

CHAPTER 8

Functions and properties of dyeing and printing auxiliaries

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8.1 THE NEED FOR AUXILIARIES

There is hardly a dyeing or printing process of commercial importance that can be adequately operated by the use of dyes and water alone. Practically every colorant–substrate system requires the use of additional products, known as auxiliaries, to ensure its reliable functioning and control. This was the case even centuries ago, when the use of natural vat and mordant dyes depended entirely on the proper, albeit rule of thumb, use of additives. These controlled pH, reduction, oxidation and mordanting to enable the dyes to be applied to the natural fibres of those days. Many of the auxiliaries, like the dyes and fibres, were of natural origin. Dung and urine [1] were among the agents used, and soap was clearly the first surfactant to be employed. Indeed, from the standpoint of today, one can only wonder at the degree of purely empirical expertise so successfully developed and applied by the ancient dyers and printers.

Our current level of understanding is clearly a phenomenal advance on the ancient arts, yet our need for auxiliaries remains. For example, even before dyeing or printing the substrate must be cleaned and wetted. Products are needed to convert non-substantive vat and sulphur dyes to substantive forms, to help stabilise the conditions that bring about the substantivity, and then to reconvert the dyes to their insoluble forms in the substrate (sections 1.6.1 and 1.6.2). Mordant dyes still require the appropriate chelating agents, as well as other agents to create and maintain the optimum chelating conditions (section 5.8). Printers still need thickening agents to facilitate the localised application of dyes. Inevitably, however, the present-day plethora of dyes, fibres and coloration processes has created additional reasons for the use of auxiliaries, whilst the concurrent evolution of the chemical industry has satisfied these needs as they arose. Moreover, a vastly more comprehensive understanding of the physico–chemical processes involved has enabled auxiliaries to be precisely engineered for specific purposes.

Hand in hand with this theoretical knowledge, practical evaluation has become increasingly sophisticated. Nevertheless, it is often difficult to differentiate between auxiliaries promoted purely for commercial reasons and those that serve a definite technical need. Dye manufacturers are acutely aware of the positive part played by auxiliaries in helping to sell dyes, and dyers today are under constant pressure to use more of them. Some additives offer cost savings by improving reproducibility and minimising reprocessing; nevertheless it is all too tempting to incorporate too many products without critically evaluating their efficacy, thus inevitably and unnecessarily increasing processing costs. Consequently it is more important than ever that the dyer or printer understands the

functions of auxiliary products and is equipped to evaluate their use realistically and to monitor it continually.

As has been implied already, functional demands for auxiliaries continue to grow, with each dye–fibre system and dyeing or printing process having particular needs. The primary functions of auxiliaries are:

- (a) to prepare or improve the substrate in readiness for coloration by
 - scouring, bleaching and desizing
 - wetting
 - enhancing the whiteness by a fluorescent brightening effect
- (b) to modify the sorption characteristics of colorants by
 - acceleration
 - retardation
 - creating a blocking or resist effect
 - providing sites for sorption
 - unifying otherwise divergent rates of sorption
 - improving or resisting the migration of dyes
- (c) to stabilise the application medium by
 - improving dye solubility
 - stabilising a dispersion or solution
 - thickening a print paste or pad liquor
 - inhibiting or promoting foaming
 - forming an emulsion
 - scavenging or minimising the effects of impurities
 - preventing or promoting oxidation or reduction
- (d) to protect or modify the substrate by
 - creating or resisting dyeability
 - lubricating the substrate
 - protecting against the effects of temperature and other processing conditions
- (e) to improve the fastness of dyeings, as in
 - the aftertreatment of direct or reactive dyes
 - the aftertreatment of acid dyes on nylon
 - the chroming of mordant dyes on wool or nylon
 - giving protection against atmospheric influences, as in UV absorbers or inhibitors of gas-fume fading
 - back-scouring or reduction clearing
- (f) to enhance the properties of laundering formulations (fluorescent brightening agents).

Some auxiliaries fulfil more than one of the above functions. For example, an auxiliary to improve dye solubility may also accelerate (or retard) a coloration process, or an emulsifying agent may also act as a thickening agent; pH-control agents may both stabilise a system and also affect the rate of dye sorption.

Thus the range of auxiliaries available is very large indeed, covering a multiplicity of uses for all stages of textile processing. However, a factor which has assumed great importance regarding the use of auxiliaries in recent years is that of their effects on the environment. In view of the extensive portfolio of products and processes, it is not surprising that good

environmental management is complex. Undesirable effects from the use of auxiliaries may become evident during handling, through effluent discharge to surface waters, through discharge to the atmosphere (e.g. via stenter gases), through consumer contact with the finished product (e.g. skin sensitivity) or during the eventual disposal of solid wastes (e.g. incineration or landfill). All these factors need careful consideration in the selection of auxiliaries at all stages of processing. Compliance with good environmental practice may be voluntary (preferably) or enforced by legislation, some countries having introduced quite extensive and stringent requirements [2,3].

Many factors need to be considered: acute toxicity to mammals, toxicity to aquatic organisms (fish, daphniae, algae) and waste water bacteria, biodegradability (aerobic or anaerobic), abiotic degradability (hydrolysis, photolysis, oxidation), ground mobility, bioaccumulation, carcinogenicity, mutagenicity and teratogenicity.

The textile wet processing industry produces particularly heavy discharges of effluent; hence the responsibility placed on it for environmentally good behaviour is indeed an onerous one, both technically and financially [4]. The preparation processes of desizing, scouring and bleaching, together with their associated wash-off processes, inevitably produce a heavy biological oxygen demand in the effluent [5]. Hence there has been, and continues to be, much research effort to improve the environmental performance of these areas.

There are two general approaches to good environmental practice. The first, termed 'end-of-pipe' solutions, requires all unacceptable matter to be removed from the effluent, or at least to be reduced to acceptable levels. This is relatively difficult and expensive, requiring the appropriate treatment facilities. The second attempts to minimise the need for end-of-pipe treatments by reducing the hazardous nature of the effluent in the first place. This can be achieved, for example, by recycling and reusing useful constituents, especially reducing water volumes through the use of low liquor ratios, and reducing the toxicity of the effluent by selecting 'green' chemicals and processing methods. In some cases, the volume of effluent can be reduced by combining some processes, e.g. desizing, scouring and bleaching. The possibilities inherent in the second approach have stimulated much research work amongst manufacturers and suppliers of auxiliaries, in terms of finding 'greener' products and more acceptable processes for their use. These efforts will continue for the foreseeable future.

It is important to remember that auxiliaries nowadays are most frequently supplied as more or less complex mixtures. It is essential from an environmental point of view to consider the influence of the subsidiary components in the branded product as well as of the main substances. For example, even a small amount of solvent added to improve the stability of an auxiliary may pose problems of flammability or toxic vapours, necessitating careful storage and labelling. Constant monitoring of products and processes is necessary, since environmental requirements are continually changing as more information, matched by increasing awareness of hazards, becomes available. It has been suggested that the main concerns to date have been in response to controlling listed substances rather than in tackling fundamental environmental problems [5].

Wragg [6] has provided the following basic environmental check-list for textile wet processing:

- (1) Is the product free from species and/or by-products that are on the various control lists? Lists of controlled chemicals are being continually extended, together with controls on their use. Usage of heavy metals, solvents and AOX-containing products will gradually decrease.

- (2) Is the manufacturing process suitable for safety and environmental controls? Processing cycles are being placed under greater control in terms of machine operation. Auxiliary usage will be more specific and accurate to avoid over-consumption and to minimise waste.
- (3) Has the product or its components been assessed at any time for acute toxicity, carcinogenicity or irritant properties?
- (4) Are the materials easily dealt with in waste treatment systems?
- (5) Has the product or its components been assessed at any time for toxicity to aquatic species?

The overall result of environmental awareness has been to increase the interplay of devolution and evolution. Devolution has seen increasing restrictions, sometimes amounting to a complete ban, on the use of certain substances (e.g. alkylphenolethoxylates, which were once widely used) and a corresponding evolution of new products which, at least for the present, are environmentally acceptable. This interplay between devolution and evolution is likely to continue indefinitely. Environmental factors as they affect specific types of auxiliary will be dealt with under the relevant sections of this volume.

8.2 THE GENERAL TYPES AND CHARACTERISTICS OF AUXILIARIES

An auxiliary has been defined [7] as 'a chemical or formulated chemical product which enables a processing operation in preparation, dyeing, printing or finishing to be carried out more effectively, or which is essential if a given effect is to be obtained'. It is much harder to devise a classification system for auxiliaries than it is for dyes. This is undoubtedly one of the main reasons why there has been no incentive to produce an auxiliaries index comparable with the *Colour Index*. It is difficult enough to put together a comprehensive yet manageable list of general application types; it becomes even more difficult to classify them chemically, especially as many of them are more or less complex mixtures, are of imprecisely known structure or are the subject of a good deal of trade confidentiality. Although the Society of Dyers and Colourists has shown reluctance to be involved in this area, a very useful biennial trade publication [8] has made considerable progress in the ordered listing of currently available commercial products. This first appeared in 1967. The seventeenth edition (2000) lists currently available products by trade name, application and suppliers. Unfortunately this publication does not include a listing by chemical type. Although the first section does give whatever chemical detail the manufacturers are prepared to divulge, these tend to be bland, broadly based descriptions such as 'nonionic aqueous emulsion of modified wax' or 'quaternary ammonium compound, cationic'. In spite of these shortcomings it remains an indispensable guide to the vast range of products on the market today.

The broadest classification of auxiliaries is achieved simply by dividing them into non-surfactants and surfactants, as detailed below.

Non-surfactants include simple electrolytes, acids and bases, both inorganic and organic. Examples include sodium chloride, sodium acetate, sulphuric acid, acetic acid and sodium carbonate, together with complex salts (such as sodium dichromate, copper(II) sulphate, sodium ethylenediaminetetra-acetate, sodium hexametaphosphate), oxidising agents (hydrogen peroxide, sodium chlorite) and reducing agents (sodium dithionite, sodium sulphide). Anionic polyelectrolytes such as sodium alginate or carboxymethylcellulose, used

mainly as thickening agents and migration inhibitors, also fall within the class of non-surfactants; so too do sorption accelerants such as *o*-phenylphenol, butanol and methylnaphthalene, although they normally require an emulsifier to stabilise them in aqueous media. Fluorescent brightening agents (FBAs) form another large class of non-surfactant auxiliaries (see Chapter 11).

Surfactants are, in general, substantially organic in nature and structurally more complex than most non-surfactants. It is difficult to define surfactants in a manner sufficiently precise to satisfy everyone. However, for the purposes of this book an adequate definition of a surfactant is given by the Society's Terms and Definitions Committee [7]: 'an agent, soluble or dispersible in a liquid, which reduces the surface tension of the liquid'. In coloration processes this reduction in surface tension usually takes place at a liquid/liquid or liquid/solid interface, although liquid/gas interfaces are also occasionally important. In general, a dramatic lowering of surface tension can be brought about by a relatively small amount of surfactant; as little as 0.2 g/l of a soap such as sodium oleate will more than halve the surface tension of water. This physical effect in solution is attributed to the molecular orientation potential of a relatively small hydrophilic moiety (a hydrophile) having strong polar forces, juxtaposed with a relatively large (usually linear) hydrophobic moiety (a hydrophobe) having relatively weak electrostatic forces (Figure 8.1). In aqueous solution or dispersion the polar hydrophile tends to be oriented into the body of the aqueous phase, whilst the hydrophobe, by nature subjected to forces of repulsion by the aqueous phase, is oriented towards (or at) the interfacial boundary, which may be that between the solution and air or between the solution and a fibrous (or other) substrate.

The surfactants used as textile auxiliaries can be divided into four major groups, depending on the type and distribution of the polar forces, an arrangement broadly resembling the ionic classification of dyes. The general scheme is shown in Table 8.1.

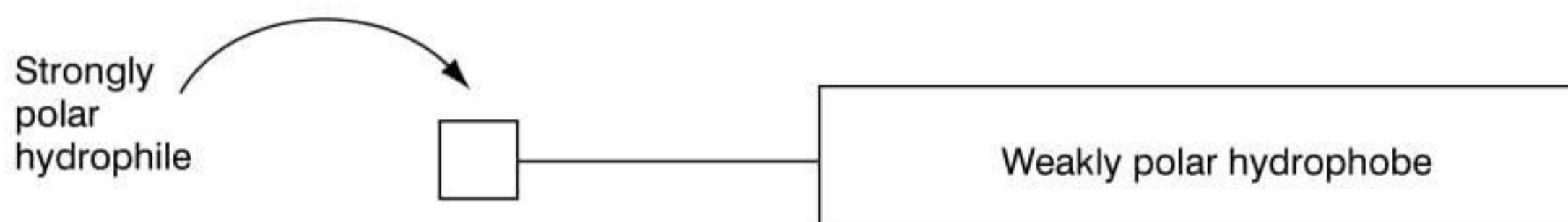


Figure 8.1 Schematic diagram of surfactant

Table 8.1 General classification of surfactants

Class of surfactant	Degree of ionic charge on the	
	Hydrophobe	Hydrophile (associated ion)
Anionic	Weakly negative	Strongly positive
Cationic	Weakly positive	Strongly negative
Nonionic	Uncharged	Uncharged
Amphoteric	These possess balanced negative and positive charges, one or other of which dominates in solution depending on the pH	

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