

4.1 Finishing:Norman 1991:HE STATES THAT Finish recipes often are made up the same way that they were originally formulated many years ago, without regard for environmental considerations. For example, mineral oil and paraffin wax softeners may still be in use even though polyethylene glycol (PEG) or polyethylene oxide (PO) products are available which do not smoke when heated, thereby reducing air emissions from dryers. Also, on another subject, the use of acrylic hand builders and stiffeners can replace formaldehyde based handbuilders.:MY COMMENTS

4.k Printing:Norman 1991:HE STATES THAT The 70% kerosene used in traditional printing past recipes is typically replaced nowadays by 2% or less of synthetic polymer thickener. Typical recipes are in Table I, page 150. If oil is still used, the biodegradable vegetable oils are preferred to mineral oils, due to their easier treatability.:MY COMMENTS This is pretty standard practice now in USA printing plants.

4.j Dyeing:Norman 1991:HE STATES THAT Lower liquor ration dyeing machines save water.:MY COMMENTS

4.g Slashing and Sizing:Norman 1991:HE STATES THAT A small amount of synthetic size material can replace a large amount of starch in warp size recipes, thus lowering BOD considerably. Synthetic sizes are also easier to remove thus saving water and energy.:MY COMMENTS

4.i Preparation:Norman 1991:HE STATES THAT Alkyl phenol (AP) surfactants are not completely degradable, and even if degraded the degradation residues are phenols which are toxic to fish. Other types (ethoxylated alcohol = LAE) are less toxic. If a mill is purchasing commodity surfactant, the decision is straightforward (see note). But when the surfactant is part of a proprietary compounded specialty, the responsibility rests with the formulator.:MY COMMENTS Straightforward if the mill has access to aquatic toxicity data (which are not easy to find), and knows how to interpret it.

2.b.v Elimination of low levels of metals from wastewater:Norman 1991:HE STATES THAT EDTA or DPTA sequesterants have been popular for years. NTA is also used, and is more biodegradable. The use of NTA provides the same in process performance, but as it degrades in the waste treatment system, it releases chelated metals, and thus they do not pass through the waste treatment system, but rather are precipitated in the sludges.:MY COMMENTS Since he presents no data or method for determining this, and since he cites no references, I suspect that he is just guessing that this is the case. I know that the performance of EDTA, DTPA and NTA are not equivalent in all conditions (of pH, metal types, etc). Still, he may be right. Whether this is correct is a judgment call, since he does not reveal the source of his information.

3.e Chemical alternatives:Norman 1991:HE STATES THAT Years ago,

acid dyes on nylon were fixed with tannic acid and tartar emetic bath which was toxic. Now, syntans (synthetic tanning agents) based on sulfone/phenolsulfonic acid/formaldehyde condensates are used, reducing toxicity. Improved syntans have reduced formaldehyde, thus are even further improved.:MY COMMENTS This is pretty standard practice now.

4.j Dyeing:Norman 1991:HE STATES THAT When dyeing fiber reactive dyes on cotton, some unfixed, hydrolyzed reactive dye remains in the fiber to be washed off. Thorough washing uses quite a lot of water. An alternative is to wash some, then fix the small remaining residue of hydrolyzed fiber reactive dye with fixing agents. For years, the standard direct dye fixing agents (DCY/formaldehyde) were used for this. Now there are cationic polymeric fixing agents which are much more efficient on fiber reactive dyes.:MY COMMENTS

# Pollution control in the textile industry – the chemical auxiliary manufacturer's role

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*In the first half of a two-part paper, the authors discuss what efforts are being made to control atmospheric and effluent pollution in the coloration industry and closely related processes such as fabric production, preparation and finishing.*

## INTRODUCTION

With pollution control in the coloration industry becoming increasingly stringent we must all address what can be done to clean up dyehouse practices. Atmospheric and effluent pollution are the two main areas of concern and it would be useful to outline what preventative measures have already been achieved in order to put future developments in perspective.

## ATMOSPHERIC POLLUTION

Drying, baking and curing often cause the majority of problems for the working environment and result in unacceptable conditions inside the factory and excessive smoke and odours outside.

## Fabric processing

In processing, for instance, such problems can often be overcome by a change in the lubricant/processing aid/softener applied to goods during earlier stages of manufacture. For example, a certain mineral oil or a paraffin wax may have been selected some years ago on technical merit alone without any environmental considerations. It is likely that there is an alternative higher boiling point oil or poly(ethylene glycol) (PEG) ester or an ethylene oxide/polyethylene oxide (EO/PO) product that will not contaminate the immediate working area or fill the locality with smoke, particularly during cold damp periods.

## Pigment printing

A particularly good example of the reduction in atmospheric pollution is in pigment printing. During the last ten years there has been a dramatic shift from emulsion thickenings to synthetics. This has come as a result of continuous research and development by chemical manufacturers. The 70% kerosene in the traditional recipe has been replaced by less than 2% of a synthetic thickener or less than 1% of an acrylic polymer, as shown by the two formulations quoted in Table 1. The aqueous system also eliminates the danger of fire and explosion.

In the early 1980s Allied Colloids chose to offer these newly developed thickeners as liquid dispersions thus giving low-viscosity, high-concentration products that are mobile, easy to use and have excellent shelf life and frost insensitivity. However, in doing so some oil was reintroduced into the system, albeit less than 1%. The next generation of liquid dispersion thickeners now use non-smoking, low VOC oils. Similar products are used as thickeners for reactive printing

TABLE 1

Thickeners for pigment printing formulations

	Emulsion	Aqueous
Water	100	815
Emulsifier	10	
Binder	150	150
Kerosene	700	
Thickener		15
Pigment	20	20
Catalyst	20	
	1000	1000

but here the thickener is washed from the fabric rather than being baked on and the problems become effluent-related rather than atmospheric. Already Allied Colloids has developed a 'green' version of the reactive dye print thickener that uses biodegradable vegetable oils rather than mineral oils as the carrier.

## EFFLUENT/WASTE WATER POLLUTION

There are a number of ways in which improvements can be made to effluents such as a reduction in volumes, lower liquor ratios, more efficient washing and recycling. There is also room to use dyes and chemicals more efficiently and to select non-toxic, more biodegradable products that are harmless and easier to deal with once they get into the effluent. In addition, there are also opportunities to make improvements at every stage of fabric production, preparation/bleaching, dyeing/printing and finishing, as can be illustrated in the following examples.

## Weaving

The most commonly used size is starch, which is usually needed at high concentrations. After weaving, the size must be removed by desizing, producing liquors containing large amounts of starch with a very high BOD. However, it is possible to use synthetic sizes as a full or partial replacement. Indeed, a small amount of acrylic polymer can replace a relatively large amount of starch with the immediate benefit of reducing costs to the manufacturer. Synthetic sizes also improve weaving efficiency, facilitate removability, and

reduce the amount of solids and BOD levels in the effluent. Total synthetic systems can actually enable size recovery, which is particularly important because this dramatically reduces effluent itself.

### Preparation and bleaching

The chemicals used in this process are commonly wetting agents, detergents, sequestrants or complexing agents, dispersants and peroxide stabilisers. One of the most commonly used product groups for wetting/detergency has been alkyl phenol ethoxylates (APEO) (Figure 1). By careful selection of the APEO it is possible to achieve the degree of biodegradability demanded by the authorities, but the decomposition products are still phenolic and therefore toxic to fish. Fortunately there are alternative non-ionic products, in particular ethoxylated fatty alcohols (Figure 2), which are more readily degradable and whose metabolites are non-toxic. Another eliminable dispersing agent is low molecular weight polyacrylate (Figure 3).

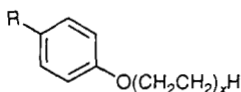


Figure 1 - Structure of alkylphenol ethoxylates

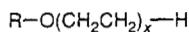


Figure 2 - Structure of ethoxylated fatty alcohols

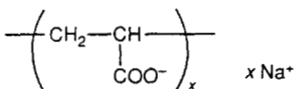


Figure 3 - Structure of polyacrylate

It is easy when buying a straightforward detergent to choose a bioeliminable product as an alternative to APEO, but not so easy to make the judgement when buying blended products aimed at speciality end uses. Allied Colloids, as a supplier, must take on board these considerations when formulating blended products for fabric preparation and make these 'green' alternatives available.

### Sequestering agents/chelates

EDTA and DTPA have been widely used for many years but are now causing some concern. They form stable highly water-soluble complexes with heavy metals, that are capable of passing through an effluent treatment plant and into the water courses. These complexes will eventually break down leaving the highly toxic metals in the environment. The less stable NTA can be a suitable alternative in some instances. Although the complex produced will be less stable than that from EDTA or DTPA, if it is adequate for the task then that is all that matters. The bonus is that NTA and its complexes are more readily degraded than EDTA/DTPA.

Polymers based on acrylic acid can also exhibit mild sequestering action as one might expect from the proximity of carboxyl groups along the polymer chain (Figure 4). Low molecular weight uncross-linked polymers can be degraded and adsorbed onto activated sludge and are therefore readily bioeliminable.

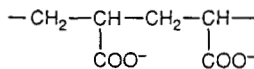


Figure 4 - Structure of acrylic acid based polymer

### Dispersants

Although phosphonates behave as complexing agents, they are also used as dispersants, as are polyphosphates. Both have a low bioeliminability and have been banned already in some countries because of the eutrophication they cause (growth of algae and plant life in rivers and lakes). However, carefully selected acrylic polymers will be bioeliminable without causing eutrophication. It is worth noting that some of the major domestic detergent manufacturers are changing from phosphates as detergent builders to acrylic copolymers such as sodium acrylate/sodium maleate (Figure 5).

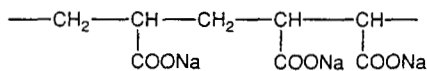


Figure 5 - Structure of sodium acrylate/sodium maleate polymer

### Peroxide stabilisers

These are complex blends of a selection of materials serving a number of functions. They can include any of the following:

- Alkali, e.g. silicate/caustic soda/carbonate
- Dispersants, e.g. acrylates/phosphonates
- Sequestrants, e.g. EDTA/DTPA/heptonates/gluconates
- Inorganics, e.g. magnesium salts
- Colloid stabilisers, e.g. acrylic polymers.

The alkalis and the inorganic salts are not bioeliminable but are not regarded as harmful to the environment. The problems could arise with the dispersants, sequestrants and colloid stabilisers. In recent years acrylates have been used in preference to phosphates and phosphonates whilst leptonates and gluconates have replaced EDTA and DTPA.

### Dyeing

For a good example of how the chemical manufacturers have contributed to cleaning up the effluent from dyehouses we need look no further than the dyeing of nylon. By fixing acid dyes using a 'full back tan' using tannic acid and tartar emetic, the dyer poured large volumes of toxic pollutants into his effluent. Syntans, usually based on sulphone/phenolsulphonic acid/formaldehyde condensation products, were a great improvement on this. Over the years these have been further improved to give more efficient, less coloured products with lower levels of formaldehyde.

An ever-increasing amount of cotton is being dyed with reactive dyes, and although the dye manufacturers have constantly improved them, together with the associated dyeing techniques, there is still a proportion of the dye that is hydrolysed and attached to the fibre in a non-covalent manner. If this is not dealt with the wet fastness will be poor. The problem can be overcome either by ensuring complete removal of hydrolysed dye by washing-off or by fixation of the hydrolysed dye.

The former will probably demand a large consumption of liquor, the use of detergents and result in the discharge of large volumes of highly coloured liquor. The latter has been

addressed by auxiliary manufacturers for many years in their attempts to improve the fastness properties of reactive dyes. Initially fixing agents used on direct dyes were tried but these were dyestuff dependent, relatively ineffective (particularly for improving wash fastness), adversely affected shade and light fastness, and, being based on dicyandiamide/formaldehyde condensation products, could impart some residual formaldehyde to the fabric.

Allied Colloids has overcome all these objections by using cationic polymer chemistry. However, what is more relevant in the context of this paper is that the amount of washing-off can be considerably reduced because of the very efficient fixation, thus minimising the volume of coloured effluent and additional detergent.

### Finishing

One of the most widely used ranges of finishing agents is that based on urea/formaldehyde and melamine/formaldehyde.

These products serve a whole host of functions including imparting easy-care properties, crease resistance, crease recovery, stiffening, fabric stabilising and anti-pilling properties. They have been, and still are, used at the rate of thousands of tonnes per year. However, one of the major criticisms is the generation of formaldehyde during application and the possibility of retained formaldehyde on the finished goods.

Again acrylic polymers could be regarded as formaldehyde-free alternatives. The sort of handle achievable will depend on the amount applied, but the chemist also has the opportunity to vary the handle by means of changes in molecular weight, the degree of cross linking and comonomer ratios.

Next month the authors take a look at the issue of waste water management within the coloration industry and how improvements can be made as economically as possible.

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## BOOK REVIEW

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**New fibres**, by Tatsuya Hongu and Glyn O Philips (Chichester: Ellis Horwood Limited, 1990) pp xii + 221. Price: £25.00.

This is a fascinating survey of recent (mainly Japanese) developments in biomimetic polymers, super-strong fibres, and 'high-touch' and 'high-tech' textiles. These descriptive terms for 'third-generation' fibres are defined mainly from application properties.

Impressive by any standards are the advances in biomimetic polymers: deodorant viscose fibres containing an iron phthalocyanine artificial enzyme, Furtastic (Toray) artificial fur to imitate the composite structure of natural mink, water-repellent Super-Microft (Teijin) to resemble the lotus leaf surface, Morpho-structured fabrics (Kuraray) to reproduce the brilliant colours of morpho butterfly alae, and black Super-microcrater fibre (Kuraray) emulating the cornea of the night-moth.

The biopolymer frontier between natural polymers and their biomedical applications, such as biomimetic enzyme/coenzyme systems, anti-tumour function and mutagen absorption or elimination, artificial skin tissues, biocosmetics, bacterially produced cellulose and copolyesters, collagen contact lenses and slow-release drug delivery is another scene of rapid progress.

High-tenacity gel-spun polyethylene, liquid crystalline para-aramid and carbon fibres are important in advanced composite materials for aircraft, ocean and space technologies. Liquid crystalline fully aromatic polyesters such as poly-*p*-hydroxybenzoic acid and polyallylate fibres are also challenging these established high-performance polymers.

'High-tech' fibres appeal specifically to the human senses. ultra-fine filaments for artificial leather and glass-cleaning cloths, protein plastics resembling animal skin and skin-like permeable protective outerwear. Enclosing microparticle of zirconium carbide in a nylon or polyester core enable outerwear garments made from these composite filaments to absorb solar radiation efficiently, converting it to infra-red heat released within the clothing. Iridescent effects arise from light interferences, photochromic (u.v. induced) and thermochromic (heat induced) colour changes have been exploited in chameleonic fabrics. Not necessarily universally appealing may be the scented bed linen fibre Cripny (Mitsubishi) and the perfumed pantyhose fibre Esprit (Flours *sic*) (Kanebo), perfume being 'often used in traditional religious ceremonies' (p. 73).

'High-tech' is a collective term for fibres produced by special methods and intended for 'high-tech' applications. Some examples are: blood purification devices (artificial kidney, liver, lung and blood-vessel tissue), virus isolation membranes, ultra-clean rooms for electronics production, design space suits and nuclear protection equipment, improved materials for sportswear, fishing gear and geotextiles.

Presentation and layout of the book are attractive, with numerous clear illustrations and reliable indexes. The style and liberal use of trade names (in capitals) regrettable has a breathless urgency at times. Transitional and print casualties, e.g. 'rhythmn' for rhythm, 'pedal' for petal, 'puffiness', 'irridescence' and 'chromism', are rare. There are 112 references (90% in English) in the concluding bibliography. Students of polymer chemistry and computer technology, as well as many research scientists with fringe involvement in these areas, will benefit by the Japanese inheritors of the Carothers legacy.

JOHN SHC