EUROPEAN COMMISSION



Integrated Pollution Prevention and Control (IPPC)

Reference Document on Best Available Techniques for the Textiles Industry

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This document is one of a series of foreseen documents as below (at the time of writing, not all documents have been drafted):

Full title	BREF code
Reference Document on Best Available Techniques for Intensive Rearing of Poultry and Pigs	ILF
Reference Document on the General Principles of Monitoring	MON
Reference Document on Best Available Techniques for the Tanning of Hides and Skins	TAN
Reference Document on Best Available Techniques in the Glass Manufacturing Industry	GLS
Reference Document on Best Available Techniques in the Pulp and Paper Industry	РР
Reference Document on Best Available Techniques on the Production of Iron and Steel	I&S
Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries	CL
Reference Document on the Application of Best Available Techniques to Industrial Cooling Systems	CV
Reference Document on Best Available Techniques in the Chlor – Alkali Manufacturing Industry	САК
Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry	FMP
Reference Document on Best Available Techniques in the Non Ferrous Metals Industries	NFM
Reference Document on Best Available Techniques for the Textiles Industry	TXT
Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries	REF
Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry	LVOC
Reference Document on Best Available Techniques in the Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector	CWW
Reference Document on Best Available Techniques in the Food, Drink and Milk Industry	FM
Reference Document on Best Available Techniques in the Smitheries and Foundries Industry	SF
Reference Document on Best Available Techniques on Emissions from Storage	ESB
Reference Document on Best Available Techniques on Economics and Cross-Media Effects	ECM
Reference Document on Best Available Techniques for Large Combustion Plants	LCP
Reference Document on Best Available Techniques in the Slaughterhouses and Animals By-products Industries	SA
Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities	MTWR
Reference Document on Best Available Techniques for the Surface Treatment of Metals	STM
Reference Document on Best Available Techniques for the Waste Treatments Industries	WT
Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals (Ammonia, Acids and Fertilisers)	LVIC-AAF
Reference Document on Best Available Techniques for Waste Incineration	WI
Reference Document on Best Available Techniques for Manufacture of Polymers	POL
Reference Document on Energy Efficiency Techniques	ENE
Reference Document on Best Available Techniques for the Manufacture of Organic Fine Chemicals	OFC
Reference Document on Best Available Techniques for the Manufacture of Specialty Inorganic Chemicals	SIC
Reference Document on Best Available Techniques for Surface Treatment Using Solvents	STS
Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals (Solids and Others)	LVIC-S
Reference Document on Best Available Techniques in Ceramic Manufacturing Industry	CER

EXECUTIVE SUMMARY

INTRODUCTION

This reference document on best available techniques in the textile industry reflects an information exchange carried out according to Article 16(2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface, which describes the objective of the document and its use.

This document covers the industrial activities specified in section 6.2 of Annex I of the IPPC Directive 96/61/EC, namely: "Plants for pretreatment (operations such as washing, bleaching, mercerisation) or dyeing of fibres or textiles where the treatment capacity exceeds 10 tonnes per day".

In addition, the BREF contains a number of annexes, which provide supplementary information about textile auxiliaries, dyes and pigments, textile machinery, typical recipes, etc.

The objective of this executive summary is to summarise the main findings of the document. However, since it is impossible to reflect all its complexities in a short summary, only the main text in its entirety should be used as a reference in the determination of BAT for any particular installation.

THE TEXTILE INDUSTRY

The textile industry is one of the longest and most complicated industrial chains in manufacturing industry. It is a fragmented and heterogeneous sector dominated by SMEs, with a demand mainly driven by three main end-uses: clothing, home furnishing and industrial use.

Italy is by far the leading European producer for textiles, followed by Germany, the UK, France and Spain (in that order), together accounting for over 80 % of the production in the EU. Belgium, France, Germany and the UK are the main European producers in the carpets sector.

In 2000 the European textile and clothing industry represented 3.4 % of the EU manufacturing industry's turnover, 3.8 % of the added value and 6.9 % of the industrial employement.

The textile industry is composed of a wide number of sub-sectors, covering the entire production cycle from the production of raw materials (man-made fibres) to semi-processed (yarn, woven and knitted fabrics with their finishing processes) and final products (carpets, home textiles, clothing and industrial use textiles). As the scope of the document is confined to those activities that involve wet processes, three main sub-sectors have been identified: wool scouring, textile finishing (excluding floor-covering) and the carpet sector.

APPLIED PROCESSES AND TECHNIQUES

The textile chain begins with the production or harvest of raw fibre. The so-called "finishing processes" (i.e. pretreatment, dyeing, printing, finishing and coating, including washing and drying) represent the core of the applied processes and techniques in this BREF. Upstream processes such as, for example, synthetic fibre manufacturing, spinning, weaving, knitting, etc. are also briefly described in the document as they may have a significant influence on the environmental impact of the subsequent wet processing activities. The "finishing processes" can take place at different stages of the production process (i.e. on fabric, yarn, loose fibre, etc.), the sequence of treatments being very variable and dependent on the requirements of the final user.

Firstly the finishing treatments are described as unit processes without considering the possible sequences in which they can be applied. Later in Chapter 2, some typical categories of industries have been identified within the wool scouring, the textile finishing and the carpet sector and the process sequences briefly described.

ENVIRONMENTAL ISSUES AND CONSUMPTION & EMISSION LEVELS

The main environmental concern in the textile industry is about the amount of water discharged and the chemical load it carries. Other important issues are energy consumption, air emissions, solid wastes and odours, which can be a significant nuisance in certain treatments.

Air emissions are usually collected at their point of origin. Because they have long been controlled in different countries, there are good historical data on air emissions from specific processes. This is not the case with emissions to water. The various streams coming from the different processes are mixed together to produce a final effluent whose characteristics are the result of a complex combination of factors such as, the types of fibres and make-ups processed, the techniques applied and the types of chemicals and auxiliaries used.

Since data available about water effluents from specific processes is very poor, it has proved appropriate to identify narrow categories of textile mills and to compare the overall mass streams between mills belonging to the same category. This approach allows a preliminary rough assessment in which, by comparing the specific consumption and emission levels of mills within the same category, it is possible to verify given data and identify macroscopic differences between the different activities. Input/output considerations are therefore addressed in the BREF for a number of typical categories of mills, starting from overviews of the overall mass streams and ending in a more detailed analysis of single processes when data is available. The key findings about some processes of particular concern are reported in this summary.

<u>Wool scouring with water</u> leads to the discharge of an effluent with a high organic content (2 to 15 l/kg of greasy wool at about 150 - 500g COD/kg of wool) and variable amounts of micropollutants resulting from the pesticides applied on the sheep. The most common pesticides are organophosphorous (OP), synthetic pyrethroids (SP) and insect growth regulators (IGR). Organochlorine (OC) pesticides are still found on wool from certain grower countries.

A large percentage of the total emission load from textile industry activities is attributable to substances that are already on the raw material before it enters the finishing mill (e.g. impurities and associated materials for natural fibres, preparation agents, spinning lubricants, sizing agents, etc.). All these substances are usually removed from the fibre during the <u>pretreatment</u> process before colouring and finishing. The removal of auxiliaries such as, spinning lubricants, knitting oils and preparation agents by <u>wet treatment</u> may lead to the discharge not only of hard-to-biodegrade organic substances such as mineral oils, but also of hazardous compounds such as polyaromatic hydrocarbons, APEO and biocides. Typical COD loads are in the order of 40 - 80 g/kg fibre. When the substrate is submitted to a <u>dry process</u> (heat-setting) before washing, the auxiliaries present on the substrate become airborne (emission factors of 10 - 16 g C/kg are typical of mineral oil-based compounds).

The washing water from the <u>desizing</u> of cotton and cotton-blend fabrics may contain 70 % of the total COD load in the final effluent. The emission factor can well be in the order of 95 g COD/kg of fabric, with COD concentrations often above 20000 mg COD/l.

<u>Sodium hypochlorite bleaching</u> gives rise to secondary reactions that form organic halogen compounds commonly measured as AOX (trichloromethane accounts for the bulk of the compounds formed). For the combined application of hypochlorite (1^{st} step) and hydrogen peroxide (2^{nd} step) values of 90 - 100 mg Cl/l of AOX have been observed from the exhausted NaClO-bleaching bath. Concentrations up to 6 mg Cl/l can still be found in the spent H₂O₂-bleaching bath, due to the carry over of the substrate from the previous bath.

Compared to sodium hypochlorite, the amount of AOX formed during <u>chlorite bleaching</u> is much lower. Recent investigations have shown that the formation of AOX is not caused by the sodium chlorite itself, but rather by the chlorine or hypochlorite present as impurities or are used as activating agents. The handling and storage of sodium chlorite needs particular attention because of toxicity, corrosion and explosion risks. In <u>hydrogen peroxide bleaching</u> the environmental concerns are associated with the use of strong complexing agents (stabilisers).

A strong alkaline effluent (40 - 50 g NaOH/l) is produced if the rinsing water after <u>mercerising</u> is not recovered or re-used.

Apart from a few exceptions (e.g. the thermosol process, pigment dyeing, etc.), most of the emissions originating from the <u>dyeing process</u> are emissions to water. Water-polluting substances can originate from the dyes themselves (e.g. aquatic toxicity, metals, colour), auxiliaries contained in the dye formulation (e.g. dispersing agents, anti-foaming agents, etc.), basic chemicals and auxiliaries used in dyeing processes (e.g. alkali, salts, reducing and oxidising agents, etc.) and residual contaminants present on the fibre (e.g. residues of pesticides on wool, spin finishes on synthetic fibres). Consumption and emission levels are strongly related to the type of fibre, the make-up, the dyeing technique and the machinery employed.

In <u>batch dyeing</u>, the concentration levels vary greatly in the dyeing sequence. Generally, spent dye baths have the highest concentration levels (values well above 5000 mg COD/l are common). The contribution of dyeing auxiliaries (e.g. dispersing and levelling agents) to the COD load is especially noticeable when dyeing with vat or disperse dyes. Operations like soaping, reductive aftertreatment and softening are also associated with high values of COD. Rinsing baths show concentrations 10 - 100 times lower than the exhausted dyeing bath and water consumption 2 to 5 times higher than for the dyeing process itself.

In <u>continuous and semi-continuous dyeing</u>, the water consumption is lower than in batch dyeing processes, but the discharge of highly concentrated residual dyeing-liquors can result in higher pollution load when short runs of material are processed (COD attributable to the dyestuffs may be in the order of 2 - 200 g/l). The padding technique is still the most commonly applied. The quantity of liquor in the padder can range from 10 - 15 litres for modern designs to 100 litres for conventional padders. The residual amount in the preparation tank can range from a few litres under optimised control conditions to up to 150 - 200 l. The total quantity of residual liquor increases with the number of batches per day.

Typical emission sources in <u>printing</u> processes include printing paste residues, waste water from wash-off and cleaning operations and volatile organic compounds from drying and fixing. Losses of printing pastes are particularly noticeable in rotary screen printing (losses of 6.5 - 8.5 kg per colour applied are common for textiles). With short runs (i.e. less than 250 m) the amount of losses may be higher than the quantity of paste printed on the textile substrate. Water consumption levels for cleaning of the equipment at the end of each run are in the order of about 500 l (excluding water for cleaning the printing belt). Printing pastes contain substances with high air emission potential (e.g. ammonia, formaldehyde, methanol and other alcohols, esters, aliphatic hydrocarbons, monomers such as, acrylates, vinylacetate, styrene, acrylonitrile, etc.).

Since most <u>continuous finishing</u> processes do not require washing operations after curing, water emissions are restricted to the system losses and to the water used to clean the equipment. The amount of residual liquors is in the range of 0.5 to 35 % of the total amount of finishing liquor prepared (the lower value is for integrated mills, whereas higher values are typical of textile mills processing small lots and different types of substrates). Too often these liquors are drained and mixed with other effluents. The COD concentration can easily be in the range of 130 - 200 g/l. Often the ingredients of the finishing formulations are non-biodegradable, nonbioeliminable and sometimes also toxic (e.g. biocides). In the drying and curing operations, air emissions are associated with the volatility of the ingredients of the formulations and with the carry-over from upstream processes (e.g. textiles previously treated with chlorinated carriers or perchloroethylene). <u>Water washing</u> processes contribute to water and energy consumption. The polluting load of the washing water is related to the pollutants carried by the water stream (e.g. impurities removed from the fabric, chemicals from previous processes, detergents and other auxiliaries used during washing). The use of organic halogenated solvents (persistent substances) for <u>dry cleaning</u> may give rise to diffuse emissions, resulting in groundwater and soil pollution and may also have negative effects on the air emissions from high-temperature downstream processes.

TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

General good management practices

General good management practises range from <u>staff education and training</u> to the <u>definition of</u> <u>well-documented procedures</u> for equipment maintenance, chemical storage, handling, dosing and dispensing. <u>Improved knowledge of the inputs and outputs of the process</u> is also an essential part of good management. This includes inputs of textile raw material, chemicals, heat, power and water, and outputs of product, waste water, air emissions, sludge, solid wastes and by-products. Monitoring process inputs and outputs is the starting point for identifying options and priorities for improving environmental and economic performance.

Measures for <u>improving the quality and quantity of chemicals used</u> include regular revision and assessment of the recipes, optimal scheduling in production, use of high quality water in wet processes, etc. Systems for automated control of process parameters (e.g. temperature, liquor level, chemicals feed) allow a tighter control of the process for improved right-first-time performance, with minimum surplus of applied chemicals and auxiliaries.

<u>Optimising water consumption</u> in textile operations starts with controlling water consumption levels. The next step is reducing water consumption, through a number of often-complementary actions. These include improving working practices, reducing liquor ratio in batch processing, increasing washing efficiency, combining processes (e.g. scouring and desizing) and re-using/recycling water. Most of these measures allow significant savings not only in water consumption, but also in energy consumption because energy is used to a great extent to heat up the process baths. Other techniques are specifically focused on <u>optimising the use of energy</u> (e.g. heat-insulation of pipes, valves, tanks and machines, segregation of hot and cold waste water streams and recovery of heat from the hot stream).

Quality management of incoming fibre

Information about textile raw materials is the first step to tackle pollution carried over from upstream processes. Information from the supplier should include not only the technical characteristics of the textile substrate, but also the type and amount of preparation agents and sizing agents, residual monomers, metals, biocides (e.g. ectoparasiticides for wool) present on the fibre. Various techniques are available that can significantly reduce the environmental impact originating from upstream processes.

As for <u>pesticides residues</u> on raw wool fibre, a number of organisations maintain information on the pesticides content of greasy and scoured wool. Manufacturers can use this information to minimise at source any legally used pesticides such as OP and SP ectoparasiticides, and to avoid processing wool contaminated with the most hazardous chemicals, such as OC pesticides, unless an analytical certificate is provided. In the absence of information, samples should be assayed to confirm their pesticide content, but this option entails higher costs for the manufacturer. Currently co-operation programmes between trade associations and leading grower countries have resulted in a progressive reduction of the average OP and SP residues on wool, along with the development of low-residue certification schemes.

Improvements are also possible for auxiliaries, such as, preparation agents, spinning lubricants and knitting oils. <u>Substitutes for mineral oils</u> are now available for most applications. Alternative compounds have a high level of biodegradability or at least bioeliminability; they are also less volatile and more thermally stable than mineral oils. This helps to reduce odour nuisance and air emissions, which can occur when the substrate is submitted to high-temperature treatments such as thermofixation.

The combination of low add-on techniques such as <u>pre-wetting of the warp yarns</u> or <u>compact</u> <u>spinning</u>, with the targeted <u>selection of sizing agents</u> helps to reduce the environmental impact of the desizing process. It is now accepted that readily biodegradable or bioeliminable compounds are available, covering all needs. Moreover, latest generation-polyacrylates are highly efficient with lower add-on and can be completely and easily removed from the fabric.

In general, integrated mills have the means to control the source of their raw material and chemicals applied on the fibre. For non-integrated companies (particularly for commission companies), it is more difficult to influence the up-stream suppliers. Conventional formulations are typically cheaper. Raw material suppliers (e.g. spinning, knitting mills) look mainly at the economic aspects and at the performance of the given substance in their own process, rather than at the environmental problems produced in the downstream processes (at the finishing mill). In these cases it is necessary to work with clients to eliminate these materials from the supply chain.

Selection and substitution of chemicals used

A number of schemes for ecotoxicological assessment and classifications of chemicals have been proposed by the TWG for consideration in the determination of BAT. Based on these tools, substitution of the harmful substances is often an available option to reduce the environmental impact of a process.

<u>Surfactants</u> are used for many different purposes in the textile industry (e.g. detergents, lubricants, etc.). Some surfactants are considered problematic because of their poor biodegradability and toxicity to aquatic species. Concerns currently focus on APEO and in particular NPE. The main alternatives for APEO are fatty alcohol ethoxylates, but also for other surfactants substitutes are often available that are readily biodegradable or bioeliminable in the waste water treatment plant and that do not form toxic metabolites.

<u>Complexing agents</u> can often be avoided. Nevertheless, when they need to be used, compounds are available as an alternative to conventional sequestering agents that are readily biodegradable or at least bioeliminable and that do not contain N or P in their molecule (e.g. polycarbonates, polyacrylates, gluconates, citrates and some sugar-acrylic acid copolymers). Costs are comparable, although higher quantities may be necessary in some cases.

<u>Antifoaming agents</u> are often based on mineral oils. Typical active ingredients in mineral oilfree products are silicones, phosphoric esters, high molecular alcohols, fluorine derivatives and mixtures of these components. Silicones are eliminated only by abiotic processes in waste water and above certain concentrations they hinder the transfer/diffusion of oxygen into the activated sludge. Tributylphosphates are odour intensive and strongly irritant and high molecular-weight alcohols are odour intensive and cannot be used in hot liquors.

Wool scouring

The implementation of <u>dirt removal/ grease recovery loops</u> allows water and energy savings (net specific water consumption figures of 2 - 4 l/kg greasy wool have proven to be achievable for coarse and fine wool). Additionally, a valuable by-product is obtained (25 to 30 % of the grease estimated to be present in the wool scoured), along with a significant reduction of the organic load sent to the effluent treatment plant. If the <u>dirt removal/ grease recovery loop is combined</u> with evaporation of the effluent and incineration of the sludge, with full recycling of the water and energy, additional environmental benefits are achieved in terms of water savings and amount of solid waste to be disposed of. Nevertheless, the technology is complex and is reported to involve very high capital costs and high running costs.

<u>Wool scouring with organic solvents</u> avoids the use of water in the actual cleaning process. The only source of water emission is moisture introduced with the wool, steam used in vacuum ejectors and moisture recovered from air drawn into the equipment. This water is contaminated with perchloroethylene (PER). To avoid any risk of diffuse emissions, the water stream is treated in two steps, comprising a solvent air stripping unit and a residual solvent destruction

unit. Since pesticides partition strongly to the solvent and are removed with the grease, the clean wool is reported to be pesticide free. This has beneficial implications for the downstream processes where the wool is finished. Another positive effect of this technique is the reduced energy consumption, due to the low latent heat of an organic solvent compared to water.

Pretreatment

Water-soluble synthetic sizing agents such as PVA, polyacrylates and CMC can be recovered from washing liquor by UF and re-used in the process. Recently, it has been confirmed that modified starches such as carboxymethyl starch can also be recycled. However, re-use in the weaving plant is not always without problems. To date, the weavers' acceptance of recovered sizes is still limited. Furthermore, long-distance shipments cancel out any ecological advantages because the liquor needs to be transported in adequate conditions in insulated tankers. For these reasons, sizing agents are usually only recovered in integrated mills which have a weaving and a finishing section at the same site.

For non integrated mills that deal with many different types of fabrics and find it more difficult to have a direct control on the source of the raw fabric, a viable option is the <u>oxidative route</u>. Under specific conditions (i.e. above pH 13), H₂O₂ will generate free radicals which efficiently and uniformly degrade all sizes and remove them from the fabric. The process produces shorter and less branched pre-oxidised molecules, which are easier to wash out (with a reduced amount of water) and easier to degrade in the waste water treatment plant. It is desirable to combine alkaline peroxide bleaching with scouring and regulate the counter-current flow of alkali and peroxide through the different pretreatment steps, so as to save water, energy and chemicals.

<u>Hydrogen peroxide</u> is now the preferred bleaching agent for cotton and cotton blends as a substitute for <u>sodium hypochlorite</u>, although it is claimed that sodium hypochlorite is still necessary for high whiteness and for fabrics that are fragile and would suffer from depolymerisation. In these cases, a two-stage process first with hydrogen peroxide and then with sodium hypochlorite can be applied, in order to reduce AOX emissions (the impurities on the fibre – which act as precursors in the haloform reaction – are removed in the first step). A two-stage bleaching process using only hydrogen peroxide is also possible today, which completely avoids the use of hypochlorite. This option is however reported to be from two to six times more expensive.

There is also increasing support for peroxide bleaching under strong alkaline conditions, which can achieve a high degree of whiteness after careful removal of catalysts by a reduction/extraction technique. The additional advantage claimed is the possible combination of scouring and bleaching. The reduction/extraction followed by a strong oxidative combined bleaching/scouring step is applicable for bleaching highly contaminated textiles in all make-ups and on all types of machines (discontinuous and continuous).

<u>Chlorine dioxide</u> (from sodium chlorite or chlorate) is an excellent bleaching agent for synthetic fibres and for flax, linen and other bast fibres that cannot be bleached using peroxide alone. Recent technologies (using hydrogen peroxide as the reducing agent of sodium chlorate) are now available to produce ClO_2 without generation of AOX (elemental chlorine-free bleach).

The rinsing water after the <u>mercerising</u> treatment (so-called "weak lye") can be recycled in the process after being concentrated by evaporation.

Dyeing

Well-known PES dyeing <u>carriers</u> can be avoided (except for PES/WO and elastane/WO blends) by dyeing under high-temperature conditions. Another attractive option is the use of non-carrier dyeable PES fibres, such as polytrimethylene terephthalate (PTT) polyester fibres. However, due to differences in physical and mechanical properties, these fibres do not cover exactly the same product market and cannot be regarded as "substitutes" for PET-based polyester fibres. When carriers cannot be avoided, conventional active substances - based on chlorinated aromatic compounds, o-phenylphenol, biphenyl and other aromatic hydrocarbons - can be replaced with less harmful compounds such as, benzylbenzoate and N-alkylphthalimide.

In order to avoid the use of sodium hydrosulphite in <u>PES after-treatment</u>, two different approaches are proposed: the use of reducing agents based on a special short-chain sulphinic acid derivatives or the use of disperse dyes that can be cleared in alkaline medium by hydrolytic solubilisation instead of reduction. Short-chain sulphinic acid derivatives are biodegradable, non-corrosive, have very low toxicity and, unlike hydrogen hydrosulphite, they can be applied in acidic conditions without the need for repeated bath changes and shifts in pH (water and energy savings). With alkali-clearable dyes the use of hydrosulphite or other reducing agents can be avoided altogether.

<u>Dispersing agents</u> typically present in disperse, vat and sulphur dye formulations have been improved by: 1) their partial substitution with optimised products based on fatty acid esters, or 2) the use of mixtures of modified aromatic sulphonic acids. The first option is only applicable for liquid formulations of disperse dyes (the dyestuff pallette is currently limited). These dispersing agents are bioeliminable and their amount in the formulation can be significantly reduced compared to conventional formulations. The dispersing agents indicated in the second option show a higher degree of bioelimination compared to the conventional condensation products of naphthalene sulphonic acid with formaldehyde. They can be used both for disperse and vat dyes (solid and liquid formulations).

Pre-reduced <u>sulphur dyestuffs</u> (liquid formulations with sulphide content <1 %) or non-prereduced sulphide-free dyestuffs are available in various different forms (water-soluble in the oxidised, powder, liquid form, or in stable suspension). All these dyestuffs can be reduced without any sodium sulphide, using glucose alone (only in one case) or in combination with dithionite, hydroxyacetone or formamidine sulphinic acid. Stabilised non-pre-reduced sulphidefree dyestuffs are reported to be more expensive than the other types of sulphur dyes.

Poor dye fixation has been a long-standing problem with reactive dyeing in particular in batch dyeing of cellulose fibres, where a significant amount of salt is normally added to improve dye exhaustion. With the use of sophisticated molecular engineering techniques it has been possible to design <u>bifunctional</u> and <u>low-salt reactive dyes</u> that can attain >95 % fixation rate even for cellulosic fibres, with considerably higher performance (reproducibility and level dyeing) than traditional reactive dyes. Hot rinsing avoids <u>the use of detergents and complexing agents</u> in the rinsing and neutralisation steps after dyeing. Substituting cold rinsing with hot rinsing leads to higher energy consumption, unless thermal energy from the rinsing effluent is recovered.

The use of sodium silicate in <u>pad-batch dyeing of cellulosic fabrics</u> can be avoided thanks to silicate-free highly concentrated aqueous solutions, which are ready-made products easily applicable with modern dosing systems. An alternative process is also described, which doesn't require the addition of substances such as urea, sodium silicate and salt, or long dwell-time to fix the dyes. The process itself is simple and highly versatile and is applicable to a wide variety of fabrics, regardless of the size of the lot. Significant savings can be achieved thanks to higher productivity, reduced consumption of chemicals and energy and the reduced waste water pollution to treat. Nevertheless due to the initial high capital investment, this technique fits better in new installations and in those seeking to replace equipment.

Quite recently, <u>new reactive dyestuffs</u> have come on the market that can provide very good levels of fastness, even equivalent with those achievable with chrome dyes, even for dark shades. However, the importance of reactive dyes is only slowly increasing due to a number of reasons, including difficulties of the operators accepting radical changes to a well-established procedure. Moreover, some finishers still consider that chrome dyes are the only ones that can guarantee the level of fastness required for overdyeing. When chrome dyes are used, <u>low-chrome and ultra-low stoichiometric chrome dyeing</u> techniques can be adopted to minimise the amount of residual chromium in the final effluent. With ultra-low chroming an emission factor of 50 mg chromium per kg of wool treated is achieved, which corresponds to a chromium concentration of 5 mg/l in the spent chroming bath when a 1:10 liquor ratio is used.

In general, with pH-controllable dyes (e.g. acid and basic dyes) it is advantageous to dye at isothermal conditions imposing a pH profile. One of the advantages over temperature-controlled dyeing processes is that maximum exhaustion of dyes and insect resist agents can be achieved with only a minimum use of organic levelling agents. When dyeing wool with metal-complex dyes, higher levels of exhaustion and fixation rate can be achieved by controlling the pH and by using special auxiliaries with high affinity for the fibre and dyestuff. The higher exhaustion rate directly correlates with the reduced residual chromium levels in the spent dye bath (10 - 20 mg/kg of treated wool, corresponding to 1 - 2 mg/l of chromium in the spent dye bath with 1:10 L.R.). The referenced technique has been designed for dyeing loose wool fibre and combed tops, but the same performances can also be achieved with other make-ups by using pH-controlled methods to maximise final bath exhaustion.

Various techniques are described in the BREF aimed at improving the environmental performance of batch and continuous dyeing processes in general. A distinct trend has developed among <u>batch dyeing machinery</u> manufacturers toward reducing bath ratios. Moreover, an outstanding feature of modern machines is that they can be operated at approximately constant liquor ratio whilst being loaded much below their nominal capacity. This is especially advantageous for commission companies, who typically need high production flexibility. Furthermore, various functions typical of continuous processing have been transferred to batch machines, which allow maximum cut-off between different batches and thereby open up further options for re-use of the dye bath and improved treatment of the concentrated streams.

As for <u>continuous dyeing processes</u>, reduction of system losses can be achieved by carrying out the impregnation step in a nip or by minimising the capacity of the dip trough (e.g. flex-shaft, U-shaft). Additional improvements are obtained by dispensing the dyestuff and auxiliaries as separate streams and by dosing the padding liquor based on measurement of the pick-up. The amount of dyeing liquor consumed is measured by reference to the quantity of processed fabric. The resulting values are automatically processed and used for the preparation of the next comparable batch in order to minimise residues of unused dyeing liquor. This system, however, cannot avoid the presence of residual dye liquor in the feeding tank. The rapid batch dyeing technique represents a further improvement because, rather than being prepared in a single step (for the whole batch) before starting the dyeing batch, the dyestuff solution is prepared just in time, in several steps, based on on-line measurement of the pick-up.

Printing

Minimising the volume of the printing paste supply system (i.e. diameters of pipes and squeegees) has major effects in reducing printing paste losses in <u>rotary-screen printing</u>. A further reduction can be achieved by improving paste recovery from the supply system itself. A recent technique consists in inserting a ball in the squeegee, before filling the system. At the end of a print run, the ball is pressed back, thus pumping the printing paste in the supply system back into the drum for re-use. Today, computer-assisted systems offer more opportunities for recycling printing pastes. Printing paste recovery and recycling systems are applied in textile finishing mills (for flat fabrics), but not for carpets. The main reason is that guar-gum (the most common thickener used for carpets) has a limited shelf-life (biodegradable compound) and therefore it cannot be stored for a long time before re-use.

Screens, buckets and the print paste feed systems need careful <u>cleaning</u> before being used for new colours. There are several inexpensive ways of reducing water consumption (e.g. start/stop control of cleaning of the printing belt, re-use of the rinsing water from the cleaning of the printing belt, etc.).

An alternative to analogue printing is the use of <u>digital techniques</u>, which are gaining importance in the textile and in the carpet sector. In digital printing the selected dyes are dosed on-demand, based on computed requirements. This avoids printing paste residues at the end of each run.

Digital <u>ink-jet printing</u> is suitable for flat fabrics. However, production speeds are still too low to allow this technique to replace traditional analogue printing. Nevertheless ink-jet printing can already offer significant advantages over analogue printing in the production of short runs.

The latest improvement in jet printing machines for carpet and bulky fabrics is now represented by machines in which the colour is injected with surgical precision deep into the face of the fabric without any machine parts touching the substrate. Here, the control of the quantity of liquor applied to the substrate (which may vary for example from lightweight articles to heavy quality fabrics) is achieved by varying not only the "firing time" but also the pumping pressure.

Urea content in <u>reactive printing</u> paste can be up to 150g/kg paste. Urea can be substituted in the one-step process by controlled addition of moisture either by the foaming technique or by spraying a defined quantity of water mist. However, for silk and viscose articles, it is not possible to avoid the use of urea with the spraying system. The technique is not reliable enough to ensure a uniform dosage of the low moisture add-on required for these fibres.

The foaming technique, on the contrary, has proven successful for viscose in complete elimination of urea. This technique should in principle be technically viable also for silk, although it has not yet been proven. Silk is known to be less problematic as a fibre than viscose, but it is typically processed in smaller runs. Without using the foam technique, the amount of urea consumed can be reduced to about 50 g/kg of printing paste for silk and 80 g/kg for viscose.

Another option for avoiding the use of urea, although more complex and slower, is the two-step printing method.

Although water-in-oil thickeners seem no longer to be applied in Europe and half-emulsion printing pastes (oil in water) are only occasionally used, hydrocarbons (predominantly aliphatic) are still found in exhaust air, mainly arising from mineral oils contained in synthetic thickeners. Their emission potential can be up to 10 g Org.-C/kg textile. New generation <u>thickeners</u> contain minimal amounts of volatile organic solvents, if any. Furthermore, optimised printing pastes are APEO-free, have a reduced ammonia content and contain formaldehyde-poor binders.

Finishing

In order to reduce pick-up, so-called <u>minimum application techniques</u> (e.g. kiss-roll, spray and foaming application systems) are gaining importance as substitutes for padding systems. In addition, various techniques are available for reducing <u>energy consumption in stenter frames</u> (e.g. mechanical dewatering equipment to reduce water content of the incoming fabric, optimising control of exhaust airflow through the oven, installation of heat recovery systems).

For each finishing process there are techniques for the reduction of the environmental impact associated with the specific substances used. The BREF focuses only on a few finishing processes. In <u>easy-care treatments</u>, emissions of formaldehyde (suspect carcinogenic) can be significantly reduced with low-formaldehyde or formaldehyde-free products (<75 mg/kg textile, or even lower than 30 ppm for consumer requirement).

General techniques to minimise emissions of <u>mothproofing agent</u> include handling procedures to minimise spillage during dispensing and transport of mothproofing agent concentrates within the dyehouse, as well as special operating techniques to achieve lowest residues of active substance in the spent dyeing liquor and rinse water. Two effective measures are 1) to ensure that a pH<4.5 is reached at the end of the dyeing process (when and if this is not possible, apply the insect resist agent in a separate step with re-use of the bath) and 2) to avoid the use of dyeing auxiliaries that exert a retarding action on the uptake of insect resist agents, (e.g. levelling agent, PA blocking agent).

Other techniques include proportional overtreatment, application of the mothproofer from the low-volume bowl at the end of the yarn scouring line, application of the IR agent directly to the pile of the carpet during back-coating or latexing operation, etc. The application of these techniques is specific for each of the three identifiable routes for yarn manufacture, i.e. by the "dry spinning route", "loose fibre dyed/ yarn scoured production" and "yarn dyed production".

The application of <u>softeners</u> by pad mangles or by spraying or foaming application systems give better environmental performance than batch softening directly in the dyeing machine after dyeing. The use of cationic softening agents can be avoided and any chemical loss can be reduced to a few percent. Another advantage is that it is then possible to re-use the dyeing or rinse baths as there is no longer a problem with the presence of residual cationic softeners, which would otherwise limit the adsorption of the dye in the subsequent dyeing process.

Washing

"Drain and fill" and "smart rinsing" are both more efficient <u>batch washing</u> techniques than conventional overflow rinsing. Moreover, modern machines are equipped with time-saving devices and other special systems in order to avoid typical limitations of the traditional "drain and fill" method (e.g. longer production cycle time, etc.). With both "smart rinsing" and "drain & fill" it is possible to keep the exhausted concentrated dye liquor and the rinsing waters as separate streams (waste streams segregation and water and energy recovery).

In <u>continuous washing</u>, water and energy conservation should start from the application of simple good housekeeping measures. These can range from the definition of the optimum flow by means of flow control devices on washers, to the installation of stop valves that shut off the water flow as soon as a stoppage occurs. Further improvements can be achieved by increasing the washing efficiency, mainly by counter-current washing and reduction of carry-over (e.g. vacuum extractors). Installing heat recovery equipment on a continuous washer is usually a simple and effective measure.

New installations for <u>washing with halogenated organic solvents</u> are fitted with closed-loop active charcoal filters, thereby avoiding any air-stream exhaustion to the outside environment. In order to minimise emissions of water contaminated with PER, most of the water-dissolved PER is extracted and recovered through a two-stage process involving air-stripping and absorption on active charcoal (PER <1 mg/l in the final effluent). Since the water flow is fairly low ($\leq 0.5 \text{ m}^3$ /h) advanced oxidation processes (e.g. the Fenton process) are suitable for treating this effluent on site. Furthermore the complete redesign of the main distilling section has drastically reduced the solvent residue in the sludge (1 % by weight compared to over 5 % in conventional installations).

Waste water treatment

Hardly-biodegradable compounds can still be degraded in biological plants under low food-tomass-ratio (F/M) conditions, but non-biodegradable substances are not degraded in biological plants. Concentrated waste water streams containing such compounds should be treated at source. For the textile finishing industry, advanced oxidation with a Fenton-like reaction is proposed as a viable pretreatment technique (depending on the type of effluent, COD removal can reach 70 - 85 % and the residual COD, which is largely biodegradable because of the modification of the compounds, is suitable for biological treatment). However, very strong residues such as residual printing paste and padding liquors can more conveniently be kept out of the waste water stream altogether and other disposal routes used.

For waste water containing pigment printing paste or latex from carpet backing, precipitation/flocculation and incineration of the resulting sludge is a viable alternative to chemical oxidation. Moreover, for azo-dyes, anaerobic treatment of padding liquor and printing pastes before a subsequent aerobic treatment is effective for colour removal.

The following techniques are proposed in order to achieve equivalent performance when treating a mixed effluent:

- tertiary treatments following the biological treatment process, such as adsorption on activated carbon with recycling of the activated carbon to the activated sludge system and destruction of the adsorbed non-biodegradable compounds by incineration or radical treatment of the excess sludge (biomass and spent activated carbon)
- combined biological physical and chemical treatments with the addition of powdered activated carbon and iron salt to the activated sludge system with reactivation of the excess sludge by "wet oxidation" or "wet peroxidation" (if hydrogen peroxide is used)
- ozonation of recalcitrant compounds prior to the activated sludge system.

For <u>wool scouring waste water</u> a number of different scenarios are discussed. The environmental performance of an evaporation plant is far superior to that of a flocculation plant. However, the initial cost of the evaporation plant seems to be much higher and payback (versus discharge to sewer) takes 4 - 5 years for small mills (3500 t/yr of wool). For medium-sized mills (15000 t/yr of wool), evaporation is slightly cheaper than flocculation over 10 years. The use of a dirt removal/grease recovery loop in combination with evaporation makes evaporation even more attractive because a smaller evaporator can be installed, which thereby reduces initial capital outlay. The use of a recovery loop also allows a reduction in running costs thanks to the proceeds from the sales of the grease (this effect is more significant for fine wool scouring mills).

The combination of a dirt removal/ grease recovery loop with evaporation of the effluent and incineration of the sludge with full recycling of water and energy is the best option from an environmental point of view. However, the complexity of the technique and the initial capital cost make it more suitable for 1) new installations, 2) existing installations with no on-site effluent treatment and 3) installations seeking to replace life-expired effluent treatment plant.

In the case of effluent treatment by biological processes it is known that there are scourers in Europe (particularly in Italy) using biological processes as their main methods of effluent treatment. However, no precise information has been submitted.

<u>Wool scour sludge</u> has been proven to have excellent technical properties when mixed with clay for brick-making. The economics are greatly dependent on the deal between the scourer and the brick-maker. According to reported information, the technique should be cheaper than landfilling, composting and incineration. No information is submitted in the BREF about other recycling options available.

GENERIC BAT (WHOLE TEXTILE INDUSTRY)

Management

It is recognised that technology improvements need to go together with environmental management and good housekeeping. Management of an installation that uses potentially polluting processes requires the implementation of many of the elements of an Environmental Management System (EMS). The implementation of a monitoring system for process input and output is a prerequisite for identifying priority areas and options for improving environmental performance.

Dosing and dispensing of chemicals (excluding dyes)

BAT is to install automated dosing and dispensing systems which meter the exact amounts of chemicals and auxiliaries required and deliver them directly to the various machines through pipework without human contact.

Selection & use of chemicals

BAT is to follow certain general principles in selecting chemicals and managing their use:

- where it is possible to achieve the desired process result without the use of chemicals, then avoid their use altogether
- where this is not possible, adopt a risk-based approach to selecting chemicals and their utilisation mode in order to ensure the lowest overall risk.

There are a number of lists and classification tools for chemicals. Modes of operation that ensure the lowest overall risk include techniques such as closed-loops and the in-loop destruction of pollutants. Of course, it is essential that due recognition be given to relevant Community legislation.

Following these principles, a number of detailed BAT conclusions arise in particular for surfactants, complexing and antifoaming agents. More details are found in Chapter 5.

Selection of incoming fibre raw material

It is recognised that knowledge of the quality and quantity of substances (e.g. preparation agents, pesticides, knitting oils) applied on the fibre during the upstream processes is essential to enable the manufacturer to prevent and control the environmental impact resulting from these substances. BAT is to seek collaboration with upstream partners in the textile chain in order to create a chain of environmental responsibility for textiles. It is desirable to exchange information on the type and load of chemicals that are added and remain on the fibre at each stage of the product's life cycle. A number of BAT were identified for different raw materials:

- man-made fibres: BAT is to select material treated with low-emission and biodegradable/ bioeliminable preparation agents
- cotton: the main issues are the presence of hazardous substances such as PCP and the quality and quantity of sizing agents used (selection of material sized with low add-on techniques and high-efficiency bioeliminable sizing agents). Preference should be given to organically grown cotton when market conditions allow
- wool: emphasis is given to using available information and to encouraging collaboration initiatives between competent bodies in order to avoid processing wool contaminated with OC pesticides and minimise at the source any legally used sheep ectoparasiticides. The selection of wool yarn spun with biodegradable spinning agents instead of formulations based on mineral oils and/or containing APEO is also part of BAT.

All measures assume that the fibre raw materials for textile processing are produced with some sort of quality assurance scheme, so that the finisher can get the appropriate information about the types and amounts of contaminants.

Water & energy management

Water and energy savings are often related in the textile industry because the main use of energy is to heat up the process baths. BAT starts from the monitoring of water and energy consumption in the various processes along with improved control of process parameters. BAT includes the use of machinery with reduced liquor ratio in batch processing and low add-on techniques in continuous processing, applying the latest techniques to improve washing efficiency. BAT is also to investigate possibilities for water re-use and recycling by a systematic characterisation of quality and volume of the various process streams.

WOOL SCOURING

Wool scouring with water

BAT is to use recovery loops for grease and dirt. BAT-associated values for water consumption are 2 to 4 l/kg of greasy wool for medium and large mills (15000 tonnes/year of greasy wool) and 6 l/kg for small mills. Associated values for grease recovery range between 25 and 30 % of the grease estimated to be present in the scoured wool. Likewise, BAT-associated values for energy consumption are 4 - 4.5 MJ/kg greasy wool processed, comprising approximately 3.5 MJ/kg thermal energy and 1 MJ/kg electrical energy. However, due to the lack of data it is

not possible to define whether the above-mentioned BAT associated values for water and energy consumption are also applicable to extra-fine wool (fibre diameter typically in the order of $20\mu m$ or less).

Wool scouring with organic solvent

Scouring with organic solvent is determined as BAT, provided that all measures are taken to minimise fugitive losses and prevent any possible contamination of groundwater arising from diffuse pollution and accidents. Details about these measures are described in Section 2.3.1.3.

TEXTILE FINISHING AND CARPET INDUSTRY

Pretreatment

Removing knitting lubricants from fabric

BAT is to do one of following:

- select knitted fabric that has been processed using water-soluble and biodegradable lubricants instead of the conventional mineral oil-based lubricants (see Section 4.2.3). Remove them by water washing. With knitted fabrics made of synthetic fibres the washing step needs to be carried out before thermofixation (to remove the lubricants and avoid them being released in the form of air emissions)
- carry out the thermofixation step before washing and treat the air emissions generated from the stenter frame by dry electrofiltration systems that allow energy recovery and separate collection of the oil. This will reduce the contamination of the effluent (see Section 4.10.9)
- remove the non-water soluble oils using organic solvent washing. The requirements described in Section 2.3.1.3 are then taken, along with provisions for the in-loop destruction of the persistent pollutants (e.g. by advanced oxidation processes). This will avoid any possible contamination of groundwater arising from diffuse pollution and accidents. This technique is convenient when other non water-soluble preparation agents, such as silicone oils, are present on the fabric.

Desizing

BAT is to do one of the following:

- select raw material processed with low add-on techniques (e.g. pre-wetting of the warp yarn, see 4.2.5) and more effective bioeliminable sizing agents (see 4.2.4) combined with the use of efficient washing systems for desizing and low F/M waste water treatment techniques (F/M <0.15 kg BOD₅/kg MLSS·d, adaptation of the activated sludge and temperatures higher than 15 °C see 4.10.1) to improve the bioeliminability of the sizing agents
- adopt the oxidative route when it is not possible to control the source of the raw material (see Section 4.5.2.4)
- combine desizing/scouring and bleaching in one single step, as described in Section 4.5.3.
- recover and re-use the sizing agents by ultrafiltration as described in Section 4.5.1.

Bleaching

BAT is to:

- use hydrogen peroxide bleaching as preferred bleaching agent combined with techniques for minimising the use of hydrogen peroxide stabilisers, as described in Section 4.5.5, or using biodegradable/bioeliminable complexing agents described in Section 4.3.4
- use sodium chlorite for flax and bast fibres that cannot be bleached with hydrogen peroxide alone. A two-step hydrogen peroxide-chlorine dioxide bleaching is the preferred option. It must be ensured that elemental chlorine-free chlorine dioxide is used. Chlorine-free chlorine dioxide is produced using hydrogen peroxide as the reducing agent of sodium chlorate (see Section 4.5.5)
- limit the use of sodium hypochlorite only to cases in which high whiteness has to be achieved and to fabrics that are fragile and would suffer depolymerisation. In these special cases, to reduce the formation of hazardous AOX, sodium hypochlorite bleaching is carried out in a two-step process in which peroxide is used in the first step and hypochlorite in the second. Effluent from hypochlorite bleaching is kept separate from the other streams and mixed effluents in order to reduce formation of hazardous AOX.

Mercerising

BAT is to either:

- recover and re-use alkali from mercerising rinsing water as described in Section 4.5.7
- or re-use the alkali-containing effluent in other preparation treatments.

Dyeing

Dosage and dispensing of dye formulations

BAT is to do all the following:

- reduce the number of dyes (one way to reduce the number of dyes is by using trichromatic systems)
- use automated systems for dosage and dispensing of dyes, only considering manual operation for dyes that are used infrequently
- in long continuous lines where the dead volume of the distribution line is comparable with the volume in the padder, give preference to decentralised automated stations that do not premix the different chemicals with the dyes before the process and that are fully automatically cleaned.

General BAT for batch dyeing processes

BAT is to:

- use machinery fitted with: automatic controllers of fill volume, temperature and other dyeing cycle parameters, indirect heating & cooling systems, hoods and doors to minimise vapour losses
- choose the machinery that is most fitted to the size of the lot to be processed to allow its operation in the range of nominal liquor ratios for which it is designed. Modern machines can be operated at approximately constant liquor ratio whilst being loaded at a level as low as 60 % of their nominal capacity (or even 30 % of their nominal capacity with yarn dyeing machines) (see Section 4.6.19)
- select new machinery according as far as possible to the requirements described in Section 4.6.19:
 - ➢ low- or ultra-low liquor ratio
 - ➢ in-process separation of the bath from the substrate
 - > internal separation of process liquor from the washing liquor
 - > mechanical liquor extraction to reduce carry-over and improve washing efficiency
 - \blacktriangleright reduced duration of the cycle.
- substitute overflow-flood rinsing method in favour of drain and fill or other methods (smart rinsing for fabric) as described in Section 4.9.1
- re-use rinse water for the next dyeing or reconstitution and re-use the dye bath when technical considerations allow. This technique (see Section 4.6.22) is easier to implement in loose fibre dyeing where top-loading machines are used. The fibre carrier can be removed from the dyeing machine without draining the bath. However, modern batch dyeing machines are equipped with built-in holding tanks allowing for uninterrupted automatic separation of concentrates from rinsing water

BAT for continuous dyeing processes

Continuous and semi-continuous dyeing processes consume less water than batch dyeing, but highly concentrated residues are produced.

BAT is to reduce losses of concentrated liquor by:

- using low add-on liquor application systems and minimising volume capacity of the dip trough when using pad dyeing techniques
- adopting dispensing systems where the chemicals are dispensed on-line as separate streams, being mixed only immediately before being fed to the applicator
- using one of the following systems for dosing the padding liquor, based on measurement of the pick up (see 4.6.7):
 - measure the amount of dyeing liquor consumed by reference to the quantity of processed fabric (length of the fabric multiplied by its specific weight); the resulting values are automatically processed and used for the preparation of the next comparable batch
 - use the rapid batch dyeing technique, where rather than being prepared for the whole batch before starting the dyeing batch, the dyestuff solution is prepared just in time, in several steps, based on on-line measurement of the pick up. This second technique is preferred when economic considerations allow (see 4.6.7)
- increase washing efficiency according to the principles of counter-current washing and reduction of carry-over described in Section 4.9.2.

PES & PES blends dyeing with disperse dyes

BAT is to:

- avoid the use of hazardous carriers by (in order of priority):
 - using non-carrier dyeable polyester fibres (modified PET or PTT-type) as described in Section 4.6.2, when product market considerations allow
 - dyeing in HT conditions without use of carriers. This technique is not applicable to PES/WO and elastane/WO blends
 - substituting conventional dye carriers with compounds based on benzylbenzoate and Nalkylphthalimide, when dyeing WO/PES fibres (see Section 4.6.1)
- substitute sodium dithionite in PES aftertreatment, by applying one of the two proposed techniques (as described in Section 4.6.5):
 - replace sodium dithionite with reducing agent based on sulphinic acid derivatives. This should be combined with measures in order to ensure that only the strict amount of reducing agent needed to reduce the dyestuff is consumed (e.g. by using nitrogen to remove oxygen from the liquor and from the air in the machine)
 - use of disperse dyes that can be cleared in alkaline medium by hydrolitic solubilisation instead of reduction (see Section 4.6.5)
- use optimised dye formulations that contain dispersing agents with high degree of bioeliminability as described in Section 4.6.3.

Dyeing with sulphur dyes

BAT is to (see 4.6.6):

- replace conventional powder and liquid sulphur dyes with stabilised non-pre-reduced sulphide-free dyestuffs or with pre-reduced liquid dye formulations with a sulphide content of less than 1 %
- replace sodium sulphide with sulphur-free reducing agents or sodium dithionite, in that order of preference
- adopt measures to ensure that only the strict amount of reducing agent needed to reduce the dyestuff is consumed (e.g. by using nitrogen to remove oxygen from the liquor and from the air in the machine)
- use hydrogen peroxide as preferred oxidant.

Batch dyeing with reactive dyes

BAT is to:

- use high-fixation, low-salt reactive dyes as described in Sections 4.6.10 and 4.6.11
- avoid the use of detergents and complexing agents in the rinsing and neutralisation steps after dyeing, by applying hot rinsing integrated with recovery of the thermal energy from the rinsing effluent (see Section 4.6.12).

Pad-batch dyeing with reactive dyes

BAT is to use dyeing techniques that perform at equivalent levels to those described in Section 4.6.13. The technique described is more cost effective than pad-batch dyeing in terms of total processing costs, but the initial capital investment in switching to the new technology is significant. However, for new installations and those seeking to replace equipment the cost factor is not so significant. In all cases, BAT is to avoid the use of urea and to use silicate-free fixation methods (see Section 4.6.9).

Wool dyeing

BAT is to:

- substitute chrome dyes with reactive dyes or, where not possible, use ultra-low chroming methods that fulfil all the following requirements as defined in Section 4.6.15:
 - an emission factor of 50 mg chromium per kg of wool treated is achieved, which corresponds to a chromium concentration of 5 mg/l in the spent chroming bath when a 1:10 liquor ratio is used
 - no chromium (VI) is detectable in the waste water (using a standard method able to detect Cr VI at concentrations <0.1 mg/l)</p>
- ensure minimum discharge of heavy metals in the waste water when dyeing wool with metal complex dyes. BAT associated values are emission factors of 10 20 mg/kg of treated wool, which correspond to 1 2 mg/l of chromium in the spent dye bath when a 1:10 liquor ratio is used. These performances can be achieved by:
 - using auxiliaries that enhance dye uptake like, for instance, the process described in Section 4.6.17 for loose wool and tops
 - using pH control methods to maximise final bath exhaustion for other make-ups
- give preference to a pH-controlled process when dyeing with pH-controllable dyes (acid and basic dyes) so that level dyeing is obtained with maximum exhaustion of dyes and insect resist agents and minimum use of organic levelling agents (see Section 4.6.14).

Printing

Process in general

BAT is to:

- reduce printing paste losses in rotary screen printing by:
 - minimising the volume of printing paste supply systems (see 4.7.4)
 - recovering printing paste from the supply system at the end of each run by adopting the technique described in Section 4.7.5
 - recycling residual printing paste (see Section 4.7.6)
- reduce water consumption in cleaning operations by a combination of (see Section 4.7.7):
 - start/stop control of cleaning of the printing belt
 - re-use of the cleanest part of the rinsing water from the cleaning of the squeegees, screens and buckets
 - > re-use of the rinsing water from cleaning of the printing belt
- use digital ink-jet printing machines for the production of short runs (less than 100 m) for flat fabrics, when product market considerations allow (see Section 4.7.9). It is not considered BAT to flush with solvent to prevent blocking while the printer is not in use
- use digital jet printing machines described in Section 4.7.8 for printing carpet and bulky fabrics, except for resist and reserve printing and similar situations.

Reactive printing

BAT is to avoid the use of urea by either:

• the one-step process with the controlled addition of moisture, where the moisture is applied either as foam or by spraying a defined quantity of water mist (see Section 4.7.1)

OR

• the two-steps printing method (see 4.7.2).

For silk and viscose, with the one-step process, the spraying technique is not reliable due to the low moisture add-on required for these fibres. The foaming technique with complete elimination of urea is proven for viscose, but not yet for silk. There is a high initial investment cost of about 200000 euros for a foaming machine related to a production capacity of up to about 80000 linear metres per day. The technique has been operated under economically viable conditions in plants of capacity of about 30000, 50000 and 140000 linear metres per day. There is a question whether the technique is economically viable for smaller plants.

Where the foam technique is not used, the amount of urea consumed can be reduced to about 50 g/kg of printing paste for silk and to 80 g/kg for viscose.

Pigment printing

BAT is to use optimised printing pastes that fulfil the following requirements (see 4.7.3):

- thickeners with low-emission of volatile organic carbon (or not containing any volatile solvent at all) and formaldehyde-poor binders. The associated air emission value is <0.4 g Org.-C/kg textile (assuming 20 m³ air/kg textile)
- APEO-free and high degree of bioeliminability
- reduced ammonia content. Associated emission value: 0.6 g NH₃/kg textile (assuming 20 m³ air/kg textile).

Finishing

Process in general

BAT is to:

- minimise residual liquor by:
 - using minimal application techniques (e.g. foam application, spraying) or reducing volume of padding devices
 - > re-using padding liquors if quality is not affected
- minimise energy consumption in stenter frames by (see Section 4.8.1):
 - ▶ using mechanical dewatering equipment to reduce water content of the incoming fabric
 - optimising exhaust airflow through the oven, automatically maintaining exhaust humidity between 0.1 and 0.15 kg water/kg dry air, considering the time taken to reach equilibrium conditions
 - installing heat recovery systems
 - fitting insulating systems
 - > ensuring optimal maintenance of the burners in directly heated stenters
- use low air emission optimised recipes. An example for classification/ selection of finishing recipes is the "Emission factor concept" described in Section 4.3.2.

Easy-care treatment

BAT is to use formaldehyde-free cross-linking agents in the carpet sector, and formaldehyde-free or formaldehyde-poor (<0.1 % formaldehyde content in the formulation) cross-linking agents in the textile industry (see 4.8.2).

Mothproofing treatments

• Process in general

BAT is to:

- > adopt appropriate measures for material handling as described in Section 4.8.4.1
- > ensure that 98 % efficiency (transfer of insect resist agent to the fibre) is achieved
- adopt the following additional measures when the insect resist agent is applied from a dye bath:
 - ensure that a pH<4.5 is reached at the end of the process and if this is not possible, apply the insect resist agent in a separate step with re-use of the bath
 - add the insect resist agent after dye bath expansion in order to avoid overflow spillages
 - select dyeing auxiliaries that do not exert a retarding action on the uptake (exhaustion) of the insect-resist agent during the dyeing process (see Section 4.8.4.1).

• Mothproofing of yarn produced via the dry spinning route

BAT is to use one or both of these techniques (described in Section 4.8.4.2):

- combine acid aftertreatment (to increase the uptake of mothproofer active substance) and reuse of the rinse bath for the next dyeing step
- apply proportional over-treatment of 5 % of the total fibre blend combined with dedicated dyeing machinery and waste water recycling systems to minimise active substance emissions to water.

• Mothproofing of loose fibre dyed / yarn scoured production

BAT is to (see Section 4.8.4.3):

- use dedicated low-volume application systems located at the end of the yarn scouring machine
- recycle low-volume process liquor between batches and use processes designed specifically to remove active substance from spent process liquor. These techniques may include adsorptive or degradative treatments
- > apply mothproofer directly to the carpet pile (when mothproofing during carpet manufacture) using foam application technology.

• Mothproofing of yarn dyed production

BAT is to (see Section 4.8.4.4):

- use a separate aftertreatment process to minimise emissions from dyeing processes which are carried out under less than optimum conditions for mothproofer uptake
- > use semi-continuous low-volume application machinery or modified centrifuges
- recycle low-volume process liquor between yarn batches and processes designed specifically to remove active substance from spent process liquor. These techniques may include adsorptive or degradative treatments
- > apply mothproofer directly to the carpet pile (when mothproofing during carpet manufacture) using foam application technology.

• <u>Softening treatments</u>

BAT is to apply the softening agents by pad mangles or better, by spraying and foaming application systems, instead of carrying out this treatment by exhaustion directly in the batch dyeing machine (see Section 4.8.3).

Washing

BAT is to:

- substitute overflow washing/rinsing with drain/fill methods or "smart rinsing" techniques as described in Section 4.9.1
- reduce water & energy consumption in continuous processes by:
 - installing high-efficiency washing machinery according to the principle described in Section 4.9.2. The associated values for high-efficiency continuous washing of cellulosic and synthetic fabric in open-width are reported in Table 4.38
 - introducing heat recovery equipment
- when halogenated organic solvent cannot be avoided (e.g. with fabrics that are heavily loaded with preparations such as silicone oils that are difficult to remove with water), use fully closed-loop equipment. It is essential that the equipment fulfil the requirements described in Section 4.9.3 and provisions be taken for in-loop destruction (e.g. by advanced oxidation processes) of the persistent pollutants in order to avoid any possible contamination of groundwater arising from diffuse pollution and accidents.

Waste water treatment

Waste water treatment follows at least three different strategies:

- central treatment in a biological waste water treatment plant on site
- central treatment off site in a municipal waste water treatment plant
- decentralised treatment on site (or off site) of selected, segregated single waste water streams

All three strategies are BAT options when properly applied to the actual waste water situation. Well-accepted general principles for waste water management and treatment include:

- characterising the different waste water streams arising from the process (see Section 4.1.2)
- segregating the effluents at source according to their contaminant type and load, before mixing with other streams. This ensures that a treatment facility receives only those pollutants it can cope with. Moreover, it enables the application of recycling or re-use options for the effluent
- allocating contaminated waste water streams to the most appropriate treatment
- avoiding the introduction of waste water components into biological treatment systems when they could cause malfunction of such a system
- treating waste streams containing a relevant non-biodegradable fraction by appropriate techniques before, or instead of, a final biological treatment.

According to this approach, the following techniques are determined as general <u>BAT for the</u> treatment of waste water from the textile finishing and carpet industry:

- treatment of waste water in an activated sludge system at low food-to-micro organisms ratio as described in Section 4.10.1, under the prerequisite that concentrated streams containing non-biodegradable compounds are pretreated separately
- pretreatment of highly-loaded (COD>5000 mg/l) selected and segregated single waste water streams containing non-biodegradable compounds by chemical oxidation (e.g. Fenton reaction as described in Section 4.10.7). Candidate waste water streams are padding liquors from semi-continuous or continuous dyeing and finishing, desizing baths, printing pastes, residues from carpet backing, exhaust dyeing and finishing baths.

Certain specific process residues, such as residual printing pastes and residual padding liquors are very strong and, where practicable, should be kept out of waste water streams.

These residues should be disposed of appropriately; thermal oxidation can be one suitable method because of the high calorific value.

For the specific cases of waste water containing pigment printing paste or latex from carpet backing, precipitation/flocculation and incineration of the resulting sludge is a viable alternative to chemical oxidation (as described in Section 4.10.8).

For azo-dyes, anaerobic treatment of padding liquor and printing pastes as described in Section 4.10.6 before a subsequent aerobic treatment can be effective for colour removal.

If concentrated water streams containing non-biodegradable compounds cannot be treated separately, additional physical-chemical treatments would be required to achieve equivalent overall performance. These include:

- tertiary treatments following the biological treatment process. An example is adsorption on activated carbon with recycling of the activated carbon to the activated sludge system: this is followed by destruction of the adsorbed non-biodegradable compounds by incineration or treatment with free-radicals (i.e. process generating OH^{*}, O₂^{*-}, CO₂^{*-}) of the excess sludge (biomass along with the spent activated carbon) (see plant 6 in Section 4.10.1)
- combined biological, physical and chemical treatments with the addition of powdered activated carbon and iron salt to the activated sludge system with reactivation of the excess sludge by "wet oxidation" or "wet peroxidation" (if hydrogen peroxide is used), as described in Section 4.10.3
- ozonation of recalcitrant compounds prior to the activated sludge system (see plant 3 in Section 4.10.1).

For effluent treatment in the wool scouring sector (water-based process) BAT is to:

- combine the use of dirt removal / grease recovery loops with evaporative effluent treatment, with integrated incineration of the resulting sludge and full recycling of water and energy for: 1) new installations 2) existing installations with no on-site effluent treatment 3) installations seeking to replace life-expired effluent treatment plant. This technique is described in Section 4.4.2
- use coagulation/flocculation treatment in existing mills already using it in conjunction with discharge to sewerage system employing aerobic biological treatment.

Whether or not biological treatment can be considered as BAT must remain an open question until better information on its costs and performance can be assembled.

Sludge disposal

For sludge from waste water treatment of wool scouring effluent BAT is to:

- use sludge in brick-making (see 4.10.12) or adopt any other appropriate recycling routes
- incinerate the sludge with heat recovery, provided that measures are taken to control emissions of SO_x, NO_x and dust and to avoid emissions of dioxins and furans arising from organically bound chlorine from pesticides potentially contained in the sludge.

CONCLUDING REMARKS

The main general conclusions are:

- the information exchange was successful and a high degree of agreement was reached following the second meeting of the TWG
- due to the nature of the textile industry (very complex and variegated sector) the impact of the implementation of the BAT identified will depend on the characteristics of each mill. The speed of implementation will therefore be a particularly sensitive issue for this industry
- mindful of the current difficulties that certain companies may have in controlling/ selecting the source of the fibre raw material, it was recognised that a quality assurance system for incoming textile material is necessary in order to produce an adequate application for an IPPC permit. BAT is therefore to seek collaboration with upstream partners in the textile chain, not only at site-specific level, but also at industry sector level, in order to create a chain of environmental responsibility for textiles.

The main recommendations for future work are:

- more systematic collection of data is needed about the current consumption and emission levels and about the performance of techniques to be considered in the determination of BAT, especially for water effluents
- a more detailed assessment of the costs and savings associated with techniques is needed to further assist the determination of BAT
- the collection of information about areas that have not been properly covered by the BREF due to a lack of information. More details about specific areas in which data and information are lacking are mentioned in Chapter 7.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).