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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
- they are chemically diverse and perform many essential operations
 - the precise mode of action of many auxiliaries is unclear
- 20

19

21 keywords

- 22 fibres; auxiliaries; dyeing; finishing
- 23

24 abbreviations

- 25 PA: polyamide; PES: poly(ethylene) terephthalate; COD: Chemical Oxygen Demand; BOD₅
- 26 Biological Oxygen Demand; TDS: Total Dissolved Solids

27 1 Introduction

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

34

In this context, an auxiliary can be defined as a chemical or formulated chemical product which 35 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 chemicals (eg acids, surfactants, reductants, etc.), as illustrated by the data presented in Table 1. 53 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 CH₃COOH and 58 inorganic such as HCl, etc.), reducing and oxidising agents (eg Na₂S₂O₄, H₂O₂, 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)

| process | auxiliary | effect | chemical type |
|-----------------|--|---------------------------------|---|
| | dye solubilising agents; | promote dissolution of dyes in | alcohols; polyols; fatty alcohol ethoxylates; |
| | hydrotopes | water | esters |
| | | | naphthalene sulfonic acid formaldehyde |
| dissolving dyes | diaparaing aganta | promote formation and stability | condensates; naphthalene sulfonates; |
| | aispersing agents; | promote formation and stability | lignosulfonates; fatty alcohol ethoxylates; |
| | protective colloids | or dye dispersions | alkylsulfonates; alkylaryl sulfonates; |
| | | | polyacrylates |
| | wetting agents; | increase wetting conscitutef | alkylsulfates; alkanesulfonates; |
| exhaust dyeing | | the dve liquere: increase dve | alkylarylsulfonates; salts of sulfosuccinic acid; |
| | deaeration agents | adsorption | esters; fatty alcohol ethoxylates; alcohols; |
| | | ausorption | phosphoric acid esters; hydrocarbons |
| | dye protecting agents; boil-down protecting | protect dyes during application | buffers and/or oxidants (nitrobenzene |
| | agents | | Sunonate, urea, any ary sunonates |
| | | oxidiise reduced forms of vat | peroxo compounds; sodium perborate; sodium |
| | ovidicing agonts | and sulphur dyes; strip dyes | persulfate; sodium chromate; salts of m- |
| | oxidising agents | and auxiliaries from | nitrobenzene sulfonic acid; bromite; sodium |
| | | the fibre | chlorite |

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

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

63

A large number of commercial auxiliary products are available, as exemplified by a 2008 publication 64 (16) that lists >6500 commercial products derived from 400-600 active compounds. Consumption of 65 66 dyeing auxiliaries is estimated to be 60-70% of that of dyes (12), which, in 2012, would have corresponded to 0.96–1.2 x 10⁶ T of auxiliary consumed in textile dyeing, according to an estimated 67 global dye consumption of 1.6 x 10^6 T (1). However, auxiliary usage varies according to several 68 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 | |
|---------|-----------|--------|---------------|--|
| | | | | |

| | 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; |
| | protoctive colleide | of due dispersions | lignosulfonates; fatty alcohol ethoxylates; |
| | protective colloids | of dye dispersions | alkylsulfonates; alkylaryl sulfonates; |
| | | | polyacrylates |
| | | increase wetting capacity of | alkylsulfates; alkanesulfonates; |
| | wetting agents; | the due ligues increase due | alkylarylsulfonates; salts of sulfosuccinic acid; |
| | deaeration agents | adsorption | esters; fatty alcohol ethoxylates; alcohols; |
| | | ausorption | phosphoric acid esters; hydrocarbons |
| | dye protecting agents; | protect dyes during application | buffers and/or oxidants (nitrobenzene |
| | agents | | sulfonate); urea; alkylarylsulfonates |
| | oxidising agents | oxidiise reduced forms of vat | peroxo compounds; sodium perborate; sodium |
| | | and sulphur dyes; strip dyes | persulfate; sodium chromate; salts of <i>m</i> - |
| exhaust dyeing | | and auxiliaries from | nitrobenzene sulfonic acid; bromite; sodium |
| | | the fibre | chlorite |
| | | | sodium dithionite; sulfonic acid |
| | | reduce vat and sulphur dyes; | derivatives; sodium sulphide; glucose and |
| | reducing agents | reduction clearing; dye | mixtures thereof; thiourea dioxide; |
| | | stripping | sodium or zinc formaldehyde |
| | | | sulfonic acids |
| | | | polyvinylpyrrolidone; polyglycol ether; |
| | brightening agents | partial removal of adsorbed | cellulases; alkyl aryl sulfonates; alkyl amine |
| | | dye | ethoxylates; reducing agents and oxidising |
| | | | agents |
| | | | protein hydrolysates; polyglycol ether; protein |
| | | and the second | fatty acid condensates; lignosulfonates; |
| | fibre-protective agents | prevent or reduce tibre | formaldehyde eliminating products (urea |
| | C | aarnage auring dyeing | 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/Wool | carriers | accelerate dye adsorption, dye diffusion | aromatic hydrocarbons; chlorinated aromatic compounds; benzoic acid esters; phthalic acid esters; alkyl phthalimides; alkylphenolethoxylates |
| 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 /a ka ⁻¹ textile | light shade | medium shade | dark shade |
|---------------------------------------|-------------|--------------|------------|
| component /g kg textile | light shade | medium snade | |
| 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 dyeing procedures can be adjusted by controlling machine-dependent factors (eg rate and extent of 94 95 dye-substrate interchange, heating rate, etc.) and by manipulating both the nature and extent of dye-dye and dye-substrate interactions within the dyebath via, for example, pH adjustment, 96 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 CH₃COOH/CH₃COONa 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 Novacron LS (Huntsman) reactive dyes to cellulosic fibres, which are intended, for example, to 106 107 improve levelness and appearance (penetrating/de-aerating/defoaming products), to avoid problems that arise from impurities in the dyebath (reduction penetrant, dispersing agent, Ca inactivation, 108 protective colloid and lubricant) and also to ensure that fastness is optimised (wash-off agents and 109 cationic fixing agents) (17). Routinely, commercial dyeing recipes include the use of several 110 111 auxiliary products, as exemplified by the procedures displayed in Figures 1 and 2.



127 from their deployment. For example, in the application of direct dyes and reactive dyes to cellulosic

- fibres, inorganic electrolytes such as NaCl or Na_2SO_4 are used to promote dye exhaustion and, in the case of reactive dyes, to promote dye fixation.
- 130



136

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 improve the fastness properties of dyeings, such as fixing agents (aka cationic fixing agents) which 146 147 impart improved wet fastness to direct dyes on cellulosic fibres, or UV absorbers which provide improved protection towards fading by light, must remain within the dyed substrate in order for their 148 149 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.

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

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

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

163

Although water is of fundamental importance in immersion dyeing, the amount of water employed 164 varies, according to, for example, the type of machine used, the type of fibre used, the physical form 165 166 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 assuming an average liquor ratio of 1:8 for dyeing and a cumulative average 1:10 liquor ratio for wet 168 processes associated with dyeing (eg wetting, rinsing, wash-off, etc.). Using this approach, in 2015, 169 as world textile fibre production totalled 90.64 x 10^6 T (19), of which PES fibres accounted for ~59% 170 (53.1 x 10⁶ T) and cotton & man-made cellulosic fibres ~31% (28.1 x 10⁶ T), the amount of water 171 172 used in dyeing (assuming that all fibre production was dyed) would have been of the order of 16.3 x 173 10¹¹ I, of which 9.6 x 10¹¹ I can be ascribed to that of PES dyeing and 5.1 x 10¹¹ I 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 I per kg of fibre, may be somewhat modest, when compared to reported water usage in commercial dyeing processes, such as the 72-96 I kg⁻¹ of water 176 177 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)

| DIOCESS | | | dye |
|---------------------|-----------------|---------------|-------------------------|
| ŀ | proceed | | Remazol RGB |
| | | scour/bleach: | accur/bloach: 00°C |
| | porotion | 98°C | Scourbleach. 96 C |
| pre | eparation | rinse: 80°C | rinse: 80°C |
| | | rinse: 60°C | rinse: 60°C |
| | | migration | R |
| | dyeing | dyeing: | isothermal dyeing: 60°C |
| | | 80/60°C | |
| | | rinse: 50°C | rinse: 50°C |
| | | rinse: 70°C | rinse: 50°C |
| | /ash_off | boil off | rinse: 80°C |
| v | a31-011 | rinse: 80°C | boil off |
| | | rinse: 60°C | rinse: 80°C |
| | | | rinse: 25°C |
| proces | ss time/ mins | 691 | 649 |
| | dyebath water | 16400 | 16400 |
| water consumption/1 | cooling water | 16380 | 21060 |
| | total | 32000 | 37460 |
| | per kg of fibre | 160 | 187.3 |
| energy consumption/ | total | 3974 | 3639 |
| MJ | per kg of fibre | 19.87 | 18.12 |
| chemicals consumed/ | total | 253 | 260 |
| kg | per kg of fibre | 1.27 | 1.3 |
| dves consumed/ kg | total | 5.55 | 7.35 |
| dyes consumed/ kg | per kg of fibre | 0.028 | 0.036 |

182

183 assumptions made in Table 4:

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
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 ⁻¹ fibre | water used/ I kg ⁻¹ fibre |
|---|---------------------------------------|--------------------------------------|
| bleach, light biowash without enzyme stop, extra | 2 93 | 36 17 |
| dark shade with HT drain | 2.00 | |
| bleach, Remazol Ultra RGB, dark red | 2.8 | 48.13 |
| bleach, Drimaren CL, medium shade with HT | | A Company |
| drain | 1.77 | 35.18 |
| bleach at 950C, biowash, light shade 60° C | Ċ | |
| without HT drain | 2.34 | 38.25 |
| | | |

190

Such data clearly shows that very large amounts of water are utilised in immersion dyeing. It is, 191 192 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

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

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

-..

214

dyes (1:10 liquor ratio) (26) using disperse dyes (1:10 liquor ratio) (27)

215

| process | component | input factor/ g COD | output factor: emission to |
|----------------|------------------|--------------------------|--|
| process | component | kg ⁻¹ textile | wastewater/ g COD kg ⁻¹ textile |
| | dye | 1-100 | 0.5-50 |
| | dispersing agent | 6 | 5 |
| dyeing | 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;
- as very small amounts of dispersing agent and defoaming agent remain on the textile, they reach wastewater
 nearly quantitatively;
- 221 3. as carriers are substantive towards PES fibres, ~50% remains on the substrate;
- 4. UV absorber is substantive towards PES fibres and only ~20% reach wastewater;
- 5. as reducing agents are partially oxidised (30% assumed), COD contribution to wastewater is lower than the input.
- 224

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

physical form, the class of dye used, the nature of the dyeing machine employed, etc., as well as the particular water management philosophy in use. Dyeing wastewater is invariably highly coloured, contains various types of both organic and inorganic compounds (see Tables 1 and 2 for chemicals that could be present), and displays typically high values of COD, *biological oxygen demand* (*BOD₅*), *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 treating dyeing effluent including both traditional treatment methods, such as adsorption, filtration 237 238 and coagulation, as well as oxidation, biological degradation, photocatalysis, biosorption and lowcost adsorbents [see for example (24, 25, 29-36)], no single treatment method has yet been 239 240 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

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

production and assuming an average of 2% on mass of fibre dye is employed for exhaust dyeing (1). Accordingly, in 2015, as world cotton & man-made cellulosic fibre production was 28.1.6 x 10⁶ T (19) than ~300,000 T of reactive dyes would have been used to dye cellulosic fibres. Despite the very large global popularity of reactive dyes for cotton and other cellulosic fibres, their usage in immersion dyeing processes presents manifold environmental challenges that arise because of the inherent inefficiency of the exhaust reactive dyeing process.

261

By way of explanation, for any dye-fibre system, all of the dye that is applied to the textile substrate 262 263 during immersion dveing 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 dyeing and associated processes, is referred to as dye *fixation* (1). In practice, 100% dye fixation is 265 266 rarely achieved in immersion dyeing, as demonstrated by the data shown in Table 7; in this context, it has been estimated that ~2 x 10⁵ T of the dyes produced annually are lost during dyeing and 267 finishing because of inefficient dyeing procedures (45). Levels of dye fixation vary for different dye-268 fibre systems (Table 7), with that typically achieved for reactive dyes on cellulosic fibres being 269 270 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 |

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 (eq 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, referred to generically as wash-off, is employed, which commonly takes the form of successive 279 280 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 types of fibre that contain suitable nucleophilic groups, such as PA, silk and wool). To achieve this, 286 reactive dyes are applied to cotton and other cellulosic fibres under aqueous alkaline (eq NaOH, 287 288 Na₂CO₃) conditions so that electrophilic groups in the dye can form a covalent bond with the more 289 strongly nucleophilic, ionised hydroxyl groups (Cell-O) that are generated within the substrate under alkaline conditions, rather than the less nucleophilic cellulosic hydroxyl groups (Cell-OH). 290 Unfortunately, such aqueous alkaline application conditions result not only in covalent bond 291 292 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 st | rinse: 10 mins @ 50°C | |
|-----------------|---|--|
| 2 nd | neutralise: 10 mins @ 50°C (with CH3COOH) | |
| 3 rd | soap: 15 mins @ 95°C; 0.5-2 gl ⁻¹ <i>Eriopon R liq</i> or 1-2 gl ⁻¹ <i>Albatex DS</i> | |
| 4 th | rinse: 10 mins @ 50°C | |
| 5 th | rinse: 10 mins cold | |
| | | |

300

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

302

301

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





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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

This was demonstrated in a study that determined the COD and BOD₅ loads obtained for the wash-332 333 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, BOD₅ and COD/BOD₅ environmental indicators 335 secured for a five-stage, commercially-recommended wash-off process employed for 2% omf dyeings of three bis(aminochlorotriazine) dyes (27). It is apparent that the magnitude of the COD 336 values followed the order: 1st wash-off stage > 2nd wash-off stage <<< 3rd wash-off stage >> 4th 337 wash-off stage >> 5th wash-off stage, for each of the three dyes used. It is widely acknowledged that 338 339 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 attributed to the presence of 'easily detached' unfixed reactive dye molecules. Further dye removal 343 occurred during the 2nd wash-off stage, but lower amounts of unfixed dye were removed than during 344 the 1st wash-off stage. The electrolyte level in the dyed fibre would be further reduced during the 2nd 345 wash-off stage, which would aid removal of additional unfixed reactive dye during subsequent wash-346 off stages. The finding that the highest COD values were recorded for the 3rd wash-off stage, in 347 348 which the proprietary wash-off auxiliary, Sera Sperse C-SN was used, can be attributed to both the effectiveness of the wash-off auxiliary in expediting unfixed dye removal as well as the presence of 349 350 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 observation that the COD values obtained for the residual liquor from the 4th wash-off stage were 352 higher than those obtained for the final (5th) wash-off stage can also be ascribed to the presence of 353 354 the wash-off auxiliary. The values of the BOD₅ environmental indicator obtained for the five different wash-off stages (Figure 3) followed the general order: 1st wash-off stage > 2nd wash-off stage <<< 355 3^{rd} wash-off stage >> 4^{th} wash-off stage < 5^{th} wash-off stage, for each of the three dves used, which 356 was very similar to that obtained for the COD values. The very high BOD₅ values obtained for the 3rd 357 wash-off stage can be assumed to reflect both high dye removal and the presence of the 358 359 commercial wash-off auxiliary. It is apparent that the values of COD were much higher than the 360 corresponding BOD₅ 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

The COD/BOD₅ ratio is an indicator of the relative biodegradability of wastewater, an inverse 363 relationship existing between the ratio and biodegradability. A ratio of between 3 and 7 implies 364 moderate biodegradability whereas values >10 denote biologically untreatable wastewater and 365 366 indicate that additional treatment of the organic components may be required to achieve a 'biodegradable' COD/BOD₅ value of <3 (48). The COD/BOD₅ ratio obtained for the five wash-off 367 stages (Figure 3) clearly demonstrate the influence of the wash-off auxiliary agent upon the quality 368 of the wastewater generated for each of the three dyes, as shown by the very high ratios presented 369 by both the 3rd and, especially, the 4th wash-off stages; the very high COD/BOD₅ ratios secured for 370 the 3rd and 4th wash-off stages can be attributed to the presence of the auxiliary wash-off agent. 371 372 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/BOD₅ ratios were >10.

374

The chemical composition of wastewater will vary according to the dyeing system under consideration, type of dye used, machine employed, etc. By way of example, the typical composition of the wastewater COD load for cotton yarn dyed mainly using vat dyes was 16% dyes and 46% 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)

| | estimated amount of | |
|--|--------------------------------------|--|
| substance | the substance in wastewater/ kg yr-1 | |
| NacSO | 10540 | |
| Nd2004 | | |
| CH₃COOH | 10206 | |
| fatty alcohol ethoxylate | 7512 | |
| naphthalene sulfonic acid condensation product | 7070 | |
| NaOH | 6344 | |
| fatty acid ethoxylate | 6180 | |
| Na ₂ CO ₃ | 6173 | |
| butylbenzoate | 4680 | |
| NaCl | 4641 | |
| polyacrylate | 3879 | |
| H ₂ O ₂ | 2093 | |

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 ⁻¹ | total suspended solids (TSS) /mg | inorganic substances | organic substances | |
|----------|------------------------|----------------------------------|----------------------|--------------------|--|
|----------|------------------------|----------------------------------|----------------------|--------------------|--|

³⁸⁵

^{386 *} the reaction of reducing agents and oxidising agents, lyes and acids in the wastewater is not considered in the estimation 387

 $|^{-1}$

| | | | | | acetate; anionic surfactants; antistatic agents; |
|---------|---------|-----------|-----------|--|--|
| | | | | No ⁺ · NH ⁻ · CI ⁻ · S ₂ O ₂ ²⁻ | dispersing agents; carriers; EDTA; ethylene |
| PES | - | 480-27000 | - | $100^{-1}, 100^{-1}, 200^{-2}$ | oxide condensates; formate; mineral oils; |
| | | | | , NO_3 , CIO , SO_3 | nonionic |
| | | | | | surfactants; residual dye; soaps; solvents |
| | | | | | acetate; formate; residual dye; |
| PA | 8.4 | 368 | 641 | Na'; CI; CO₃² | sulfonated oils |
| | | | | | naphthols; acetate; amides of naphthoic acid; |
| | | | | Na ⁺ ; Cr ³⁺ ; Cu ²⁺ ; Sb ³⁺ ; | anionic dispersing agents; anionic surfactants; |
| cotton; | | | | K ⁺ ; NH4 ⁺ ; Cl ⁻ ; O ₃ ²⁻ ; | cationic fixing agents; chloro amines; |
| linen; | 5-10 | 11-1800 | 500-14100 | CO ₄ ²⁻ ; F ⁻ ; NO ₂ ⁻ ; O ₂ ²⁻ ; | formaldehyde; formate; nitro |
| CV | | | | S ²⁻ ; ₂ O ₃ ²⁻ ; SO ₃ ²⁻ ; | amines; nonionic surfactants; residual dye; |
| | | | | SO4 ²⁻ | soaps; soluble oils; sulfated oils; tannic acid; |
| | | | | | tartrate; urea |
| | | | | + | acetate; aromatic amines; formate; levelling |
| PAN | 1.5-3.7 | 175-2000 | 833-1968 | Na; NH ₄ ; Cu ⁻⁺ ; | agents; phenolic compounds; residual dye; |
| | | | | 504 | retardants; surfactants; thiourea dioxide |
| | | | | Na ⁺ ; Cr ³⁺ ; Cu ²⁺ ; Sb ³⁺ ; | |
| | 4.0.0 | 000 0000 | | K ⁺ ; NH₄ ⁺ ; Al ³⁺ ; Cl ⁻ ; | acetate; dispersing agents; formate; lactate; |
| WOOI | 4.8-8 | 380-2200 | 3855-8315 | CO ₃ ²⁻ ; S ₂ O ₄ ⁻ ; SO ₃ ²⁻ ; | residual dye; sulfated oils; tartrate |
| | | | | SO4 ²⁻ | |
| | | | | | |

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

399

393

400

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

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

401

402

average of data obtained for: ¹ five mills; ² three mills; ³ four mills

403

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/BOD₅ 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).

411

412 **4** economic aspects associated with the use of dyeing auxiliaries

413 From the above discussion, it is clear that the widespread use of auxiliaries in immersion dyeing will 414 make a major contribution to the cost of dyeing not only directly, via the cost of the dyeing auxiliaries 415 themselves, but also indirectly, because of the expense of treating the wastewater that contains 416 auxiliaries. By way of example, as mentioned, the immersion dyeing of cotton and other cellulosic 417 fibres requires the use of electrolyte, commonly in the form of either NaCl or Na₂SO₄, which is 418 added to the dyebath to promote dye uptake. The amount of added electrolyte employed varies 419 according to the particular type of dye used (eg reactive dyes, direct dyes, etc.), the nature of the 420 fibre, liquor ratio employed, etc. For example, direct dyes are applied in the presence of typically 5-421 20 gl⁻¹ electrolyte whilst the dyeing of cotton with reactive dyes typically requires larger amounts of 422 electrolyte, as high as 100 gl⁻¹ in the case of dark shades (50) and leuco dyeing with vat dyes can 423 utilise 10-20 gl⁻¹ electrolyte depending on dyeing method. Such routine usage of high amounts of 424 NaCl or Na₂SO₄ 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 Na₂SO₄ 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 Na₂SO₄) and that TDS and chloride contents of the treated effluent were in the range 5000–7000 mg l⁻¹ and 2000–3500 mg l⁻¹, respectively, as compared to tolerance limits of 2100 mg l⁻¹ for TDS 448 and 1000 mg l^{-1} for chlorides. However, such ZLD treatment systems are, typically, complex, 449 450 expensive and entail high running costs. By way of example, in 2015 (62) the establishment costs of installing a typical ZLD system to service an installed fabric dyeing capacity of 12 T dav¹ was 451

452 €1,165,000 whilst the cost of treating the ensuing wastewater was €21.06 per m³ (Table 12) of 453 which >95% related to TDS (electrolyte).

454

Table 12 typical costs of wastewater treatment (62)

| stage of treatment | cost/€ m ⁻³ |
|----------------------------|------------------------|
| 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

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

462

463

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

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

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|-----------|-------------------|----------|--|
| | 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 | |
| | scouring & dyeing | 17-33 | |
| viscose | salt bath | 4-13 | |
| cellulose | scouring & dveing | 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 water used. For example, a liquor ratio of 1:8 describes a dyeing process in which 1 kg or 1 T of 467 468 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

It follows therefore, that in the case of dyeing recipes that are based on liquor ratio as opposed to mass of fibre (ie omf), liquor ratio determines the amount of chemicals (dye, wetting agent, electrolyte, etc.) used for dyeing. For example, consider the case of the batchwise dyeing of 250 kg of cotton with reactive dyes. Table 14 shows that using a 1:8 liquor ratio would require the use of ~2000 I (~2000 kg) of water whereas the use of a 1:5 liquor ratio would necessitate the use of 1250 I of water. Clearly, the lower the liquor ratio then the lower the amount of water used in dyeing (and 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 <u>dry mass</u> of the textile material.

483

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

485

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

486

As illustrated by the data displayed in Table 14, the liquor ratio that is employed for dyeing and the 487 488 amount of the auxiliaries that are used in dyeing, are linked, insofar as, the larger the liquor ratio, the greater the amount of auxiliaries required for dyeing. It follows therefore, that the amount of 489 490 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 related perspective of the amounts of water, steam and energy consumed (75-79), as illustrated by 495 496 the data shown in Table 15 (79).

- 497
- 498 499
- Table 15 estimated cost savings of ultra low liquor ratio (1:3 for synthetic fibres and 1:5 for cotton) dyeing equipment compared to conventional (1:10 liquor ratio) equipment (79)

| cost factor | change/% |
|-------------|----------|
| water | -37.0 |
| steam | -50.3 |

| CCEPTED N | IANUSCF |
|---------------|---------|
| 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 kg of fibre. If a 1:10 liquor ratio is used for dyeing, the auxiliary would have a concentration in the 506 dyebath of 5 gl⁻¹ whereas at a 1:6 liquor ratio, the concentration of the fibre protective agent would 507 be 8 gl⁻¹. It is common for dye makers to prescribe the amount of auxiliaries (and dye) required 508 depending on the particular ratio selected for dyeing (Table 16) (18). 509

| 511 | Table 16 amounts of added electrolyte and alklai r | equired for immersion dyeing using Novacron FN dyes | s (18) |
|-----|--|---|--------|
| | | dve/% omf | |

| liquor ratio | | | | | dye/% omf | | | | |
|----------------|---|-------|-----|----|-----------|----|-----|-----|--|
| | electrolyte & alkali | < 0.5 | 0.5 | 1 | 2 | 3 | 4 | ≥5 | |
| ≤ 1:6 | NaCl/ gl ⁻¹ | 10 | 20 | 30 | 40 | 50 | 60 | 70 | |
| | NaHCO₃/ gl ⁻¹ | 14 | 16 | 18 | 20 | 20 | 20 | 20 | |
| 1:6 < LR ≥ 1:8 | NaCl/ gl ⁻¹ | 20 | 30 | 40 | 50 | 60 | 70 | 80 | |
| | NaHCO₃/ gl ⁻¹ | 10 | 12 | 14 | 16 | 18 | 20 | 20 | |
| > 1:8 | NaCl/ gl⁻¹ | 30 | 40 | 50 | 60 | 80 | 90 | 100 | |
| | NaHCO ₃ / gl ⁻¹ | 8 | 10 | 12 | 14 | 16 | 18 | 18 | |
| ≤ 1:6 | NaCl/ gl⁻¹ | 10 | 20 | 30 | 40 | 50 | 60 | 70 | |
| | NaHCO₃/ gl ⁻¹ | 10 | 10 | 5 | 50 | 5 | 5 | 5 | |
| | NaOH 36⁰Bé/ cm ³ l ^{⁻1} | 0.5 | 1 | 2 | 2.5 | 3 | 3.5 | 4 | |
| 1:6 < LR ≥ 1:8 | NaCl/ gl ⁻¹ | 20 | 30 | 40 | 50 | 60 | 70 | 80 | |
| | NaHCO ₃ / gl ⁻¹ | 10 | 5 | 5 | 5 | 5 | 5 | 5 | |

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|---------------------|---|----|------|------|------|-----|-----|-----|--|--|--|
| | NaOH 36°Bé/ cm ³ l ⁻¹ | - | 0.75 | 1.25 | 1.5 | 2 | 2.5 | 3 | | | |
| | NaCl/ gl⁻¹ | 30 | 40 | 50 | 60 | 80 | 90 | 100 | | | |
| > 1:8 | NaHCO₃/ gl⁻¹ | 8 | 5 | 5 | 5 | 5 | 5 | 5 | | | |
| | NaOH 36°Bé/ cm ³ l ⁻¹ | - | 0.5 | 1 | 1.25 | 1.5 | 2 | 2.5 | | | |

512

As discussed previously, the amount of water consumed in dyeing has major environmental implications. For example, in the case of China, where shortage of water resources is severe, insofar as >300 of the 640 major cities face water shortages and 100 cities face severe scarcities (40), textile dyeing and finishing processes are characterised by high water consumption, with some 150 m³ of water being consumed per tonne of cloth processed (40). Clearly, the use of lower liquor ratios in dyeing can result in lower amounts of wastewater that contain smaller amounts of auxiliaries.

520

521 6 summary

The many types of dyeing auxiliary that are commercially available vary, not only in terms of the nature of the assistance they furnish in immersion dyeing processes, but also from the viewpoints of their environmental credentials and the costs associated with their us. Despite their widespread 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