Although water is often considered as a renewable resource owing to its replenishment by rainfall,  
157 the total volume of water on earth is, of course, constant and, therefore, its availability for industrial,  
158 agricultural and urban usage, is finite. Furthermore, as both the freshwater resources available  
159 globally and the world's population are distributed unevenly, water shortages exist in many regions.  
160 Such a situation can be expected to only worsen, as an expanding global population, continued  
161 urban growth, rising industrialisation and increased food production place demands on the finite  
162 global supply of water.

163

164 Although water is of fundamental importance in immersion dyeing, the amount of water employed  
165 varies, according to, for example, the type of machine used, the type of fibre used, the physical form  
166 of the fibre, type of dye, etc. Whilst precise figures are not available for global water usage in  
167 dyeing, an indicative estimate has been proposed (1) based on global textile fibre consumption and  
168 assuming an average liquor ratio of 1:8 for dyeing and a cumulative average 1:10 liquor ratio for wet  
169 processes associated with dyeing (eg wetting, rinsing, wash-off, etc.). Using this approach, in 2015,  
170 as world textile fibre production totalled  $90.64 \times 10^6$  T (19), of which PES fibres accounted for ~59%  
171 ( $53.1 \times 10^6$  T) and cotton & man-made cellulosic fibres ~31% ( $28.1 \times 10^6$  T), the amount of water  
172 used in dyeing (assuming that all fibre production was dyed) would have been of the order of  $16.3 \times$   
173  $10^{11}$  l, of which  $9.6 \times 10^{11}$  l can be ascribed to that of PES dyeing and  $5.1 \times 10^{11}$  l to the dyeing of  
174 cotton and other cellulosic fibres. However, as pointed out (1) such an estimated level of water  
175 consumption, which corresponds to 18 l per kg of fibre, may be somewhat modest, when compared  
176 to reported water usage in commercial dyeing processes, such as the 72-96 l kg<sup>-1</sup> of water  
177 consumed in typical batchwise jet dyeing processes (20) or that used in the batchwise, immersion  
178 dyeing of cotton with reactive dyes (Table 4 and Table 5) (21).

179

180 Table 4 Water, chemicals and energy consumed in jet dyeing of cotton using reactive dyes (21)

181

process	dye		
	<i>Novocron FN</i>	<i>Remazol RGB</i>	
preparation	scour/bleach: 98°C	scour/bleach: 98°C	
	rinse: 80°C	rinse: 80°C	
	rinse: 60°C	rinse: 60°C	
	migration		
dyeing	dyeing: 80/60°C	isothermal dyeing: 60°C	
wash-off	rinse: 50°C	rinse: 50°C	
	rinse: 70°C	rinse: 50°C	
	boil off	rinse: 80°C	
	rinse: 80°C	boil off	
	rinse: 60°C	rinse: 80°C	
	rinse: 50°C	rinse: 25°C	
process time/ mins	691	649	
water consumption/ l	dyebath water	16400	16400
	cooling water	16380	21060
	total	32000	37460
	per kg of fibre	160	187.3
energy consumption/ MJ	total	3974	3639
	per kg of fibre	19.87	18.12
chemicals consumed/ kg	total	253	260
	per kg of fibre	1.27	1.3
dyes consumed/ kg	total	5.55	7.35
	per kg of fibre	0.028	0.036

182

183 *assumptions made in Table 4:*184 *200 kg fibre; 10:1 liquor ratio; cold water at 20°C; no hot fill (all heating done in machine); liquor retention: 2x mass of fibre*185 *on draining; standard fill / drain; no parallel rinsing/draining; 100% right first time (no additions); all hot baths cooled to*

186 60°C before draining; 50% efficiency of heating (steam energy transfer); 50% efficiency of cooling (heat transfer to cold  
 187 water); no water recycling; no use of renewable energy

188

189 Table 5 jet dyeing machine: steam and water consumption; reactive dyes; 100% cotton (22)

process	steam used/ kg kg <sup>-1</sup> fibre	water used/ l kg <sup>-1</sup> fibre
bleach, light biowash without enzyme stop, extra dark shade with HT drain	2.93	36.17
bleach, <i>Remazol Ultra RGB</i> , dark red	2.8	48.13
bleach, <i>Drimaren CL</i> , medium shade with HT drain	1.77	35.18
bleach at 95°C, biowash, light shade 60°C without HT drain	2.34	38.25

190

191 Such data clearly shows that very large amounts of water are utilised in immersion dyeing. It is,  
 192 therefore, perhaps unsurprising, that immersion dyeing processes routinely generate very large  
 193 amounts of wastewater, as exemplified by the finding (23) that in the Indian city of Tirupur, dyeing  
 194 and bleaching plants generated 87,000 T of wastewater per day. Unfortunately, such high levels of  
 195 water consumption and wastewater generation in dyeing is not especially remarkable when it is  
 196 recalled that immersion dyeing is only one of several wet processes that are used in the conversion  
 197 of raw materials into finished textile products and, also, that the textile industry characteristically  
 198 consumes extraordinarily large amounts of water and generates vast amounts of wastewater. For  
 199 example, it is reported that in the Indian textile industry, each 200 kg of water per kg of textile that is  
 200 consumed in textile manufacture results in 200–350 kg of wastewater generation per kg of finished  
 201 product (24).

202

203 In view of the previously mentioned high levels of auxiliary consumption in dyeing, the wastewater  
 204 created during immersion dyeing is likely to contain a wide variety of auxiliary chemicals. Indeed, as  
 205 many of the auxiliaries that are employed in immersion dyeing are intended to be removed from the  
 206 dyed material at the end of dyeing, such chemicals will be present in the wastewater that ensues

207 from dyeing processes [eg (8, 10, 25)]. This is illustrated by the data presented in Table 6 which  
 208 shows the low contribution that both dye and UV absorber make towards wastewater *chemical*  
 209 *oxygen demand (COD)* as these particular components of the disperse dye/PES dyeing system are  
 210 intended to be adsorbed by the substrate.

211

212 Table 6 Typical input and calculated output factors for the exhaust dyeing of PES knitted fabric using disperse

213 dyes (1:10 liquor ratio) (26)

214 using disperse dyes (1:10 liquor ratio) (27)

215

process	component	input factor/ g COD kg <sup>-1</sup> textile	output factor: emission to wastewater/ g COD kg <sup>-1</sup> textile
dyeing	dye	1-100	0.5-50
	dispersing agent	6	5
	carrier	23	11
	UV absorber	19	4
	defoaming agent	17	16
aftertreatment	reducing agent	7	5
	sequestrant	3	3

216

217 *Notes to Table 6:*

218 1. *as disperse dye formulations contain 40-60% dispersing agents, the output factor is 0.5-50;*

219 2. *as very small amounts of dispersing agent and defoaming agent remain on the textile, they reach wastewater*  
 220 *nearly quantitatively;*

221 3. *as carriers are substantive towards PES fibres, ~50% remains on the substrate;*

222 4. *UV absorber is substantive towards PES fibres and only ~20% reach wastewater;*

223 5. *as reducing agents are partially oxidised (30% assumed), COD contribution to wastewater is lower than the input.*

224

225 The wastewater obtained from immersion dyeing processes varies, in terms of both volume and  
 226 composition, depending on factors such as, for example, the type of fibre being dyed and its

227 physical form, the class of dye used, the nature of the dyeing machine employed, etc., as well as  
228 the particular water management philosophy in use. Dyeing wastewater is invariably highly  
229 coloured, contains various types of both organic and inorganic compounds (see Tables 1 and 2 for  
230 chemicals that could be present), and displays typically high values of COD, *biological oxygen*  
231 *demand (BOD<sub>5</sub>)*, *total suspended solids (TSS)* and *total dissolved solids (TDS)*.

232

233 Although dyeing wastewater is subjected to some form of effluent treatment, because the  
234 wastewater from dyeing processes characteristically displays marked resistance towards  
235 biodegradation (27, 28), such treatment is, typically, not only complex but also entails substantial  
236 expenditure of time, energy and chemicals. Although many strategies have been explored for  
237 treating dyeing effluent including both traditional treatment methods, such as adsorption, filtration  
238 and coagulation, as well as oxidation, biological degradation, photocatalysis, biosorption and low-  
239 cost adsorbents [see for example (24, 25, 29-36)], no single treatment method has yet been  
240 developed which can deal with the complex and varied nature of dyeing wastewater. Furthermore,  
241 the impact of dyeing auxiliaries on the effectiveness of wastewater decolourisation and re-use has  
242 received attention [eg (37-39)], as has the toxicity of auxiliaries used in reactive dyeing (40), whilst  
243 the environmental impact of surfactants is a well-discussed area [eg (41-44)].

244

245 Clearly, from an environmental perspective, the less water used in immersion dyeing the better.

246

### 247 *3.1 reactive dyes and cellulosic fibres*

248 An example of the scale of the environmental challenges posed by the routine usage of auxiliaries in  
249 dyeing processes is provided by reactive dyes that are used in the dyeing of cellulosic fibres such  
250 as cotton, lyocell, rayon, etc. Reactive dyes are one of five classes of dye (direct dyes, sulphur  
251 dyes, vat dyes, azoic colorants and reactive dyes) that can be used to dye cotton and other  
252 cellulosic fibres using immersion dyeing processes. Owing to their world-wide popularity, reactive  
253 dyes nowadays account for around ~55% of global dye consumption for cellulosic fibres. An  
254 estimate can be made of the scale of this usage based on published statistics for world fibre

255 production and assuming an average of 2% on mass of fibre dye is employed for exhaust dyeing  
 256 (1). Accordingly, in 2015, as world cotton & man-made cellulosic fibre production was  $28.1.6 \times 10^6$  T  
 257 (19) than  $\sim 300,000$  T of reactive dyes would have been used to dye cellulosic fibres. Despite the  
 258 very large global popularity of reactive dyes for cotton and other cellulosic fibres, their usage in  
 259 immersion dyeing processes presents manifold environmental challenges that arise because of the  
 260 inherent inefficiency of the exhaust reactive dyeing process.

261

262 By way of explanation, for any dye-fibre system, all of the dye that is applied to the textile substrate  
 263 during immersion dyeing should, ideally, be physically and/or chemically retained by the substrate.  
 264 The proportion of dye originally applied to a substrate that remains on the substrate after exhaust  
 265 dyeing and associated processes, is referred to as dye *fixation* (1). In practice, 100% dye fixation is  
 266 rarely achieved in immersion dyeing, as demonstrated by the data shown in Table 7; in this context,  
 267 it has been estimated that  $\sim 2 \times 10^5$  T of the dyes produced annually are lost during dyeing and  
 268 finishing because of inefficient dyeing procedures (45). Levels of dye fixation vary for different dye-  
 269 fibre systems (Table 7), with that typically achieved for reactive dyes on cellulosic fibres being  
 270 characteristically low.

271

272

Table 7 Estimated dye fixation achieved for different dye/fibre combinations (46)

dye/fibre combination	fixation/%
basic/PAN	97-98
pre-metallised acid/wool	93-98
azoic colorants/cellulose	90-95
disperse/PET	80-98
direct/cellulosic	80-95
vat/cellulosic	80-95
non-metallised acid/wool/PA	80-93
sulphur/cellulosic	60-70
reactive/cellulosic	50-80

273

274 For all dye-fibre systems, at the end of exhaust dyeing, unfixed, vagrant dye molecules must be  
275 removed from the dyed material, which otherwise, will desorb from the dyeing during subsequent  
276 use (eg domestic laundering), resulting in colour change and staining of adjacent materials.  
277 Although a rinse using cold water is the most rudimentary removal process that can be used, such a  
278 simple water rinse is seldom able to remove all residual dye. Thus, a more rigorous process,  
279 referred to generically as *wash-off*, is employed, which commonly takes the form of successive  
280 aqueous treatments which utilise progressions of cold/warm/hot water baths together with  
281 specialised, proprietary auxiliaries to expedite dye and auxiliary removal. In this context, the wash-  
282 off of reactive dyes on cellulosic fibres is of especial significance from a wastewater perspective.

283

284 Reactive dyes are so named because they can 'react' with appropriate groups within the cellulosic  
285 fibre and, therefore, form a covalent bond with substrate (the dyes can also covalently bind to other  
286 types of fibre that contain suitable nucleophilic groups, such as PA, silk and wool). To achieve this,  
287 reactive dyes are applied to cotton and other cellulosic fibres under aqueous alkaline (eg NaOH,  
288 Na<sub>2</sub>CO<sub>3</sub>) conditions so that electrophilic groups in the dye can form a covalent bond with the more  
289 strongly nucleophilic, ionised hydroxyl groups (Cell-O<sup>-</sup>) that are generated within the substrate under  
290 alkaline conditions, rather than the less nucleophilic cellulosic hydroxyl groups (Cell-OH).  
291 Unfortunately, such aqueous alkaline application conditions result not only in covalent bond  
292 formation with the substrate but also alkali-induced hydrolysis of the reactive dye. Thus, all  
293 commercial reactive dyes display inherently low levels of dye-fibre fixation efficiency. Consequently,  
294 in the case of reactive dyes used for dyeing of cellulosic fibres, wash-off is of fundamentally  
295 importance in achieving dyeings of satisfactory levels of fastness. As such, multiple wash-off baths  
296 and specific wash-off auxiliaries (aka wash-off agents) are utilised in exhaust reactive dyeing  
297 processes, as exemplified by the five-stage procedure shown in Table 8.

298

299 Table 8 recommended wash-off procedure for *Novacron FN* dyes on 100% cellulosic fibres (18)

wash-off stage	treatment*
----------------	------------

1 <sup>st</sup>	rinse: 10 mins @ 50°C
2 <sup>nd</sup>	neutralise: 10 mins @ 50°C (with CH <sub>3</sub> COOH)
3 <sup>rd</sup>	soap: 15 mins @ 95°C; 0.5-2 gl <sup>-1</sup> <i>Eriopon R liq</i> or 1-2 gl <sup>-1</sup> <i>Albatex DS</i>
4 <sup>th</sup>	rinse: 10 mins @ 50°C
5 <sup>th</sup>	rinse: 10 mins cold

300

301

\* for very deep shades an additional rinse at 90°C is recommended

302

303 The wash-off processes that are employed in the application of reactive dyes to cellulosic fibres  
 304 contribute markedly to the effluent load generated in dyeing not only because of the presence of  
 305 unfixed dye in the wastewater but also because of the presence of the proprietary wash-off agent  
 306 that is employed. An additional contribution to the effluent load generated in reactive dyeing  
 307 processes stems from the routine use of very large amounts of inorganic electrolyte (eg upto 100 gl<sup>-1</sup>  
 308 <sup>1</sup> NaCl) to promote dye uptake onto cellulosic fibres.

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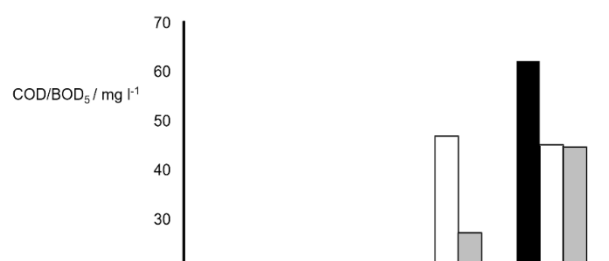
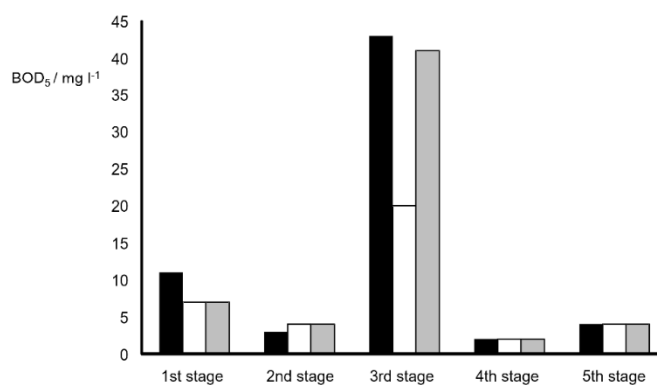
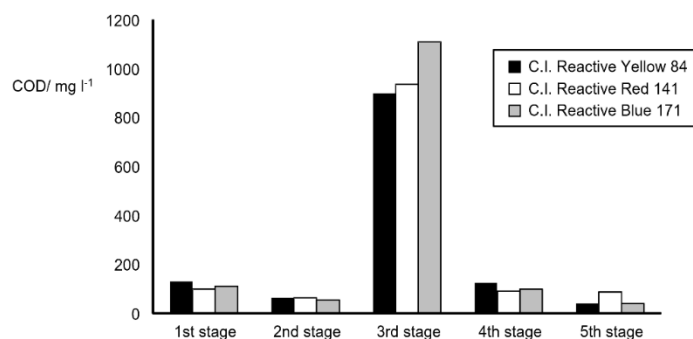
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328

329 Figure 3 Environmental indicators obtained for the five-stage, wash-off of 2% omf dyeings of three  
330 bis(aminochlorotriazine) dyes on cotton (27)

331

332 This was demonstrated in a study that determined the COD and BOD<sub>5</sub> loads obtained for the wash-  
333 off of three bis(aminochlorotriazine) (27) and three bifunctional (28) reactive dyes on cotton. By way  
334 of example, Figure 3 shows the values of the COD, BOD<sub>5</sub> and COD/BOD<sub>5</sub> environmental indicators  
335 secured for a five-stage, commercially-recommended wash-off process employed for 2% omf  
336 dyeings of three bis(aminochlorotriazine) dyes (27). It is apparent that the magnitude of the COD  
337 values followed the order: 1<sup>st</sup> wash-off stage > 2<sup>nd</sup> wash-off stage <<< 3<sup>rd</sup> wash-off stage >> 4<sup>th</sup>  
338 wash-off stage >> 5<sup>th</sup> wash-off stage, for each of the three dyes used. It is widely acknowledged that  
339 the first stage in the wash-off of reactive dyeings is important as it removes more 'easily detached'  
340 unfixed reactive dye molecules and also reduces the often very high inorganic electrolyte  
341 concentration within the dyed substrate, the latter function being important in terms of the complete  
342 of unfixed reactive dyes. Thus, the COD obtained for the first stage of the wash-off process can be  
343 attributed to the presence of 'easily detached' unfixed reactive dye molecules. Further dye removal  
344 occurred during the 2<sup>nd</sup> wash-off stage, but lower amounts of unfixed dye were removed than during  
345 the 1<sup>st</sup> wash-off stage. The electrolyte level in the dyed fibre would be further reduced during the 2<sup>nd</sup>  
346 wash-off stage, which would aid removal of additional unfixed reactive dye during subsequent wash-  
347 off stages. The finding that the highest COD values were recorded for the 3<sup>rd</sup> wash-off stage, in  
348 which the proprietary wash-off auxiliary, *Sera Sperse C-SN* was used, can be attributed to both the  
349 effectiveness of the wash-off auxiliary in expediting unfixed dye removal as well as the presence of  
350 the auxiliary in the residual wash-off bath. In this context, it is considered (47) that ~70% of the COD

351 load generated by reactive dyeing can result from the presence of such wash-off auxiliaries. The  
352 observation that the COD values obtained for the residual liquor from the 4<sup>th</sup> wash-off stage were  
353 higher than those obtained for the final (5<sup>th</sup>) wash-off stage can also be ascribed to the presence of  
354 the wash-off auxiliary. The values of the BOD<sub>5</sub> environmental indicator obtained for the five different  
355 wash-off stages (Figure 3) followed the general order: 1<sup>st</sup> wash-off stage > 2<sup>nd</sup> wash-off stage <<<  
356 3<sup>rd</sup> wash-off stage >> 4<sup>th</sup> wash-off stage < 5<sup>th</sup> wash-off stage, for each of the three dyes used, which  
357 was very similar to that obtained for the COD values. The very high BOD<sub>5</sub> values obtained for the 3<sup>rd</sup>  
358 wash-off stage can be assumed to reflect both high dye removal and the presence of the  
359 commercial wash-off auxiliary. It is apparent that the values of COD were much higher than the  
360 corresponding BOD<sub>5</sub> values, for each of the five wash-off stages used, indicating that whilst the  
361 wash-off liquors contain organic material that can be oxidised, it is not biodegradable.

362

363 The COD/BOD<sub>5</sub> ratio is an indicator of the relative biodegradability of wastewater, an inverse  
364 relationship existing between the ratio and biodegradability. A ratio of between 3 and 7 implies  
365 moderate biodegradability whereas values >10 denote biologically untreatable wastewater and  
366 indicate that additional treatment of the organic components may be required to achieve a  
367 'biodegradable' COD/BOD<sub>5</sub> value of <3 (48). The COD/BOD<sub>5</sub> ratio obtained for the five wash-off  
368 stages (Figure 3) clearly demonstrate the influence of the wash-off auxiliary agent upon the quality  
369 of the wastewater generated for each of the three dyes, as shown by the very high ratios presented  
370 by both the 3<sup>rd</sup> and, especially, the 4<sup>th</sup> wash-off stages; the very high COD/BOD<sub>5</sub> ratios secured for  
371 the 3<sup>rd</sup> and 4<sup>th</sup> wash-off stages can be attributed to the presence of the auxiliary wash-off agent.  
372 Indeed, from Figure 3 it is evident that the wastewater obtained from the majority of the wash-off  
373 stages was of very low biodegradability, as the COD/BOD<sub>5</sub> ratios were >10.

374

375 The chemical composition of wastewater will vary according to the dyeing system under  
376 consideration, type of dye used, machine employed, etc. By way of example, the typical composition  
377 of the wastewater COD load for cotton yarn dyed mainly using vat dyes was 16% dyes and 46%  
378 dyeing auxiliaries, whereas the corresponding figures for dyes and dyeing auxiliaries obtained in the

379 case of dyeing PA and PA/elastane blend fabrics was 2% and 54%, respectively (15). An estimate  
 380 of the chemical composition of wastewater from a textile finishing mill that processed mainly  
 381 synthetic fibres, (Table 9) revealed varying amounts of relatively simple inorganic compounds as  
 382 well as more complex organic auxiliary materials (10).

383

384

Table 9 Chemical composition of wastewater from a textile finishing mill (10)

substance	estimated amount of the substance in wastewater/ kg yr <sup>-1</sup>
Na <sub>2</sub> SO <sub>4</sub>	10540
CH <sub>3</sub> COOH	10206
fatty alcohol ethoxylate	7512
naphthalene sulfonic acid condensation product	7070
NaOH	6344
fatty acid ethoxylate	6180
Na <sub>2</sub> CO <sub>3</sub>	6173
butylbenzoate	4680
NaCl	4641
polyacrylate	3879
H <sub>2</sub> O <sub>2</sub>	2093

385

386 *\* the reaction of reducing agents and oxidising agents, lyes and acids in the wastewater is not considered in the estimation*

387

388 The wide range of different types of auxiliary that are likely to be present in the wastewater  
 389 generated during dyeing can be anticipated to contribute to the overall environmental load; Table 10  
 390 shows possible pollutants and pollution loads from dyeing (49).

391

392

Table 10 Possible pollutants and pollution loads from dyeing (49)

fibre	pH	BOD/mg l <sup>-1</sup>	total suspended solids (TSS) /mg	inorganic substances	organic substances
-------	----	------------------------	-------------------------------------	----------------------	--------------------

l<sup>-1</sup>

PES	-	480-27000	-	Na <sup>+</sup> ; NH <sub>4</sub> <sup>-</sup> ; Cl <sup>-</sup> ; S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> ; NO <sub>3</sub> <sup>-</sup> ; ClO <sup>-</sup> ; SO <sub>3</sub> <sup>2-</sup>	acetate; anionic surfactants; antistatic agents; dispersing agents; carriers; EDTA; ethylene oxide condensates; formate; mineral oils; nonionic surfactants; residual dye; soaps; solvents
PA	8.4	368	641	Na <sup>+</sup> ; Cl <sup>-</sup> ; CO <sub>3</sub> <sup>2-</sup>	acetate; formate; residual dye; sulfonated oils
cotton;				Na <sup>+</sup> ; Cr <sup>3+</sup> ; Cu <sup>2+</sup> ; Sb <sup>3+</sup> ; K <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Cl <sup>-</sup> ; O <sub>3</sub> <sup>2-</sup> ;	naphthols; acetate; amides of naphthoic acid; anionic dispersing agents; anionic surfactants; cationic fixing agents; chloro amines;
linen;	5-10	11-1800	500-14100	CO <sub>4</sub> <sup>2-</sup> ; F <sup>-</sup> ; NO <sub>2</sub> <sup>-</sup> ; O <sub>2</sub> <sup>2-</sup> ;	formaldehyde; formate; nitro
CV				S <sup>2-</sup> ; <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ; SO <sub>3</sub> <sup>2-</sup> ; SO <sub>4</sub> <sup>2-</sup>	amines; nonionic surfactants; residual dye; soaps; soluble oils; sulfated oils; tannic acid; tartrate; urea
PAN	1.5-3.7	175-2000	833-1968	Na <sup>+</sup> ; NH <sub>4</sub> <sup>-</sup> ; Cu <sup>2+</sup> ; SO <sub>4</sub> <sup>2-</sup>	acetate; aromatic amines; formate; levelling agents; phenolic compounds; residual dye; retardants; surfactants; thiourea dioxide
wool	4.8-8	380-2200	3855-8315	Na <sup>+</sup> ; Cr <sup>3+</sup> ; Cu <sup>2+</sup> ; Sb <sup>3+</sup> ; K <sup>+</sup> ; NH <sub>4</sub> <sup>+</sup> ; Al <sup>3+</sup> ; Cl <sup>-</sup> ; CO <sub>3</sub> <sup>2-</sup> ; S <sub>2</sub> O <sub>4</sub> <sup>-</sup> ; SO <sub>3</sub> <sup>2-</sup> ; SO <sub>4</sub> <sup>2-</sup>	acetate; dispersing agents; formate; lactate; residual dye; sulfated oils; tartrate

393

394 As might be anticipated, the contribution that auxiliaries make to the environmental load of  
 395 wastewater will vary according to the dye-fibre system in question. For example, the contribution of  
 396 dispersing agents and levelling agents is significant in the case of dyeing with vat or disperse dyes;  
 397 processes such as reduction clearing and softening are also associated with high values of COD  
 398 (8).

399

400

Table 11 Environmental indicators obtained for mills mainly processing a particular type of fibre (15)

fibre type	COD/ mg O <sub>2</sub> l <sup>-1</sup>	BOD <sub>5</sub> / mg O <sub>2</sub> l <sup>-1</sup>	COD/BOD <sub>5</sub>
wool PA and/or CV <sup>1</sup>	692	240	2.9
cotton <sup>1</sup>	709	207	3.4
PES <sup>2</sup>	1240	230	5.4

average of data obtained for: <sup>1</sup>five mills; <sup>2</sup>three mills; <sup>3</sup>four mills

Table 11 shows environmental indicators obtained for the dyeing and other wet processing of different types of fibre (15). The higher value of COD recorded for PES can be attributed to the dispersing agents and levelling agents used in dyeing with disperse dyes. As mentioned, the COD/BOD<sub>5</sub> ratio can be considered as an indicator of the relative biodegradability of wastewater (27), insofar as an inverse relationship exists between the ratio and biodegradability; the comparatively lower biodegradability of the wastewater generated from PES processing is apparent (Table 11).

#### 4 economic aspects associated with the use of dyeing auxiliaries

From the above discussion, it is clear that the widespread use of auxiliaries in immersion dyeing will make a major contribution to the cost of dyeing not only directly, via the cost of the dyeing auxiliaries themselves, but also indirectly, because of the expense of treating the wastewater that contains auxiliaries. By way of example, as mentioned, the immersion dyeing of cotton and other cellulosic fibres requires the use of electrolyte, commonly in the form of either NaCl or Na<sub>2</sub>SO<sub>4</sub>, which is added to the dyebath to promote dye uptake. The amount of added electrolyte employed varies according to the particular type of dye used (eg reactive dyes, direct dyes, etc.), the nature of the fibre, liquor ratio employed, etc. For example, direct dyes are applied in the presence of typically 5-20 gl<sup>-1</sup> electrolyte whilst the dyeing of cotton with reactive dyes typically requires larger amounts of electrolyte, as high as 100 gl<sup>-1</sup> in the case of dark shades (50) and leuco dyeing with vat dyes can utilise 10-20 gl<sup>-1</sup> electrolyte depending on dyeing method. Such routine usage of high amounts of NaCl or Na<sub>2</sub>SO<sub>4</sub> in cellulosic fibre dyeing poses severe environmental concerns, owing to the

425 presence of inorganic electrolyte in wastewater, as well as significant economic challenges. In the  
426 latter context, the electrolyte used in cotton dyeing increases the expense of dyeing not only  
427 because of the cost of the added NaCl or Na<sub>2</sub>SO<sub>4</sub> but also due to the sizeable costs involved in  
428 removing inorganic electrolyte from the dyed material at the end of dyeing via the use of lengthy  
429 wash-off procedures and the treatment and disposal of the ensuing, already chemically-loaded,  
430 saline wastewater. An idea of the scale of such treatment is provided by the water consumption  
431 figures presented in Table 4 for the processing of 200 kg of cotton using typical commercial reactive  
432 dyes.

433

434 In recent years, the treatment of wastewater generated from dyeing processes has received  
435 considerable attention and, as mentioned, a wide range of different types of wastewater treatment  
436 methods have been examined [eg (25, 35, 51-57)]. In this context, the discharge of large volumes of  
437 wastewater of *high total dissolved solids (TDS)* (ie electrolyte content) generated by cotton  
438 immersion dyeing processes are subject to stringent environmental restrictions in many parts of the  
439 world and the use of wastewater treatments that remove electrolyte for reclamation/disposal and  
440 enable recycling of some process water are nowadays unexceptional. The problems that arise from  
441 the presence of inorganic electrolyte in surface water cannot be underestimated and are illustrated  
442 by the well-publicised difficulties that have attended the dyeing industry centred around Tirupur  
443 which prompted the local government to demand the implementation of *zero liquid discharge* [ZLD]  
444 dyeing operations owing to the severe environmental impact of the use of inorganic electrolyte in  
445 cellulosic fibre dyeing [eg (58-63)]. By way of example, it was reported (63) in 2008 that the daily  
446 processing of 600–700 T of hosiery fabric required 400–500 T of inorganic electrolyte (either NaCl  
447 or Na<sub>2</sub>SO<sub>4</sub>) and that TDS and chloride contents of the treated effluent were in the range 5000–7000  
448 mg l<sup>-1</sup> and 2000–3500 mg l<sup>-1</sup>, respectively, as compared to tolerance limits of 2100 mg l<sup>-1</sup> for TDS  
449 and 1000 mg l<sup>-1</sup> for chlorides. However, such ZLD treatment systems are, typically, complex,  
450 expensive and entail high running costs. By way of example, in 2015 (62) the establishment costs of  
451 installing a typical ZLD system to service an installed fabric dyeing capacity of 12 T day<sup>-1</sup> was

452 €1,165,000 whilst the cost of treating the ensuing wastewater was €21.06 per m<sup>3</sup> (Table 12) of  
 453 which >95% related to TDS (electrolyte).

454 Table 12 typical costs of wastewater treatment (62)

stage of treatment	cost/€ m <sup>-3</sup>
effluent treatment	0.54
reverse osmosis	0.27
multiple effect evaporator	6.75
agitator thin film dryer	13.5
total treatment cost	21.06

455

456

#### 457 **5 the relationship between liquor ratio and the use of auxiliaries**

458 As recounted above, immersion dyeing consumes large amounts of water, as do the other wet  
 459 processes to which textile fibres are subjected during their conversion into a dyed textile material,  
 460 although water consumption varies markedly among such processes, as illustrated by the data  
 461 shown in Table 13.

462

463 Table 13 Average water usage for different textile wet processes (49)

fibre	process	water usage/ l kg <sup>-1</sup>
cotton	desizing	3-9
	scouring	26-43
	bleaching	3-124
	mercerising	232-308
	dyeing	8-300
wool	scouring	46-100
	dyeing	16-22
	washing	334-835
polyamide	neutralisation	104-131
	bleaching	3-22
	scouring	50-67

	dyeing	17-33
	scouring	50-67
acrylic	dyeing	17-33
	final scour	67-93
	scouring	25-42
polyester	dyeing	17-33
	final scour	17-33
viscose	scouring & dyeing	17-33
	salt bath	4-13
cellulose	scouring & dyeing	33-50
acetate		

464

465 The amount of water used in dyeing is commonly expressed by the *liquor ratio* (aka *goods:liquor*  
466 *ratio*) which simply describes the ratio of the amount of substrate used in relation to the amount of  
467 water used. For example, a liquor ratio of 1:8 describes a dyeing process in which 1 kg or 1 T of  
468 fibre is dyed using 8 kg (~8 l) or 8T (8000 l) of dye solution. Higher liquor ratios favour dye migration  
469 during dyeing (64) whilst lower values of liquor ratio increase both the rate and extent of dyeing (65-  
470 74) and, in the case of reactive dyes, the extent of covalent dye fixation (66). Various factors  
471 influence the particular liquor ratio used for dyeing, such as type of fibre and its physical form, dye  
472 type, machine used, etc. (1).

473

474 It follows therefore, that in the case of dyeing recipes that are based on liquor ratio as opposed to  
475 mass of fibre (ie omf), liquor ratio determines the amount of chemicals (dye, wetting agent,  
476 electrolyte, etc.) used for dyeing. For example, consider the case of the batchwise dyeing of 250 kg  
477 of cotton with reactive dyes. Table 14 shows that using a 1:8 liquor ratio would require the use of  
478 ~2000 l (~2000 kg) of water whereas the use of a 1:5 liquor ratio would necessitate the use of 1250 l  
479 of water. Clearly, the lower the liquor ratio then the lower the amount of water used in dyeing (and  
480 other textile wet processes). Although liquor ratio is usually based on the dry mass of the textile

481 material (fabric, yarn, etc.), some dyers and machine makers (wrongly) refer to liquor ratio on the  
 482 basis of wet or wetted-out material rather than on the dry mass of the textile material.

483

484 Table 14 amounts of water, electrolyte and alkali used in a typical reactive dyeing process for 250 kg of cotton

485

liquor ratio used in dyeing	amount of water used in dyeing/ l	amount of electrolyte used in dyeing/ kg	amount of alkali used in dyeing/ kg	total amount of electrolyte and alkali consumed in dyeing/ kg	reduction in electrolyte and alkali used in dyeing compared to conventional 1:8 liquo ratio process/ %
1:8	2000	100	40	140	-
1:5	1250	62.5	25	87.5	37.5

486

487 As illustrated by the data displayed in Table 14, the liquor ratio that is employed for dyeing and the  
 488 amount of the auxiliaries that are used in dyeing, are linked, insofar as, the larger the liquor ratio,  
 489 the greater the amount of auxiliaries required for dyeing. It follows therefore, that the amount of  
 490 water consumed in dyeing, expressed via liquor ratio, is of major economic importance, not only  
 491 from the viewpoint of the direct cost of the water used, but also, and more significantly, because of  
 492 the fact that the amount of auxiliaries utilised and their direct cost, are directly related to the amount  
 493 of water employed. Indeed, the adoption of low liquor ratios in dyeing has beneficial effects in terms  
 494 of the cost of dyeing, not only from the viewpoint of auxiliary usage but also, for example, from the  
 495 related perspective of the amounts of water, steam and energy consumed (75-79), as illustrated by  
 496 the data shown in Table 15 (79).

497

498 Table 15 estimated cost savings of ultra low liquor ratio (1:3 for synthetic fibres and 1:5 for cotton) dyeing  
 499 equipment compared to conventional (1:10 liquor ratio) equipment (79)

cost factor	change/%
water	-37.0
steam	-50.3

electricity	0
direct labour	-104
chemicals	-43.9
supplies	-1.1
overhead	-10.6

500

501 When the amount of the auxiliaries that are used in dyeing is calculated on the basis of mass of  
 502 fibre, liquor ratio has a marked effect on the effective concentration of the auxiliary that is present in  
 503 the dyebath, which, in turn, has implications in terms of, for example, the manner by which the  
 504 auxiliary functions, the treatment required for its removal from wastewater, etc. For example,  
 505 consider the use of a fibre protective agent that is deployed at 5% omf in a process for dyeing 250  
 506 kg of fibre. If a 1:10 liquor ratio is used for dyeing, the auxiliary would have a concentration in the  
 507 dyebath of 5 gl<sup>-1</sup> whereas at a 1:6 liquor ratio, the concentration of the fibre protective agent would  
 508 be 8 gl<sup>-1</sup>. It is common for dye makers to prescribe the amount of auxiliaries (and dye) required  
 509 depending on the particular ratio selected for dyeing (Table 16) (18).

510

511 Table 16 amounts of added electrolyte and alkali required for immersion dyeing using *Novacron FN* dyes (18)

liquor ratio	electrolyte & alkali	dye/% omf						
		< 0.5	0.5	1	2	3	4	≥5
≤ 1:6	NaCl/ gl <sup>-1</sup>	10	20	30	40	50	60	70
	NaHCO <sub>3</sub> / gl <sup>-1</sup>	14	16	18	20	20	20	20
1:6 < LR ≤ 1:8	NaCl/ gl <sup>-1</sup>	20	30	40	50	60	70	80
	NaHCO <sub>3</sub> / gl <sup>-1</sup>	10	12	14	16	18	20	20
> 1:8	NaCl/ gl <sup>-1</sup>	30	40	50	60	80	90	100
	NaHCO <sub>3</sub> / gl <sup>-1</sup>	8	10	12	14	16	18	18
≤ 1:6	NaCl/ gl <sup>-1</sup>	10	20	30	40	50	60	70
	NaHCO <sub>3</sub> / gl <sup>-1</sup>	10	10	5	50	5	5	5
	NaOH 36°Bé/ cm <sup>3</sup> l <sup>-1</sup>	0.5	1	2	2.5	3	3.5	4
1:6 < LR ≤ 1:8	NaCl/ gl <sup>-1</sup>	20	30	40	50	60	70	80
	NaHCO <sub>3</sub> / gl <sup>-1</sup>	10	5	5	5	5	5	5

	NaOH 36°Bé/ cm <sup>3</sup> l <sup>-1</sup>	-	0.75	1.25	1.5	2	2.5	3
	NaCl/ gl <sup>-1</sup>	30	40	50	60	80	90	100
> 1:8	NaHCO <sub>3</sub> / gl <sup>-1</sup>	8	5	5	5	5	5	5
	NaOH 36°Bé/ cm <sup>3</sup> l <sup>-1</sup>	-	0.5	1	1.25	1.5	2	2.5

512

513 As discussed previously, the amount of water consumed in dyeing has major environmental  
 514 implications. For example, in the case of China, where shortage of water resources is severe,  
 515 insofar as >300 of the 640 major cities face water shortages and 100 cities face severe scarcities  
 516 (40), textile dyeing and finishing processes are characterised by high water consumption, with some  
 517 150 m<sup>3</sup> of water being consumed per tonne of cloth processed (40). Clearly, the use of lower liquor  
 518 ratios in dyeing can result in lower amounts of wastewater that contain smaller amounts of  
 519 auxiliaries.

520

## 521 6 summary

522 The many types of dyeing auxiliary that are commercially available vary, not only in terms of the  
 523 nature of the assistance they furnish in immersion dyeing processes, but also from the viewpoints of  
 524 their environmental credentials and the costs associated with their use. Despite their widespread  
 525 usage, the precise nature of the mode of action of many auxiliaries has not been fully resolved.

526

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**Highlights**

- there are many different types of dyeing auxiliary
- they are chemically diverse and perform many essential operations
- the precise mode of action of many auxiliaries is unclear

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