EUROPEAN COMMISSION
DIRECTORATE-GENERAL JRC
JOINT RESEARCH CENTRE
Institute for Prospective Technological Studies (Seville)
Technologies for Sustainable Development
European IPPC Bureau

Integrated Pollution Prevention and Control (IPPC)

Reference Document on Best Available Techniques for the Textiles Industry

Draft dated February 2001

PREFACE

1.   Status of this document

Unless otherwise stated, references to "the Directive" in this document means the Council Directive 96/61/EC on integrated pollution prevention and control.
This document is a working draft of the European IPPC Bureau. It is not an official publication of the European Communities and does not necessarily reflect the position of the European Commission.

2.   Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term "best available techniques", are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community's industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term "best available techniques" is defined in Article 2(11) of the Directive as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." Article 2(11) goes on to clarify further this definition as follows:

"techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

"available" techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

"best" means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of "considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention". These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3.   Objective of this Document

Article 16(2) of the Directive requires the Commission to organise "an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them", and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that "the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive."

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4.   Information Sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5.   How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.

Chapters 1 and 2 provide general information on the industrial sector concerned and on the industrial processes used within the sector. Chapter 3 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapter 4 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Chapter 5 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in Chapter 5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

World Trade Center, Isla de la Cartuja s/n, E-41092 Seville, Spain
Telephone: +34 95 4488 284
Fax: +34 95 4488 426
e-mail: eippcb@jrc.es
Internet: http://eippcb.jrc.es

SCOPE

This document covers the industrial activities specified in Section 6.2 of Annex 1 of Directive 96/61/EC, namely:

"Plants for the pretreatment (operations such as washing, bleaching, mercerisation) or dyeing of fibres or textiles where the treatment capacity exceeds 10 tonnes per day".

Particular attention is given to the following processes:
- fibre preparation
- pretreatment
- dyeing
- printing
- finishing.

Upstream processes which may have a significant influence on the environmental impact of the subsequent wet processing activities are also briefly described.

The backing of carpets is included in this document because it is an intrinsic part of carpet manufacturing and has the potential to pollute the environment.

All main fibre types, namely natural fibres, man-made fibres derived from natural polymers such as viscose and cellulose acetate as well as man-made fibres derived from synthetic polymers are described, including their blends.

Non-woven fabric manufacturing is not included in this BREF.

Draft Reference Document on Best Available Techniques for the Textiles Industry

List of tables

List of figures

1   GENERAL INFORMATION

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 a majority of Small and Medium Enterprises, with a demand largely driven by three main end-uses: clothing, home furnishing and industrial use.

The importance of textile industry in the European economy is shown in Table 1.1. In 1997 the turnover was over 197 billions ECU (?) and the 116000 companies employed 2.4 (?) millions people.

1997	Turnover	Value added at f.c.	Production	Employment	Share Turnover	Share Value added	Share Production	Share Employment
	Millions ECU	Millions ECU	Millions ECU	Millions	%	%	%	%
Textile	98	31	94	0.95	2.5	2.7	2.6	4.1
Clothing	55	17	53	0.80	1.4	1.5	1.5	3.5
Textile Clothing	153 (?)	48	147	1.75 (?)	3.9	4.2	4.0	7.6
Manufacturing	3940	1141	3661	23.22	100	100	100	100
THESE FIGURES NEED TO BE CHECKED								
f.c. : factor costs Source: [EURATEX]								

Table 1.1: Share of the EU-15 textile-clothing industry in the manufacturing industry (only companies with 20 employees or more)
[EUROSTAT]

Moreover, in 1997 the European textile industry represented:
- 4.0 % of EU manufacturing industry's turnover
- 4.2 % of the valued added and
- 7.6 % of the industrial employment.

The textile industry's activities are distributed right across Europe, but concentrated in a few EU states. Italy is the leading European producer, far ahead of Germany, the UK, France and Spain (in that order). These five countries together account for over 80 % of the Community textile and clothing industry. [EURATEX]

The textile and clothing chain is composed of a wide number of sub-sectors covering the entire production cycle from the production of raw materials (chemical fibres) to semi-processed (yarns, woven and knitted fabrics with their finishing process) and final/consumer products (carpets, home textiles, clothing and industrial use textiles).

The complexity of the sector is also reflected in the difficulty of finding a clear-cut classification system for the different activities involved. The old nomenclature system (old NACE 1995) still classified textile industry's activities as follows:
- man made fibres industry
- wool
- cotton
- silk
- flax/jute
- knitting
- finishing
- carpets
- other textiles
- household linen.

The new nomenclature system (NACE 1997) identifies the following categories:
- yarn and thread
- woven fabric
- textile finishing
- home textiles
- industrial & other textiles (which includes Carpets)
- knitted fabrics & articles.

The old nomenclature reflects the historical subdivision of the textile industry's activities according to the fibre processed. This stems from the fact that historically the only textile fibres available were natural fibres, with a predominance of wool and cotton, which resulted in the development of two main sectors, wool and cotton. Because of the different physico-chemical characteristics of these two fibres, different machinery and different techniques were developed. Nowadays, with the proliferation of man-made fibres these two historical sectors both process all available fibres and it has become impractical to classify textiles activities by reference to the fibre.

As for the scope of this document, it is confined to those activities in the textile industry that involve wet processes. In addition to wool scouring, that means primarily activities falling within the following new NACE classifications:
- textile finishing
- industrial and other textiles (including Carpets)
- home textiles (?).

Because of its very specialised nature, carpet manufacturing is always considered as a stand-alone sector, even though many of the operations carried out are very close to those carried out elsewhere in textile finishing. This document follows that tradition: carpets are the only sector where the end product is taken as the point of reference.

Some general information is given below about the three macro-sectors of wool scouring, textile finishing (excluding floor-coverings) and carpets.

1.1   Wool scouring sector

1.1.1 Sector organisation

Wool is processed to yarn mainly via two systems: woollen and worsted. Scourers tend to specialise in wools for one system or the other. Woollen system scourers normally only scour the wool, though some may blend it before despatch to the customer. Worsted system scourers (referred to as combers in English) scour, card and comb the wool and their product is called top.

Within Europe, significant quantities of wool are obtained from skins of slaughtered animals by fellmongering. Fellmongers normally sell the wool they produce to merchants, who have it scoured on commission. In France there are several fellmongers who also scour the wool they produce.

The wool scouring and combing business in Western Europe is largely carried out on commission. There are a few exceptions to this system, notably in the UK, where three carpet yarn manufacturers who have their own wool scouring plants.

1.1.2 Production & economics

Table 1.2 shows estimates of the amounts of wool produced and scoured in the various Member States along with the number of existing scouring companies.

Country	Domestic production of greasy wool	Wool scoured for worsted processing (clean weight)	Wool scoured for woollen processing (clean weight)	Total wool scoured (clean weight)	Total wool scoured (approx. greasy equivalent) (c)	Estimated number of scouring mills
Austria	(a)	0	0	0	0	0
Belgium	(a)	1.8	2.0	3.8	5.4	1(?)
Denmark	(a)	0	0	0	0	0
Finland	(a)	0	0	0	0	0
France	20	56.3	9.1	65.4	93.4	(?)
Germany	13	34.2	9.2	43.4	62.0	1 (d)
Greece	9	0	0	0	0	0
Ireland	25	0	0	0	0	0
Italy	11	73.6	2.4	76.0	108.6	8 – 9
Luxembourg	(a)	0	0	0	0	0
Netherlands	(a)	0	0	0	0	0
Portugal	9	3.3	2.0	5.3	7.6	2 (?)
Spain	36	13.5	12.7	26.2	37.4	(?)
Sweden	(a)	0	0	0	0	0
UK	65	29.1	50.4	79.6	113.7	13
Other western Europe	10 (b)	0	0	0	0	0
TOTAL	198	211.8	87.8	299.7	428.1	>25

Unit: '000 tonnes/year

Notes:
(a)   Included in "Other western Europe".
(b)   Austria, Belgium, Denmark, Finland, Iceland, Luxembourg, Malta, Netherlands, Norway, Sweden and Switzerland.
(c)   Assuming an average yield of 70 %.
(d)   A second scouring/combing mill in Germany is not believed to be operational.

Table 1.2: Wool production and wool scouring production in EU Member States [INTERLAINE]

As it is possible to see from the reported data, 90 % of the EU scouring activity is concentrated in France, Germany, Italy and UK, while eight EU member states have no scouring plants.

The UK scouring and combing industry is the largest in Europe, though only slightly larger than that of Italy. About 2/3 of the UK scouring production comprises coarse wools for woollen spun carpet yarn.

Figure 1.1 shows the amounts of wool scoured in the 15 EU Member States in terms of greasy wool weight. This is the unit most often used by scourers to express their throughput.

Production, million kg greasy wool per year

Figure showing a bar chart with the y-axis labeled from 0 to 120 in increments of 20, and the x-axis listing EU Member States: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Netherlands, Portugal, Spain, Sweden, UK. Notable bars: Belgium ~5, France ~93, Germany ~62, Italy ~109, Portugal ~8, Spain ~37, UK ~114.

Figure 1.1: Estimates of the amounts of greasy wool scoured during 1997 in the 15 EU Member States
[INTERLAINE]

During the period from 1993 to 1997 the total production in EU Member States has declined almost 10 % from 326 million kg (clean wool) in 1993 to 300 million kg (clean wool) in 1997. Within this overall trend a steeper decline has been observed in northern Europe (Belgium, France, Germany and UK) alongside an increase in production in the Italy and Spain. Although the overall decline in production in the European scouring sector has been relatively slow, there have been significant structural changes. The competitive nature of the industry and the cost and technical difficulties of complying with increasingly stringent environmental legislation have driven the changes. Several large and small scouring mills have been forced beyond the limits of commercial and economic viability and have ceased trading. Often, their market share has been absorbed by competitors, so there are now fewer companies in the sector, on average processing larger amounts of wool. This tendency towards consolidation is especially the case in UK, where a large part of the scouring industry's trade is the processing of UK and Irish wools. Almost 80 %[1] of the British and Irish wool production, totalling 90000 tonnes is scoured in UK and this trade is unlikely to be lost to competitors in other countries. [INTERLAINE]

1.2 Textile finishing sector (excluding floor covering)

1.2.1 Sector organisation

?

1.2.2 Production & economics

?

---

[1] A survey of UK wool scourers, carried out by ENco in 1997, showed that they processed 71 million kg (greasy) of British and Irish wool during the previous year.

1.3   Carpet

1.3.1 Sector organisation

The strong specialisation of this well integrated sector has already been mentioned. The carpet manufacturing, carpet yarn spinning and associated dyeing industry can be divided into a number of basic sub-sectors, although there can be considerable variation on the following pattern. All sectors may process combinations of 100 % synthetic fibre, 100 % natural fibre and blends of the two, as many of the processes and techniques used are not fibre specific.

As Table 1.3 shows there are four main different categories of companies where wet processes are normally carried out:
- commission loose fibre dyehouses
- commission yarn dyehouses
- integrated yarn manufacturing companies, which in addition to the dyeing processes perform on-site conversion of the loose fibre to yarn, selling the finished yarn as end-product
- integrated carpet manufacturing industries, which carry out all the mechanical processes, dyeing and finishing operations required to convert natural and synthetic fibres into finished carpet.

Sub-Sector	Main Characteristics and Principal Wet Processes (in italics)	End Product
Commission Loose Fibre Processing	• *Loose fibre dyeing*	Dyed loose fibre for yarn manufacture
Commission Yarn Processing	• *Yarn scouring and chemical finishing* • *Yarn dyeing*	Dyed yarn for carpet manufacture
Yarn Manufacture	Raw material (fibre) purchase Conversion to yarn (Dyeing/wet processing carried out on commission) Marketing of finished yarn	Coloured and ecru yarn for carpet manufacture
Integrated Yarn Manufacture (may be on several sites)	Raw material (fibre) purchase • *Loose fibre dyeing* Conversion to yarn • *Yarn scouring and chemical finishing* • *Yarn dyeing and chemical finishing* • *Yarn setting* Marketing of finished yarn	Coloured and ecru yarn for carpet manufacture
Commission Tufting and Weaving	Conversion of yarn to carpet Backing and mechanical finishing	Finished carpet
Carpet Manufacturing	Dyed and finished yarn purchase Conversion to carpet • Foam applied chemical treatment Backing and mechanical finishing Marketing of finished carpet	Carpet for contract and retail sale
Integrated Carpet Manufacturing (may be on several sites) Note(1) Raw wool scouring may be carried out within the group or on commission	Raw material (fibre) purchase/manufacture • *Raw wool scouring* [1] • *Loose fibre dyeing* Conversion to yarn • *Yarn scouring and chemical finishing* • *Yarn dyeing and chemical finishing* • *Yarn setting* Conversion to Carpet • Carpet piece coloration • Foam applied chemical treatments • Backing and mechanical finishing Marketing of finished carpet	Carpet for contract and retail sale

Table 1.3: Basic structure of the wool and wool blend carpet yarn and carpet manufacturing industry
[ENCO]

Table 1.4 indicates the locations of trading entities within the European Community. Note that individual units may be part of a larger group, providing services to other members of the same organisation. In a similar way, a yarn spinning company with its own dyeing facilities may, if production schedules require, also have work carried out by a commission dyer or may carry out commission work for other companies if spare capacity is available.

Country	Carpet [A] Manufacturers	Yarn [B] Spinners	Commission [C] Dyers
Austria	4		
Belgium	64	12	9
Denmark	12	2	
Finland	4	1	1
France	16	1	1
Germany	38	4	2
Greece	2		
Ireland	4	1	
Italy	9	1	
Netherlands	34	1	3
Portugal	2	1	
Spain	3		
Sweden	2		
United Kingdom	87	30	9
Sources: [A] International Carpet Yearbook 2000 – includes all, product types and fibres [B] International Carpet Yearbook 2000 & Wools of New Zealand – includes spinners with dyehouses [C] ENco and Wools of New Zealand – includes all fibres			

Table 1.4: Sector Location and number of trading entities within the European Economic Community
[ENCO]

1.3.2 Production & economics

As Figure 1.2 shows, European carpet industry accounts for 38 % of world production (after the United States, with 58 %).
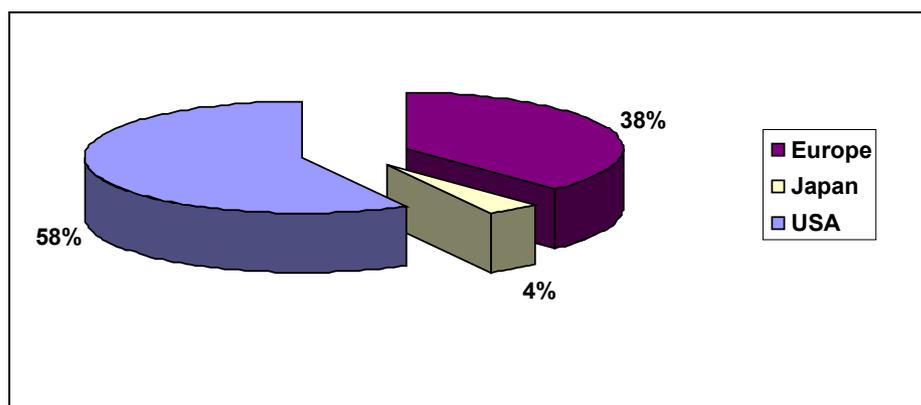
Figure 1.2: Worldwide production of carpets and rugs in 1999
[GUT]

Belgium, France, Germany, the Netherlands and the United Kingdom are all major producers for both internal EU consumption and world export markets. European carpet production exceeds carpet consumption by a significant margin (Figure 1.3), indicating the importance of export markets to the European industry.

**EU Carpet Production and Consumption 1999
(Tufted and Woven - millions of square meters)**
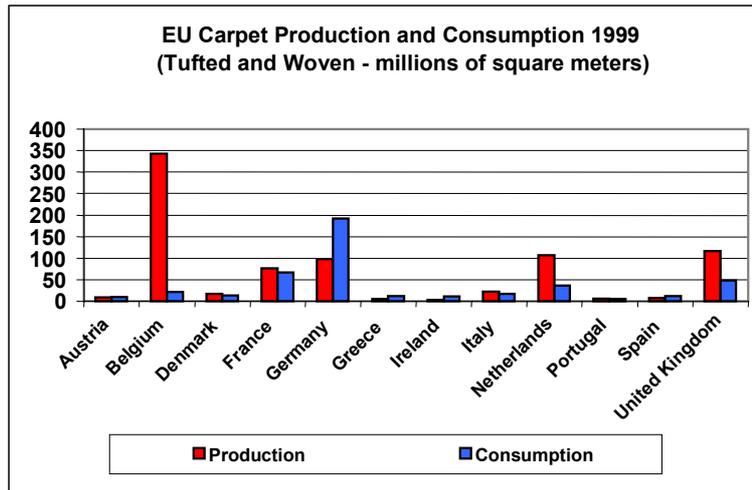
**Figure 1.3: Carpet production and consumption in EU Member States
[Intercontuft]**

Among the three typical end-products of carpet manufacturing industry - tufted carpet, woven carpet and needle felts - tufted carpet accounts for 66 % of EU production. This is shown in the 1995 production figures below.
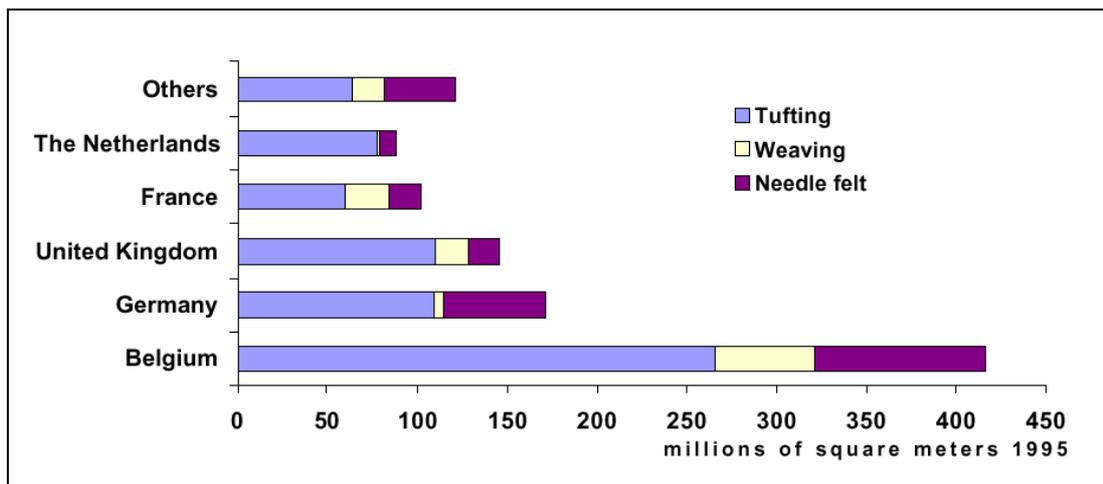
**Figure 1.4: European carpet and rug production in 1995 for the major producers of carpets and rugs in Europe
[GUT]**
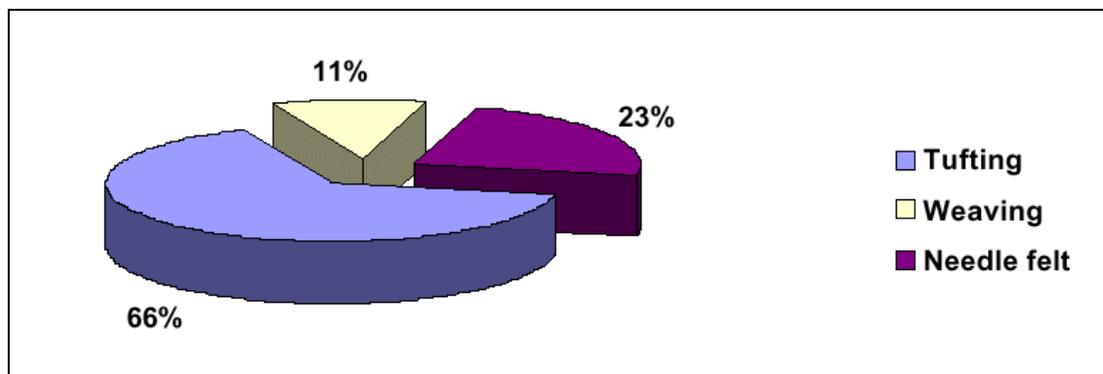
**Figure 1.5: Total carpet and rug production in Europe in 1995
[GUT]**

1.4 Main environmental issues

The main environmental issues arising from the activities in the textile industry which are covered in this document regard primarily emissions to water, air and energy consumption.

Among these, water is the most important concern. The textile industry uses water as the principal medium for removing contaminants and applying dyes and finishes and for the generation of steam.

Losses to the product are negligible, therefore, apart from a minor amount of water which is evaporated during drying, the bulk is discharged as aqueous effluent. The main concern is therefore about the amount of water discharged and the chemical load it carries.

An overview of these charging loads is given in Table 1.5. The reported data have been extrapolated to European level from the results of a research in Germany and Austria.

Substances	Charging load (t/yr)
Salts	200 - 250000
Natural fibres contaminants	50 - 100000
Sizes (mainly starch derivatives, but also polyacrylates and polyvinylalcohol)	80 - 100000
Preparation agents (mainly mineral oils, but also ester oils)	25 - 30000
Surfactants (dispersing agents, emulsifiers, detergents)	20 - 25000
Carboxylic acids (mainly acetic acid)	15 - 20000
Thickeners (starch derivatives)	10 - 15000
Urea	5 - 10000
Complexing agents	<5000
Organic solvents	?
Special auxiliaries with more or less ecotoxicological properties	<5000
Source: [EURATEX]	

Table 1.5: Main charging loads from textile industry in Europe

From the reported figures it appears that 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. These are:
- sizing agents
- natural fibres impurities
- preparation agents

Sizing agents are used to assist weaving process. They are removed from the woven fabric at the finishing mill thus producing high levels of organic load in the water.
Auxiliaries, so-called preparation agents and spinning oils, are applied to fibres in various steps of the process, from the manufacturing of the fibre itself (for synthetic fibres only) to the

formation of the yarn. These organic substances are removed during pretreatment at the finishing mill, contributing the increase of the organic load of the final effluent.

All natural fibres contain a percentage of impurities that have to be removed before the fibre can undergo the finishing processes. In the case of wool, in particular, the bulk of the natural impurities (grease, dirt, etc.) is removed before the fibre enters the finishing mill. This operation is carried out in a preparation step called wool scouring which is responsible for the generation of an effluent with a very high concentration of organic material. Moreover, wool contains other pollutants, so-called micro-pollutants, originating from the pesticides used to prevent sheep becoming infested with external parasites (ticks, lice, blow-fly maggots, etc.). These biocides are in general toxic to aquatic life and, in some cases, may be highly toxic and persistent.

In this context, the extensive industrial and agricultural use of OC pesticides (in particular lindane, dieldrin and DDT) in most wool-producing countries has left a legacy of low-level background contamination in the general environment. Consequently, wool from all sources may still contain detectable OC residues arising from this background contamination. The γ-hexachlorocyclohexane (lindane) is still used as a veterinary medicine in some former Soviet States, the Middle East and South America.

Modern sheep treatment medicines are formulated from a range or organophosphate (OP's) insecticides, synthetic pyrethroid insecticides (SP's) and insect growth regulators (IGR's). Their pattern of permitted use varies widely. These substances are lipophilic in character and strongly associate with the wool grease at shearing. They are largely removed during the scouring process, which makes them another important concern for the wool scouring sector. A very small percentage of these compounds, however, remains on the fibre, which means that wool dyeing effluents may also contain residual pesticides.

The input of chemicals and auxiliaries added at the finishing mills can be up to 1 kg per kg of processed textiles, which is high. The range of these substances is very extensive: the latest issues of TEGEWA lists more than 7000 auxiliaries. However, as shown in Figure 1.6, in a typical finishing mill, 80 % of the annual consumption is covered by only 20 % of the product types used.
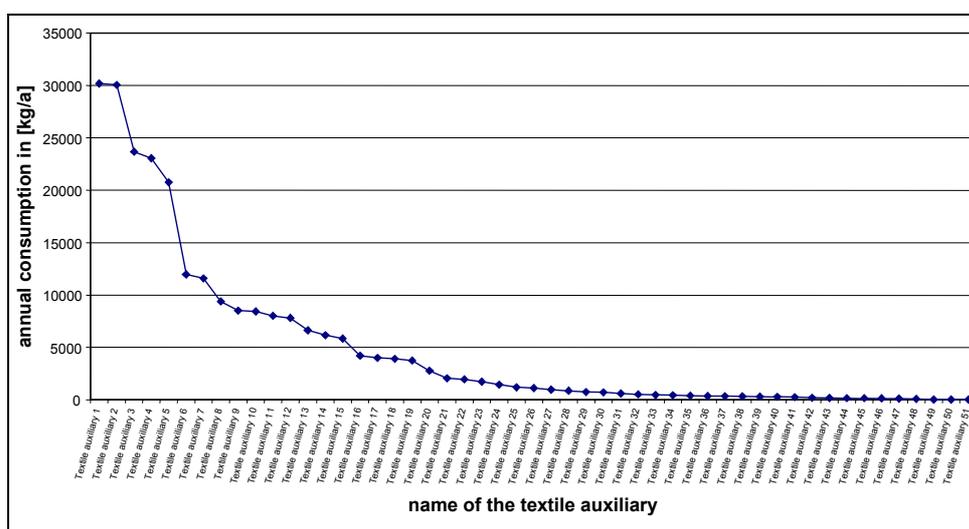
Figure 1.6: Auxiliaries pattern usage in a typical finishing mill
[UBA, 2001]

Among the products applied during the process, the highest charging loads arise from salts, detergents and organic acids (in that order).

Table 1.5 does not report dyestuffs. Although they are responsible for the colour of the effluent - a common problem for the textile industry - they do not represent a significant load compared with other substances used in the process. That said, their presence in the water is important, not only because of the colour, but also in relation with other environmental concerns (e.g. difficult-to-eliminate organic load, AOX, metals, in particular for certain classes of dyestuffs).

A number of chemicals used in the textile process are worth mentioning for their potential negative effects on the environment. These are:
- alkyl phenol ethoxylates (detergents, wetting agents, levelling agents, etc.) polybrominated diphenyl ethers and chlorinated paraffins (flame retardants), halogenated phenols and benzenes (reagents in the production of flame retardants). All these substances have proven or suspected hormonal effects
- mothproofing agents based on permethrin and cyfluthrin (carpet sector) and other biocides highly toxic to aquatic life
- poorly bioeliminable sequestering agents such as EDTA, DTPA and NTA, capable of forming very stable complexes with metals
- chlorine and chlorine-based agents such as sodium hypochlorite (bleaching agent) and sodium dichloroisocyanurate (wool anti-felting agent) capable of reacting with organic compounds to form adsorbable organic halogens (AOX)
- metal-containing compounds such potassium dichromate (oxidising agent used for the fixation of chrome dyes).

It is reported that:
- more than 90 % of the organic input in pretreatment and dyeing operations is released to the environment
- of the organic chemicals added in the finishing process, 90 % remain on the textile
- nearly 90 % of the organic load entering the process is emitted to water, the remaining amount being released to air. [EURATEX]

Concerning emissions to air, volatile organic compounds are released from particular activities such as:
- printing processes when organic solvents are used (e.g. they are contained in pigment printing pastes)
- cleaning with organic solvents
- heat treatments (e.g. thermofixation, drying, curing) when the textile materials contain oils, plasticisers and other chemicals that evaporate or degrade thermally
- vulcanisation of the backing layers (carpet sector).

Moreover, emissions of CO_2, SO_x and NO_x associated with the on-site burning of fossil fuels to produce thermal energy are to be taken into account.

Energy is consumed primarily in raising the temperature of the baths (e.g. pretreatment, dyeing, etc.) and in drying and curing operations. To this aim steam is produced on-site. Electrical energy is required for driving the machinery.

2 APPLIED PROCESSES AND TECHNIQUES

The textile chain begins with the production or harvest of raw fibre. The basic steps in this chain are schematically represented in the following diagram and will be described in this chapter.
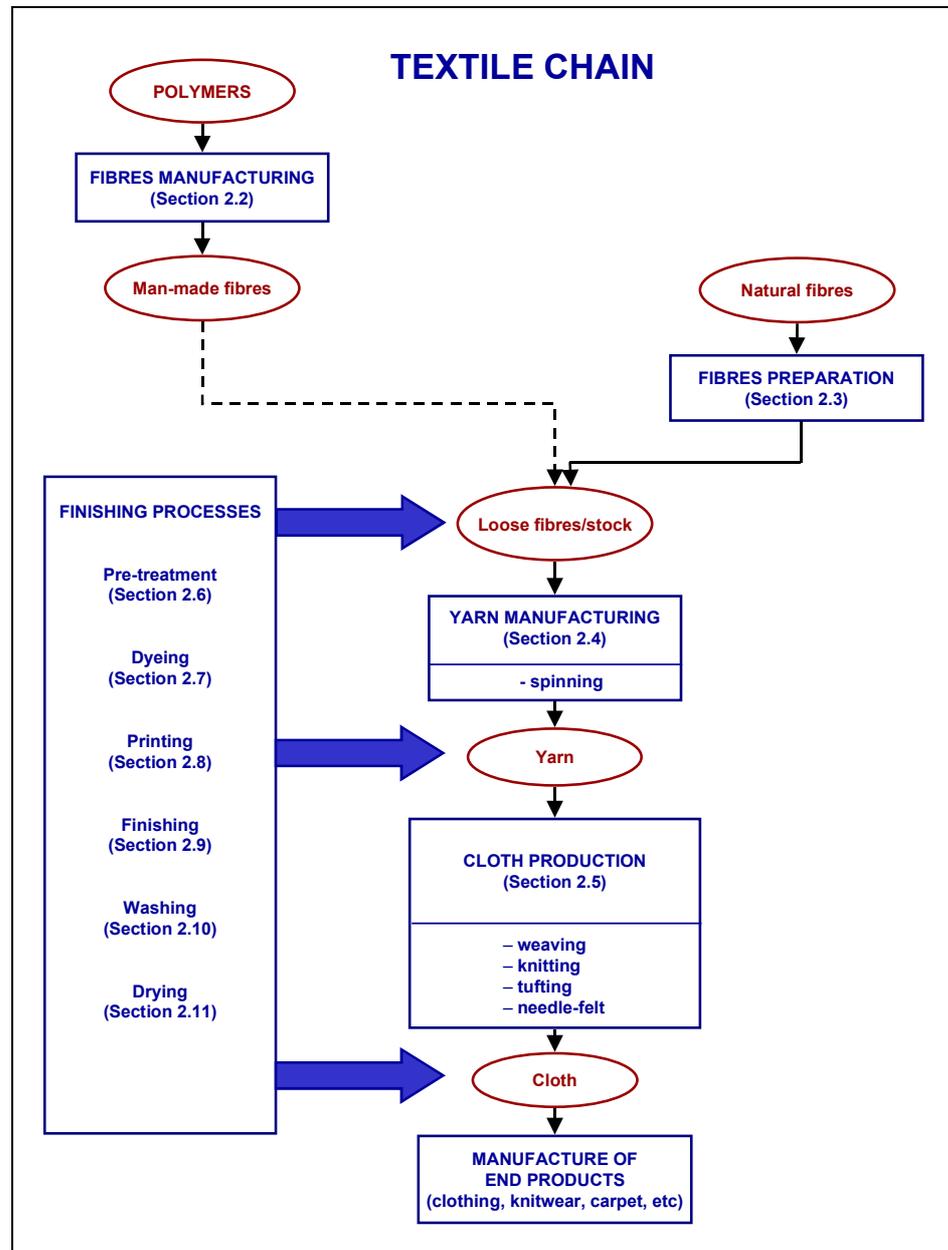
Figure 2.1: General diagram of processes in the textile industry

The main part of this chapter will describe those treatments that are broadly referred to as "finishing treatments" (pretreatment, dyeing, printing, finishing). As the diagram shows, they can take place at different stages of the production process: the substrates for finishing can be cloths, yarns or loose fibres.

"Textile finishing" cannot be defined as a standard sequence of treatments, but rather is a combination of unit processes that can be applied within the production of a textile product, depending on the requirements of the final user. For this reason finishing treatments will be described (from Section 2.6 to Section 2.11) as unit processes without considering the possible sequences in which they can be applied.

In the second part of this chapter a distinction has been made between the carpet finishing sector and the rest of the finishing industry. Some typical categories of industries have been identified within each sector. The wool scouring industry has also been identified as a stand-alone sector. These categories have typical features that are described in brief.

As well as fibres, the raw materials of the textile industry include a wide range of chemicals and auxiliaries. These chemicals and auxiliaries are often not process-specific and can be found in different steps within the process cycle. For this reason it has been considered more practical to report the description of these issues in separate annexes (ANNEX I Textile Auxiliaries and ANNEX II Dyes and Pigments). Only general information about textile raw materials, including common procedures for storage & handling is given in this chapter.

In the same way, because most of the machines have a multifunctional use within the production cycle, equipment is also described in a specific annex (ANNEX III Wet Processes: Machinery and Techniques).

2.1 Raw materials

2.1.1 Fibres

Two general categories of fibres are used in the textile industry: natural and man-made. Man-made fibres encompass both purely synthetic materials of petrochemical origin, and regenerative cellulosic materials manufactured from wood fibres. A more detailed classification of fibres is:

- Natural fibres	• Animal origin	Raw wool Silk fibre Hair
	• Vegetable origin	Raw cotton fibre Flax Jute
	• Mineral origin	Asbestos
- Half-synthetic fibres	• Vegetable origin	Viscose, cupro, lyocell Cellulose acetate Cellulose triacetate
	• Mineral origin	Glass for fibre glass Metal for metal fibre
- Synthetic fibres	• Petrochemical origin	Polyester (PES) Polyamide (PA) Polyacrylonitrile (PAC) Polypropylene (PP) Elastane (EL)

Fibres included in this document are described in more detail below, highlighting in particular the typical impurities present on them. These impurities will enter the textile process and will influence the associated emissions.

2.1.1.1 Polyester fibres (PES)

Polyester fibres are made of linear macromolecules containing at least 85 % of an ester in the chain. This ester is made through the reaction between ethylene glycol and phathalic acid derivatives (e.g. terephthalic acid or dimethyl terephthalate). During the polycondensation reaction, cyclic oligomers with very low water-solubility can be formed (1 - 3 % on the weight of the fibre [EURATEX]). These oligomers tend to migrate to the surface of the fibre during dyeing, thus affecting negatively level dyeing and rub-fastness properties.

PES fibres have a very high degree of cristallinity, which allows for excellent resistance to heat and other mechanical properties. On the other hand, this compact structure inhibits the diffusion of the colorants into the fibre during dyeing. To counteract this effect the use of dyeing accelerants (so-called carriers), which are harmful for the environment and in many cases are toxic for humans, has been common practice for many years. *Modified PES fibres* are now gaining importance in the market. Thanks to physical and chemical alterations made to the structure of the fibre during the manufacturing process, these fibres show a lower cristallinity and as a result they are easier to dye without the need for carriers.

2.1.1.2 Polyamide fibres (PA)

The starting polymer comes from the polycondensation reaction between a diamine and a dicarboxylic acid. According to the number of carbon atoms of the end product one can speak of PA 6,6 or PA 6.

PA 6,6 is made by thermal polycondensation of equimolecular amounts of adipic acid and 1,6-hexamethylendiamine. The equilibrium condensate contains small amounts of monomers and cyclic dimers (2 %).

PA 6 is made by polycondensation of the monomer epsilon-caprolactame. The caprolactame content in the polymer can be reduced to 0.2 % by extraction with hot water. During the melting process for the production of the fibre (melt spinning), the caprolactame content rises again and is partially emitted during the following thermal treatments.

2.1.1.3 Polyacrylonitrile fibres (PAC)

The polymer is obtained by radical polymerisation of acrylonitrile in aqueous emulsion or in solvent. The obtained polymer, made of 100 % acrylonitrile (also called PAN), gives fibres with insufficient dye-binding capability, due to the high glass transition temperature (above 100 ºC). For this reason this polymer is no longer used in the textile industry. Polyacrylonitrile fibres (PAC), commonly found on the market today, are anionic copolymers containing 85 – 89 % of acrylonitrile, 4 – 10 % of a non-ionic comonomer (vinyl chloride, vinyl acetate, methyl acrylate) and 0.5 – 1 % of ionic comonomers containing sulphonic or sulphate groups.

Dry and wet-spinning techniques can be used for the production of the fibre. When dry spinning is used the polymer is dissolved in dimethylformamide (DMF). If the fibre is manufactured through wet spinning, besides DMF, dimethylacetamide, dimethylsulphoxide, ethyl carbonate and aqueous solutions of inorganic salts or acids are also used. Residues of these solvents (0.2 - 2 %) are found in wastewater from pre-treatment.

2.1.1.4 Polypropylene fibres (PP)

The isotactic polymer is used for fibre production. Due to the tertiary carbon atom, PP is very sensitive to high temperature and oxidation. Alkylated phenols or p-xylols, together with suphides or thio-derivatives (dilauryl- or distearyl thiopropionate) are used as stabilizers.

Substances with benzotriazol groups, Ni complexes, anthrachinon derivatives and steric hindered diamines are used as UV-absorbents. These low molecular weight substances remain in the PP fibres and are considered as possible emission-relevant substances.

2.1.1.5 Elastane (EL)

Elastane fibres are made out of an elastomer contaning at least 85 % of polyurethane (PU). For the production of the fibre (dry spinning) the polymer is dissolved in dimethylacetamide. Residues of this solvent remain in the fibre (<1 % on the weight of the fibre) and are found in wastewater from pre-treatment.

To reduce the high adhesive characteristics and to guarantee sufficient gliding properties during processing, preparation agents are applied to the fibre (approximately 6 – 8 % add-on). These auxiliaries contain 95 % silicone oils and 5 % surfactants. The high percentage of silicone oils will cause environmental concerns during pre-treatment of the textile material, when these substances have to be removed.

2.1.1.6 Viscose (CV)

The starting material is the cellulose that is extracted from coniferous timber and supplied to the fibre manufacture in sheets about 1cm thick. The wood contains ca. 40 – 50 % cellulose that is useable to make viscose. The cellulose is first allowed to swell in a NaOH solution. The white flakes obtained are then treated with carbon disulphide until the sodium cellulose xantogenate is formed. The xantogenate is soluble in diluted sodium hydroxide and the formed solution (pulp) is already called viscose. The pulp then needs to be spun. Spinning consists in coagulating the xantogenate solution at the outlet of the spinneret in an acid bath containing sulphuric acid, sodium sulphate and zinc sulphate.

2.1.1.7 Cupro (CU)

Cellulose (wood pulp) can also be dissolved in an aqueous solution of ammonia and copper sulphate. Cupro fibres are produced by wet spinning.

2.1.1.8 Acetate fibres

The cellulose molecule contains 3 alcohol groups. When between 2 and 2.5 of the 3 groups are esterified with acetic acid, the polymer is called diacetate. When all the three alcohol groups are esterified then the polymer is called triacetate. The acetate fibres contain less that 92 % of cellulose acetate, but at least 74 % of the hydroxilic groups must be acetilated.

2.1.1.9 Wool

Wool is an animal hair from the body of sheep. This hair is normally sheared once, or sometimes twice, a year and its quality and quantity varies widely, depending on the breed of sheep and environment. Wool is a member of a group of proteins known as keratin, also found in horns, nails, etc.

In addition to wool fibre, raw wool contains:

- Natural impurities   - Wool grease   2 - 25 % of greasy wool weight
  - Suint (dried perspiration)   2 - 12 % of greasy wool weight
  - Dirt   5 - 45 % of greasy wool weight
- Residues of insecticides, acaricides or insect growth regulators used as veterinary medicines to protect sheep from ectoparasites, such as lice, mites, blowfly, etc.

The percentage of the above mentioned components may vary widely depending on the origin of wool. For example, fine wool from merino sheep, used mainly in apparel, typically contains 13 % wool grease, whereas coarser wool of the types used for carpets contains an average of about 5 % grease.

The clean fibre content of raw wool usually lies within the 60 to 80 % range, but may vary from 40 to 90 %.

Wool grease is insoluble in water, but soluble in non-polar solvents such as dichloromethane or hexane. Refined wool grease is a valuable by-product.

Suint is water-soluble material arising from the secretion of the sweat glands in the skin. Suint is soluble in polar solvent such as water and alcohol.

Dirt can include a variety of materials such as mineral dirt, sands, clay, dust and organic materials.

Ectoparasiticides have important implications for the discharge of raw wool scouring effluent and disposal of the sludge generated by the treatment of the effluent. The chemicals known to be present in raw wool include:

- Organochlorine insecticides (OCs)   - γ-Hexachlorocyclohexane (lindane)
  - Dieldrin
  - DDT

- Organophosphorous insecticides (OPs)   - Diazinon
  - Propetamphos
  - Chlorfenvinphos
  - Chlorpyriphos
  - Dichlorfenthion

- Synthetic pyrethroids insecticides (SPs)   - Cypermethrin
  - Deltamethrin
  - Fenvalerate
  - Flumethrin
  - Cyhalothrin

- Insect growth regulators (IGRs)   - Cyromazine
  - Dicyclanil
  - Diflubenzuron
  - Triflumuron

The organochlorines are hazardous due to their persistence and bioaccumulability. They are thus likely to have long-range effects. γ-Hexachlorocyclohexane (also called lindane) is the most toxic (and also the most active as pesticide) of the hexachlorocyclohexane isomers (α- and β-HCHs). The technical crude product contains α- and β-HCH, the β-isomer being the most persistent. Lindane and DDT compounds are well-studied substances with demonstrated endocrine disrupting capacity.

The synthetic growth regulators show high aquatic toxicity (predicted no-effect concentration for cypermethrin is estimated at 0.0001 µg/l, while for OPs the correspondent value is 10.9 µg/l). Organophosphates have lower aquatic toxicity than synthetic pyrethroids and are less persistent than organochlorines.

All major grower countries have banned the use of organochlorine pesticides for sheep treatment, but there is evidence that wool from some former Soviet Union States and South America contain lindane at detectable concentrations. This would suggest that either their grazing is heavily contaminated or that this compound continues to be used occasionally for sheep treatment against ectoparasites.

Wool from the majority of grower nations contains residual sheep treatment medicines which are used legally to control infestations of lice, ticks and mites. These materials may be organophosphates, typically diazinon, propetamphos and trans-chlorfenvinphos, synthetic pyrethroids, typically cypermethrin and insect growth regulators such as cyromazine. The incidence of these materials on wool is variable and depends on the permitted legal use pattern in each country.

Manufacturers can use a database containing quantitative information on the OC, OP and SP content of wool from major producing countries. ENCO maintains one such database. Manufacturers use these data to avoid processing wool from suspect sources. The system is of immediate benefit to manufacturers who purchase and process wool from known sources. Commission processors of either loose fibre or yarn may be not aware of the origin of the fibre they are processing and so find it more difficult to control their raw material inputs using this approach.

More information regarding ectoparasiticides is reported in Section 2.3.1 where the wool scouring process is discussed.

2.1.1.10 Silk

Silk accounts for only 0.2 % of the total fibre production. Nevertheless, this fibre is very important for specific "niche" articles such as ladies' shirts, jackets and scarves.

Silk is derived from the silk worm, which spins a cocoon around itself. It is a protein fibre like wool and it is the only natural filament fibre to be used with success in the textile industry (the length of the thread is in the range of 700 to 1500m).

The silk fibre is composed of fibroin filaments wrapped with sericine (silk gum), which has to be removed during the pre-treatment.

2.1.1.11 Cotton and flax

Cotton fibre consists mainly of cellulose and some other components, as shown below.

Substance	Content
Cellulose	88 - 96 %
Pectin substances	0.7 - 1.2 %
Wax	0.4 - 1.0 %
Proteins	1.1 - 1.9 %
Ash	0.7 - 1.6 %
Other organic components	0.5 - 1.0 %
Source: EURATEX	

Table 2.1: Chemical composition of cotton fibre

Cotton production may use chemicals such as pesticides, herbicides and defoliants and these may remain as a residue on raw cotton fibres that reach the textile mill. However, this is of little concern for textile industry. In fact, tests of cotton samples from around the world, performed from 1991 to 1993, reported levels of pesticides below the threshold limit values for foodstuffs. [EPA]

Flax is a bast fibre. Many economic factors have contributed to this fibre losing much of its previous importance. Nevertheless flax remains a noble fibre suitable for luxury articles.

2.1.2 Chemicals & auxiliaries

A huge number of organic dyestuffs/pigments and auxiliaries are applied in the textile industry. In this document they will be divided into the following categories:
- dyestuffs and pigments
- basic chemicals, which include all inorganic chemicals and organic reducing and oxidising agents as well as the aliphatic organic acids
- auxiliaries, which comprise all textile auxiliaries containing mainly organic compounds except organic reducing and oxidising agents and organic aliphatic acids.

To give an idea of the variety of products available on the market (in particular, auxiliaries), it is worth noting that in the "2000 Textile Auxiliaries Buyers' Guide" more than 7000 commercial products are reported, based on 400 to 600 active components. They are classified according to the well-established TEGEWA nomenclature, according to their functional use in the production process, although the chemical nature of these products is too varied to allocate them unequivocally to one category.

For practical reasons the information about dyestuffs and textile auxiliaries is reported in this document in separate annexes (see Section 8 and Section 9).

2.1.3 Materials handling and storage

Basic fibrous raw materials arrive on site in press-packed bales and are stored in covered warehousing, which may also be used to store and dispatch finished goods to customers.

Basic chemical intermediates, acids, alkalis and bulk auxiliary chemicals are normally held within a bound or contained storage area. Large bulk containers may be situated in the open. High value and moisture- or environmentally-sensitive materials are normally transferred directly to the preparation area ("colour kitchen") from where they are dispensed.

Some synthetic organic colorants are regarded as a potential health hazard. Therefore colour kitchens are normally equipped with air extraction and filter systems to suppress dust levels during dispensing.

The chemicals (dyestuffs, pigments, basic chemicals and auxiliaries) are metered out either in powder form or as solutions. This operation can be done manually or with computer-aided metering devices.

The required measured amounts of products must in general be dispersed, diluted or mixed before being fed to the finishing machinery. Various systems are found in the industry, ranging from completely manual procedures to fully automatic ones. In the case of manual systems the prepared chemicals are added directly into the machine or in a storage container near the equipment, from which they are then pumped into the machine. In larger companies the chemicals are usually mixed in a central mixing station, from which they are supplied to the various machines through a network of pipes. The quantities and the addition of chemicals and auxiliaries are normally called up automatically according to predetermined programmes.

2.2   Fibre manufacturing: synthetic and artificial fibres

Manmade fibres are typically extruded into continuous filaments. The continuous filaments can then be:
- used directly (in general, following further shaping or texturing)
- cut into staple length and then spun in a process resembling the one used for wool or cotton.

Three main methods are used to produce the continuous filaments (primary spinning):
- melt spinning
- dry spinning
- wet spinning.

Melt spinning: The polymer is melted in a melt-extruder. The liquid is forced through the spinner opening under pressure and cooled by a jet of air to form the filament. A spinning preparation (spin finish) is generally applied at the bottom of the spinning duct. The melting process is suitable for thermoplastic fibres such as polyester, polyamide, polyolefins (e.g. polypropylene) and glass fibre.

Dry spinning: The polymer is dissolved in a solvent. The dissolved polymer is extruded through a spinneret into a chamber of heated air or gas where the solvents evaporates and the filament forms. This filament is further after-treated with a spin finish. The dry spinning process is principally used for acetate, triacetate and polyacrilonitrile.

Wet spinning: The polymer is dissolved in solution. The solution is forced under pressure through an opening into a liquid bath in which the polymer is insoluble. As the solvent is dissipated the fibre forms. The solvent can be dissipated through extraction or by means of a chemical reaction between the polymer solution and a reagent in the spinning bath (reactive spinning). The residual solvent can be extracted by simple washing. After the thread is formed and the solvent is washed out, a spin finish can be applied. Wet spinning produces viscose, acrylic fibres.

Following primary spinning, the applied treatments vary, depending on the final product and the processed fibre. Two simplified process sequences can be identified for this stage:
- process for the manufacturing of continuous filament in flat or texturised form
- process for the manufacturing of staple fibres.

Continuous flat filament

Possible points of spin finish application

Primary spinning

Drawing (dry)

Continuous texturised filament

Possible points of spin finish application

Primary spinning

Drawing (dry)

Texturising
(oven up to 500 ºC)

To reestablish the amount of spin finish
lost in the texturing process

Staple fibre

Possible points of spin finish application

Primary spinning

Drawing (wet)
(in aqueous bath with
preparation agents)

Heat-setting
(170 ºC)

If needed

Crimping

Cutting

As shown in the diagrams above, preparation agents can be applied at various stages during the manufacturing of the chemical fibres. Application of preparation agents in primary spinning (fibre manufacturing) is usually followed by further additions during secondary spinning, when the yarn is manufactured (see Section 2.4).

The preparation agents need to be removed to ensure uniform penetration of dyes and finishing agents and to avoid reaction or precipitation with them. Due to their high organic content and their often-low bioeliminability, these substances are responsible for wastewater pollution and air emission in the subsequent fibre pre-treatment. Particularly relevant in this respect is the production of continuous filaments destined for the production of knitted fabric and the manufacturing of elastomeric fibres, because in this case the amount of preparation agents applied is higher.

The amount of preparation agents applied varies according to the fibre (e.g. PES, PA, etc.) and make-up (flat or texturised filament, staple fibre). Information about the chemistry of the preparation agents and the amount applied on the fibre is given in Section 8.2.

2.3 Fibre preparation: natural fibres

2.3.1 Wool

Wool is usually opened and de-dusted before it is fed to the scour. This is a mechanical process designed to shake out dirt from the wool and open the fleeces in order to improve the efficiency of the scour in removing contaminants. The process also roughly blends the wool and produces a layer of fibres suitable for presentation to the scour. The opening and de-dusting processes vary considerably in severity depending on the characteristics of the particular wool being processed. The process produces a solid waste comprising dirt, sand, fibre fragments and vegetable matter.

The object of subsequent raw wool scouring processes is to remove contaminants from the wool fibre and to make it suitable for further processing.

Almost all of the scouring plants are based upon aqueous washing. Solvent scouring is much less widely practised. According to [VITO] there are world-wide only about five companies that degrease with organic solvents.

2.3.1.1 Cleaning and washing with water

A conventional wool scouring set is shown in Figure 2.2. The process is carried out by passing the wool through a series of 4 – 8 wash bowls, each followed by a mangle or squeeze press which removes excess scouring liquor from the wool and returns it to the bowl. Clean water is added at the last bowl and passes via a counter-flow system from bowl to bowl with final disharge from the first bowl in a controlled manner to drain.
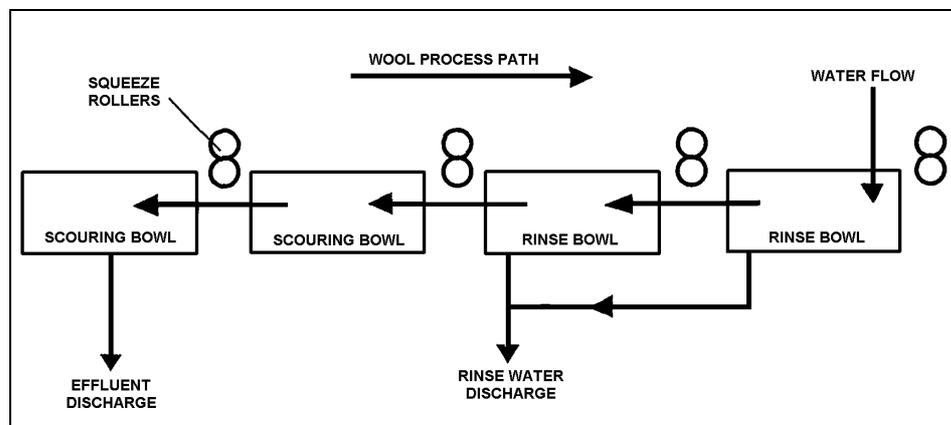
Figure 2.2: Conventional wool scouring arrangement

In the scouring bowls, suint is removed from the wool by dissolution, grease by emulsification and dirt by suspension.

For merino wools, the first bowl may be charged with water only and, in that case, its purpose is the removal of water-soluble suint before the wool enters the scouring process proper (this bowl is usually called "de-suint").

In order to achieve grease emulsification, the scouring bowls are charged with detergent and often with sodium carbonate, or other alkali, which acts as a detergent builder. Concentrations of detergent and builder are usually highest in the first scour bowl and they decrease in subsequent bowls.

Detergents used by scourers are mainly synthetic non-ionic surfactants, namely alcohol ethoxylates and alkylphenol ethoxylates. Some scourers also report the use of "solvent-assisted detergents" for the removal of marking fluids from fleeces.

Finally, the wool is rinsed by passing it through bowls containing water only.

In coarse wool scouring plants the final bowl of the scouring train is sometimes used for chemical treatments. In this case, it is isolated from the countercurrent liquor flow system and may also be isolated from the drain if the chemical treatment uses ecotoxic chemicals. The most commonly used treatment is bleaching, in which hydrogen peroxide and formic or acetic acid are added to the bowl. Other treatments sometimes applied include mothproofing, using a synthetic pyrethroid insecticide and acetic or formic acid, and sterilisation (of goat hairs) using formaldehyde.

Wool grease has a melting point around 40 ºC. Since removal of solid grease from wool by detergents is slow and difficult, 40 ºC is the lowest temperature at which aqueous scouring liquors are effective for removing grease. In addition, non-ionic detergents lose efficiency rather rapidly below 60 ºC, which means that scour and rinse bowls are typically operated at 55 - 70ºC.

After leaving the final squeeze roller the wool will contain 40 to 60 % moisture. It is therefore dried by convection in a hot-air drier. The drier is usually heated either by closed steam pipes or by direct gas firing. The heat supply to the drier may be controlled by a signal from a device which senses the humidity of the drier atmosphere or the moisture content of the wool at the output end, thus saving energy and avoiding overdrying the wool.

The mechanical design of wool scours and the arrangements for circulating the scour and rinse liquors vary widely. Since these matters have a direct influence on energy and water usage, as well as the partial removal of contaminants from the effluent, it is important to illustrate them in more detail.

New generation scouring plants like the one illustrated in Figure 2.3 have an integrated system for grease and dirt recovery.
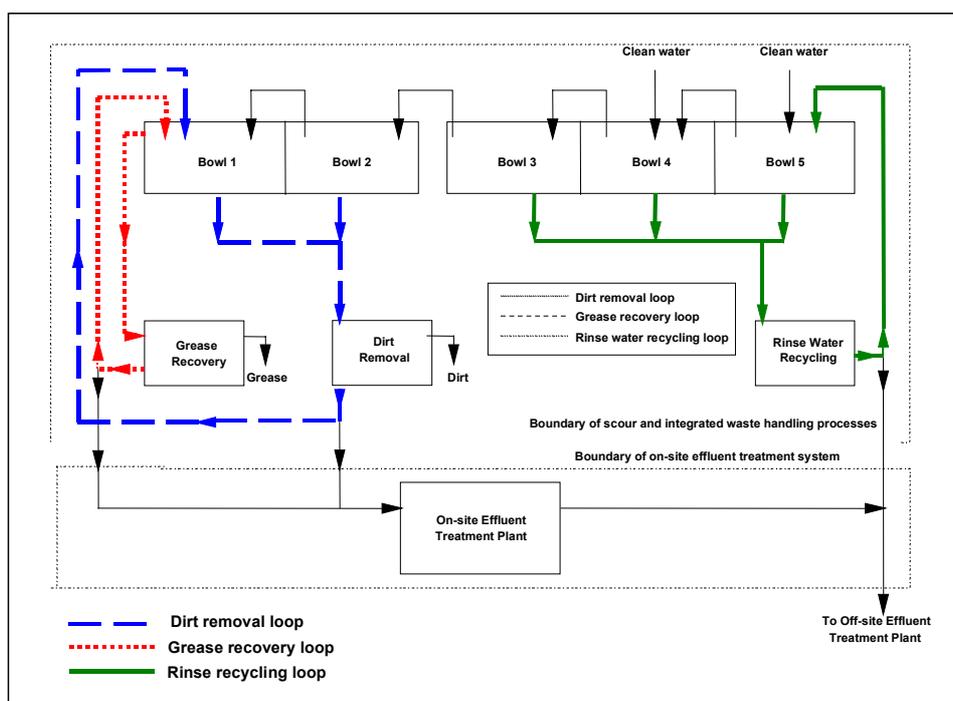
Figure 2.3: Schematic diagram showing a scour line, integrated waste handling process and on-site effluent treatment plant

The dirt tends to settle at the bottom of the bowl and modern scour bowls usually have hopper-shaped bottoms from which the sludge is removed by gravity through a valve. Opening of the valve may be under the control of a timer or may respond to a signal from a turbidity meter which senses the thickness of the dirt suspension in the hopper bottom. The discharge from the scour bowl hopper bottoms is led to a heavy solids settling tank where it is gravity-settled and the settled liquor partly recycled to scour bowl 1 and partly discharged. Flocculant may be added to the heavy solids settling tank to assist the separation of dirt, or a decanter centrifuge or hydrocyclone may be used in preference to gravity settling for dirt removal.

For grease recovery, modern scour bowls have a side tank in which the grease-rich liquors removed from the wool by the squeeze press are collected. From here, part of the flow may be pumped to the previous bowl or, in the case of bowl 1, to a primary grease centrifuge. The centrifuge separates the liquor into three phases. The top phase, referred to as the cream, is rich in grease and passes to secondary and possibly tertiary centrifuges for further de-watering, finally producing anhydrous grease; the bottom phase is rich in dirt and goes to the heavy solids settling tank; the middle phase is impoverished in both grease and dirt compared with the input and this is split, part being recycled to scour bowl 1 and part being discharged.

In a commonly used variation of the above recycling arrangements, the dirt and grease removal and recycling loops may be combined. In this case, scouring liquor may be removed from the bottoms of the bowls only, or from top and bottom, and passed first through the dirt removal equipment, then through the primary grease centrifuge.

Some scourers recycle rinse water (see Figure 2.3). The flowdown from the first rinse bowl can be treated to make it suitable for addition to the feed to the final rinse bowl. Normally, this is accomplished by removing dirt in a hydrocyclone and processing the water through a membrane filtration plant to remove other impurities.

It is normally necessary to purge dirty liquors which collect at the bottoms of the rinse bowls, but this is not always the case.

The dirt removal and grease recovery loops described above serve several purposes. They save water, by recycling effluent to the scour, and they act as a process-integrated partial effluent treatment. The recovered wool grease can be sold, although the market for this by-product has been variable in most recent years. Finally, since the discharges from the loops are the only points at which heavily contaminated scour liquors are discharged, valves and meters at these points can be used to control the rate of water usage in the scouring section.

2.3.1.2 Environmental issues associated with wool scouring (with water)

In this section we will discuss the environmental issues associated with the overall scouring process including the treatment of the process effluent.

The main environmental issues associated with the wool scouring process arise from emissions to water, but solid waste and the air emissions also need to be taken into account.

Potential for pollution of water

The removal of contaminants present on the raw fibre leads to the discharge of an effluent in which the main polluting contributors are:
- highly concentrated organic material in suspension and in solution, along with dirt in suspension
- micro-pollutants resulting from the veterinary medicines applied to protect sheep from external parasites.

There are also detergents in the discharged water, which contribute to the increase of the chemical oxygen demand of the effluent. The detergent is recycled via the grease recovery/dirt removal loop. As a result, low efficiency in this recovery system is associated with higher amounts of detergent in the effluent. Compared to the chemical oxygen demand attributable to wax, dirt, etc., the detergents can be considered minor contributors to water pollution, but this is not the case when harmful surfactants such as alkylphenol ethoxylates are used as detergents (for more detail on environmental issues, see Section 8.1).

As to the organic matter coming from wax and dirt, according to [Stewart, 1988] the COD of effluent and of greasy wool can be calculated using the following equation:

COD(mg/l or mg/kg) = 8267 x suint(%) + 30980 x oxidised grease(%) + 29326 x top grease(%) +   6454 x dirt(%) + 1536.

Since the coefficients for top grease and oxidised grease[2] in this equation are similar and since approximately equal quantities of top grease and oxidised grease are present in many wools, it is possible to combine the two grease terms the above equation as follows:

COD (mg/l or mg/kg) = 8267 x suint(%) + 30153 x total grease(%) + 6454 x dirt(%) + 1536

It is then possible to calculate the COD content of "typical" merino and crossbred wools:

-    Merino wool: suint = 8 %; grease = 13 %; dirt = 15 %

COD = (8.267 x 8) + (30.153 x 13) + (6.454 x 15) + 1.536 = 556 g/kg greasy wool

-    Crossbred wool: suint = 8 %; grease = 5 %; dirt = 15 %

COD = (8.267 x 8) + (30.153 x 5) + (6.454 x 15) + 1.536 = 315 g/kg greasy wool.

These high levels of oxygen-depleting substances must be removed from the effluent before it can be discharged without potential for harmful effects.

Organohalogen, organophosphorus compounds and biocides are among the priority substances listed for emission control in the IPPC Directive.

Worldwide, the most common ectoparasiticides used for treating sheep are diazinon (OP), propetamphos (OP), cypermethrin (SP) and cyromazine (fly-specific IGR), for control of blowfly. Insect growth regulators such as dicyclanil, diflubenzuron and triflumuron are registered only in Australia and New Zealand. Organochlorine pesticides (in particular, hexachlorocyclohexane) are still found on wool coming from the former Soviet Union, the Middle East and some South American countries. [INTERLAINE] (See also Section 2.1.1.9).

Concerning the fate of ectoparasiticides when they enter the scouring process, a distinction has to be made between lipophilic and hydrophylic compounds such as cyromazine. OCs, OPs and SPs associate strongly with the wool grease and are removed with it during scouring (although a fraction (4 %) is retained by the fibre and will be released in the subsequent finishing wet processes). This behaviour applies also to diflubenzuron (IGR). Recent studies have shown that triflumuron associates partially with the dirt and partially with the grease and that consequently a higher proportion of the residue is likely to be retained on site. [NRA] The water-soluble compounds cyromazine (11 g/l at 20 ºC) and dicyclanil are probably not removed from the effluent stream except by evaporating treatments.

---

[2]   Top grease is unoxidised grease which is readily separated from scour liquors by centrifuging; oxidised grease is less hydrophobic and is less readily separated.

In the following wastewater treatment systems an additional fraction of these residues is removed. Physico-chemical separation techniques remove the biocide residue at approximately the same rate as the grease and the dirt with which they are associated. On the other hand, evaporation systems remove OCs and SPs in significant quantities, but up to 30 % of the OPs may appear in the condensate because they are steam volatile. [INTERLAINE]

Despite these treatments, the removal of pesticides is often incomplete and there is potential for pesticides to enter the aquatic environment when the effluent is discharged. The environmental concentrations of ectoparasiticides in the receiving water depend greatly on local circumstances, in particular, the amount of scouring activity concentrated in a given catchment and the dilution available between scouring discharges and the river which receives the treated effluent.

In areas of Europe with a high concentration of scouring activity, there is a risk of high concentration levels of pesticides in the receiving water. In this case, it is preferable to define discharge limits on the basis of risk assessment models. In UK for example, statutory environmental quality standards (EQS) for the OCs and non-statutory standards for the OPs and cypermethrin have been defined. Discharge limits (given in g/tonne of greasy wool) are set up for processing mills by comparing the given EQS targets with predicted environmental concentrations based on tonnage of wool processed and typical effluent treatment systems.

The control of the discharge limits at the scouring mills is carried out by using data from the ENCO wool & hair pesticide database (to define the initial amount of residues on the incoming wool) in combination with the above mentioned water-grease partition factors for the different pesticides.

Potential for pollution of land

Two main "wastes", grease and sludge, are produced as a consequence of the scouring activities (and related effluent treatment).

Depending on its oxidation extent, it may be possible to recover from 20 to 40 % of the grease initially present on the raw wool. This is usually regarded as a by-product rather than a waste, since it can be sold to lanolin refiners. However, high levels of pesticides residues in the grease can also be a problem for the lanolin refiners, especially for the production of lanolin-based pharmaceuticals and cosmetics, since more expensive and sophisticated techniques have to be used to remove the pesticides to acceptable levels. Acid-cracked grease has no market value and has to be landfilled.

The sludge produced as a result of physico-chemical treatment of wastewater also contains grease, dirt and the portion of pesticides which are strongly associated with either grease or dirt. Concentrates and sludges from evaporation or membrane filtration may also contain suint, which is mainly potassium chloride and potassium salts of fatty acids.

Sludge and concentrate disposal may follow several routes:
- incineration (with heat recovery)
- pyrolysis/gasification
- brick manufacturing
- composting or co-composting with other organic material
- landfill.

The first three sludge disposal routes listed destroy the organic material in the sludge, including grease and pesticides. The ash from incineration may contain potassium salts, derived from suint, and heavy metals characteristic of the soil on which the sheep producing the wool have grazed. The ash is normally disposed of to landfill. The characteristics of the char from pyrolysis/gasification are unknown and this char is also typically disposed of to landfill. The use

of wool scour sludges in brick manufacture results in no residues for immediate disposal. These three sludge disposal methods probably have the least potential to pollute land.

Wool scour sludges cannot be composted alone, but require the addition of carbon-rich organic material. Green waste from agriculture or horticulture has been used. Composting is not yet regarded as a fully developed, fail-safe technique and only partly degrades the pesticides present in the sludge. However, since the pesticides present in the sludge are there because of their lipophilicity or their strong propensity to absorb onto solids, they are likely to be immobile in soil, and spreading of compost derived from wool scour sludges on agricultural land is unlikely to pose an environmental risk of any significance.

Landfill is the simplest and often cheapest method of disposal of sludges. In the longer term, however, landfill is not believed to be either economically or environmentally sustainable. The fate of wool scour sludges in landfill is not known, but there is a small potential for the ectoparasiticides present to arise in leachate. Anaerobic degradation of the organic material in the sludge will give rise to methane emissions.

Potential for pollution of air

Air pollution is not a main issue for wool scouring processes. Nevertheless two issues can be mentioned.

Hot acid cracking, which involves heating the scour effluent with sulphuric acid, when used near residential areas, has been the subject of odour complaints.

Incineration is used in conjunction with evaporation of the effluent because the surplus heat from the incinerator can be used in the evaporation process. Incineration of wool scour sludges has potential for air pollution. Since sludges contain relatively high levels of chloride (from suint) as well as organically bound chlorine from ectoparasiticides etc., there is potential for the production of polychlorodibenzodioxins and furans, when they are incinerated. The sludges also contain relatively high levels of sulphur and nitrogen and the combustion process therefore produces SO_X and NO_X.

2.3.1.3 Cleaning and washing with solvent

?

2.3.2 Cotton and flax

Cotton is a much cleaner raw fibre than wool and initial operations are mainly dry. The fibres are supplied to the spinning mill in compressed bales. The fibres are sorted by grade, cleaned to remove particles of dirt and blended with fibres from different bales to improve the consistency of the fibre mix. Sorting and cleaning is performed in machines known as openers.

With flax, the isolation of the fibre from the flax stem is done in different steps. After crop (plucking) the flax is retted (dew retting, water retting, enzymatic, microbiotic, steam or chemical retting). Pectinic and hemicellulosis substances are degraded in this step. Rovings are produced by further mechanical treatment before spinning.

2.3.3 Silk

For silk production the silk worm is killed with steam and the filament is unwound directly from the cocoon. The filament is submitted to pre-treatment processes to remove the silk gum and other organic impurities.

2.4   Yarn manufacturing

Almost all textile apparel products are made from spun yarns of either 100 % natural fibres, or 100 % man-made staple fibres or blends. Only a few apparel products, for instance smooth sportswear, are made of filament yarns exclusively. Spinning is the process by which staple fibres are transformed into yarn suitable for the textile industry. There are two main spinning processes:

- the wool spinning process
- the cotton spinning process.

2.4.1 The wool spinning system

The wool spinning process is mainly used to produce wool and wool-blend yarns. A distinction is made between the worsted and woollen process. In worsted spinning, higher-quality and longer fibres are processed and the result is a fine yarn which is used to produce worsted fabric. In the woollen spinning system, shorter fibres are processed. In both the woollen and worsted systems the various fibres (e.g. wool fibres from different sources, different types of synthetic fibres) are combined during the blending operation. In order to allow efficient mechanical processing in the subsequent operations, fibre lubricants are applied to the fibres at this stage (or later before or after carding, depending on the system applied).

In the worsted system the fibres are paralleled in a combing machine and are then drawn and spun. In the woollen system the fibres are only carded and then spun. The resulting yarn is then twisted (if required) and finally prepared for the subsequent treatments (dyeing, weaving, tufting, etc) through an operation called winding.

The environmental implications of the yarn production stage for the subsequent finishing steps of the textile chain originate from the lubricants applied in the oiling stage. Since lubricants need in general to be completely removed before dyeing, they are found in wastewater from finishing mills. Lubricants are generally sold in aqueous solution (50 % oil and 50 % water), which are further diluted before use in spinning mills. Water-soluble synthetic oils are generally used. Mineral oils are sometimes used, too, but in smaller quantities. In addition, spinning formulations contain a surfactant to improve the oil-removal during washing and, sometimes, antistatic agents, especially with of synthetic fibres. In most cases surfactants are based on APEOs. In the carpet industry, mothproofing agents can also be present in the formulations.

Emissions of hard-to-biodegrade organic substances such as mineral oils and hazardous compounds such as APEOs and pesticides (only when mothproofing agents are applied) that are, need to be taken into account. Additional information about spinning oils is given in Section 8.2. It is, however, difficult to analyse in more detail the environmental aspects associated with the use of these substances because of the large variety of commercial products. Spinning mills usually buy lubricants from dealers, who buy chemical products from large chemical producers, and mix them according to the specific needs of each spinning mill. This makes even more difficult the identification of the chemical substances present on the yarn when this enters the finishing mill.

Moreover, a distinction must be made between fabric derived from carded yarn (woollen process) and fabric manufactured using combed yarn (worsted process). There is a substantial difference, in fact, not only from a mechanical point of view, but also in the quantity of lubricants applied (which reaches approximately 5 % in the woollen process, but only 1 % in the worsted process).

2.4.2 The cotton spinning system

The cotton spinning system is generally used for cotton and man-made fibres. As has already been described in Section 2.3.2, cotton fibres are first submitted to opening and cleaning operations. The following steps, which are the same for cotton and man-made fibres, are:
- carding
- combing
- drawing
- roving
- spinning
- twisting (if required)
- winding.

In the case of synthetic fibres an extra amount of preparation agents is applied to the fibre at the yarn manufacturing stage. This amount is especially relevant in the case of elastomeric fibres where the final content of preparation agents (mainly silicone oils) can reach 6 % on the weight of the fibre. These substances will be removed during the pre-treatment processes in the finishing mills, thus increasing the organic load of the resulting emissions.

2.5 Cloth production

Raw materials for cloth production are spun yarns and filament yarns. These raw materials can then be converted into:
- woven textiles
- knitted textiles
- floor-coverings.

The last item covers a number of different end-products which are typical of the carpet industry.

2.5.1 Woven textiles

2.5.1.1 Warping

Before weaving, warp yarns are wound onto beams in a process called warping. During this operation there is no consumption of auxiliary agents that could have a negative influence on the emissions from the subsequent finishing processes.

2.5.1.2 Sizing

In order to lubricate and protect the warp yarn during weaving, sizing agents (in the form of water solutions or water dispersions) are applied after warping. The main sizing agents can be grouped into two classes:

a)   Sizing agents on base of native polysaccharides:

- starch
- starch derivates such as carboximethyl starch or hydroxiethyl starch ether
- cellulose derivates, especially carboximethyl cellulose (CMC)
- galactomannans
- protein derivates.

b)   Fully synthetic polymers

- polyvinyl alcohols (PVA)
- polyacrylates
- polyvinyl acetate
- polyester

The ratio of synthetic sizing agents to native sizing agents is about 1:3 (in Germany) (?).

It is important to bear in mind that:
- the type of sizing agent applied varies according to the fibre concerned
- sizing agent formulations are usually mixtures of the substances mentioned above.

Moreover additional auxiliaries are present in the sizing mixtures. These are mainly [ULLMANN'S]:
- viscosity regulators: complex formation between borax and the hydroxyl groups of starch increases the viscosity of the paste, while urea reduces it. Important viscosity regulators include starch-degrading agents such as oxodisulphates, peroxosulphates that act by oxidative cleavage of the macromolecules.
- sizing fats: are used to improve the weaving behaviour of the warp. Suitable materials include sulphated fats and oils and mixtures of fatty acid esters with non-ionic and anionic emulsifiers.
- antistatic agents (mainly based on polyglycol ethers).
- wetting agents: fatty alcohols poly(glycol ethers) with a low degree of ethoxylation.
- de-foaming agents: their addition is often necessary when the sizing agents tend to produce foam (e.g. with PVA) or if wetting agents are added. Suitable products are based on paraffin oils, phosphoric esters, fatty acid esters or silicone oils.
- preservatives: for sizing liquors that are stored for long periods and contain degradable components such as starch and starch derivatives, fungicides and/or bacteriocides are added. Typical preservatives include formaldehyde, phenol derivatives, heterocyclic compounds of the isothiazoline type.

Sizing agents are introduced by the weaving firm, but have to be removed by the finisher (during the operation called desizing). This desizing process results in high wastewater loads. In the case of woven fabric, sizing agents can represent 30 – 70 % of the total COD load in wastewater. The lower percentage is for finishing of woven fabric mainly consisting of flat filament yarns and the higher for staple fibres, especially for cotton and in case of native sizing agents. Therefore it is important to know the COD of these substances and their characteristics in terms of biodegradability and bio-eliminability. The additives present in the formulations also influence the aquatic toxicity and BOD of the resulting emissions.

Section 8.3 gives more details about:
- characteristics of the chemical substances commonly used as sizing agents and specific COD and BOD_5 values
- typical amounts applied on the various fibres.

2.5.1.3 Weaving

Weaving is the process by which yarns are assembled together on a loom and a woven fabric is obtained. The process only requires electricity. Lubricants and oils are used to lubricate the loom, but in particular cases they may contaminate the fabric.

2.5.2 Knitted textiles

2.5.2.1 Waxing

Before knitting, the yarn is lubricated or waxed (generally with paraffin wax) to allow knitting at higher speed and protect the yarn from mechanical stresses. Waxing may be done while re-winding the yarn onto bobbins, in which case the process is normally called "preparation for knitting".

2.5.2.2 Knitting

Like weaving, knitting is a mechanical process and involves knotting yarn together with a series of needles. Mineral oils are generally used to lubricate the needles and other parts of the knitting machinery. The quantity of oils used depends on the technology of the machine and on the speed of the needles; the value ranges between 0.2 and 0.3 % of the weight of the fabric.

The oil and the wax that remain on the final fabric will be washed out during the finishing treatments. However, their contribution to the total pollution load coming from finishing mills is not significant.

2.5.3 Textile floor-coverings

Textile floor-covering is a collective noun for articles having a usable surface of textile material. This particular class of cloths can be schematically described as composite substrates made up of the following layers:
- a *carrier layer*, which is mainly made of polypropylene strips of fabric (75 %), PP or PES webs (16 % and 8 %, respectively) and less commonly of jute fabric (1 %). [VITO]
- a *pile yarn*, which can equally well be made from filament or staple fibre yarns (mainly polypropylene, polyamide, polyester, wool).
- a *pre-coating layer*, which is typical of tufted carpet and whose function is to anchor the pile onto the carrier layer. This coating layer is made from synthetic rubber or an artificial dispersion based on carboxylated styrene-butadiene rubber latex.
- a *coating layer,* which is an additional layer applied to the bottom side of the carpet. We can distinguish between foam coating, textile backing coating and heavy coating methods. The purposes of this final layer are various. Mainly, it is intended to strengthen the attachement of the pile, improve dimensional stability of the carpet and provide the carpet with properties such as anti-slip, heat insulation, stepping elasticity, etc. (carpet coating techniques are described in more detail under the finishing treatments in Section 2.12).

This is, however, a very general definition. In fact, the characteristics of the end product and the applied manufacturing techniques can vary significantly. The principal methods of manufacturing carpet/floor-coverings are tufting, weaving and needling. The best way to describe these techniques is probably to describe the different types of carpets.

2.5.3.1 Tufted carpet

As the figure below shows, tufted carpets are made up of the following different components:
- the face yarn (pile), which can be made from either staple fibres (PA, PP, PES, PAC, wool and cotton) or synthetic filaments
- the primary backing (carrier layer)
- the pre-coating layer
- the back-coating layer (which can consist of a textile back-coating or of a foam coating layer).
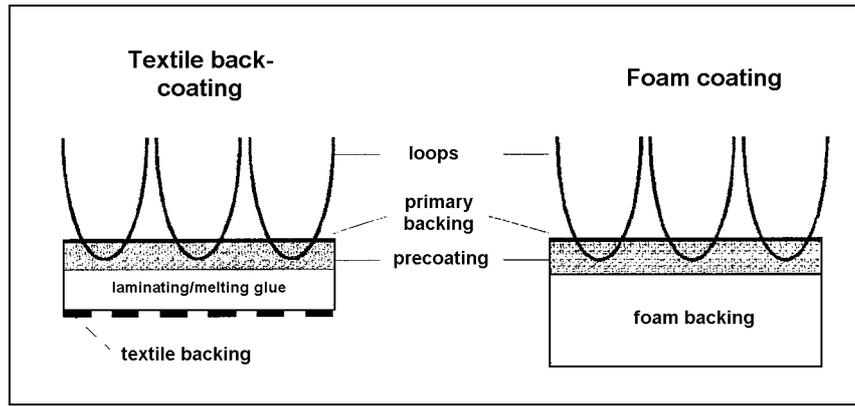
Figure 2.4: Cross-section of a tufted carpet

In the tufting process, pile yarns are inserted by needles into a woven or non-woven carrier material (primary backing), made of polypropylene, polyester or jute, across the entire width of the substrate (up to 5m). During subsequent manufacturing processes the base of the pile yarn is anchored in the back of the carpet by means of an applied coating.

Figure 2.5 is a simplified representation of a tufting plant.
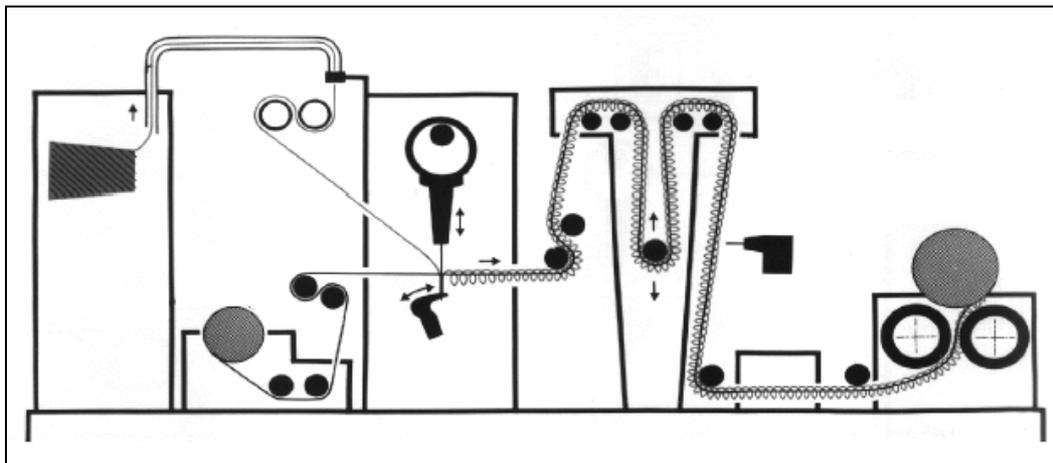
Figure 2.5: Simplified representation of a tufting plant

Through variations of the tufting technique, different three-dimensional pile structure can be produced as well as patterned carpets (e.g. level loop pile, multi-level loop pile, cut and loop, velvet and velour, saxony).
Figure 2.6 shows two examples of carpet styles are shown.
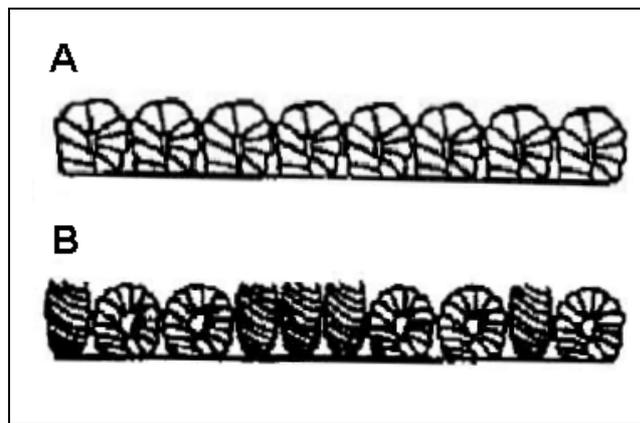
Figure 2.6: A: Level loop pile; B: Cut and loop pile

2.5.3.2 Needle-felt carpet

Figure 2.7 and Figure 2.8 show the manufacturing process for needle felt carpets. The fibres lie criss-cross to each other and are compressed with needles. This compression is fixed with binding agents [VITO]. Needle-pile carpets can consist of one or several layers, with or without a carrier layer. They may be equipped with various types of backings (textile backing, foam, heavy coating). For lasting binding of the fibres, the needled substrate is subsequently subjected to further thermal or chemical treatment (chemical reinforcement).

1) needle board with needles
2) needle bar grid
3) jute backing
4) nonwovens
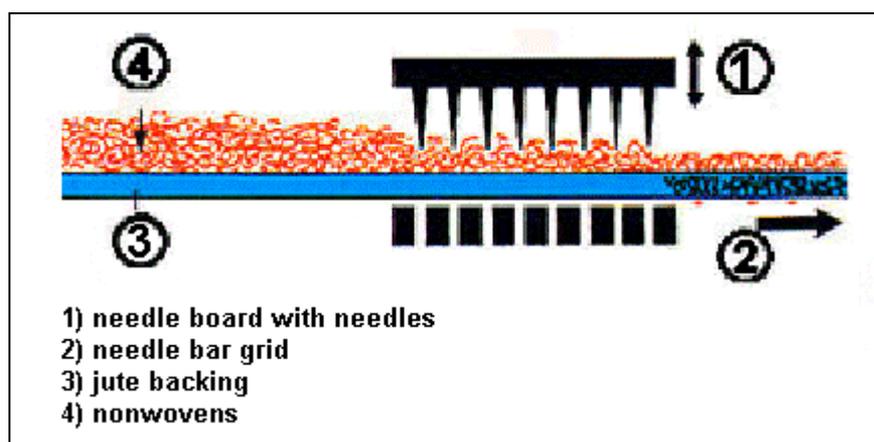
Figure 2.7: Manufacture of needle-felt carpet

Almost all fibres may be used for the production of needle felts; however, man-made fibres are mostly used (PP, PA, PES, PAC, wool, jute/sisal, viscose).
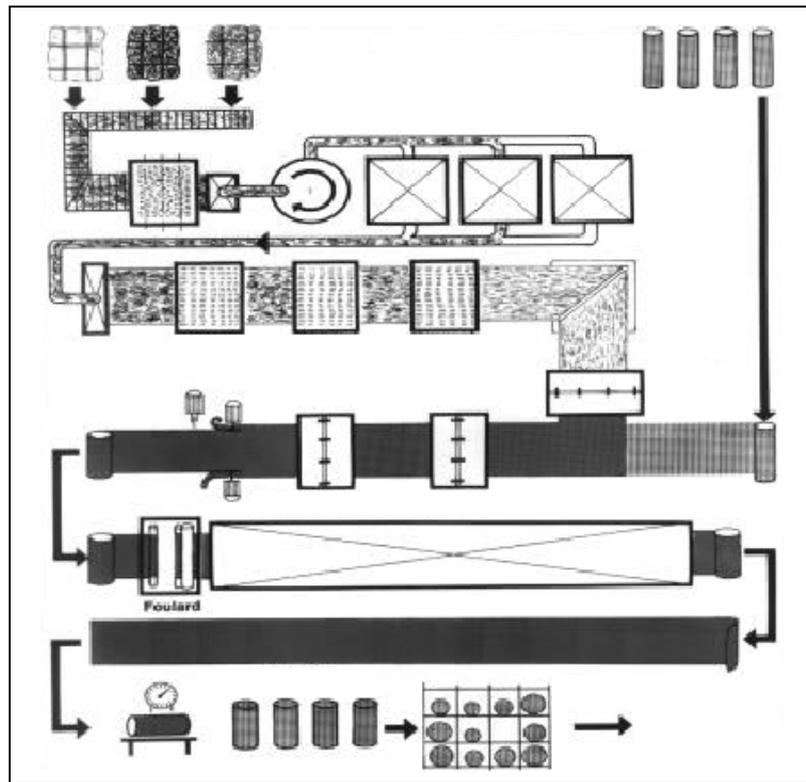
Figure 2.8: Production line for needle-felt carpets

2.5.3.3 Woven carpet

The manufacturing process for woven carpets is similar to manufacturing of any other woven good (IS THE WARP SIZED OR NOT IN THE CASE OF CARPET MANUFACTURING?). A scheme of the production process for woven carpets is reported in Figure 2.9.
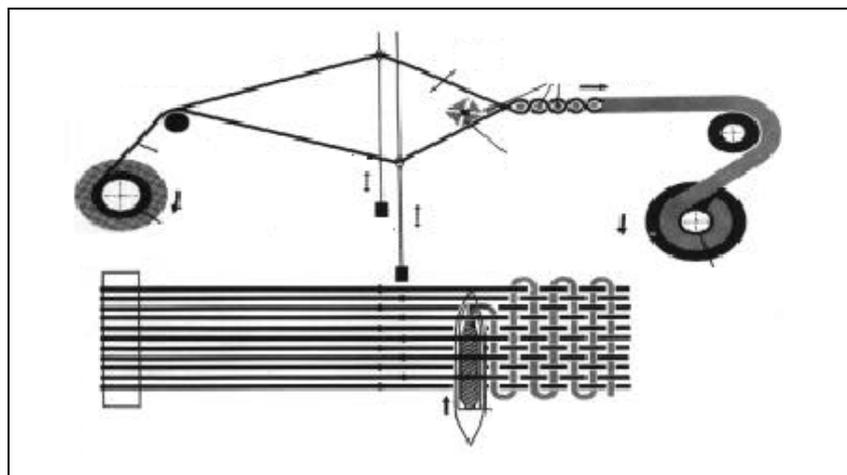
Figure 2.9: Representation of the production process for woven carpets

As a rule, woven carpets are provided with a stabilising back-coating. Only in rare cases is an additional heavy coating (e.g. PVC or bitumen) applied.

2.6   Pre-treatment before colouring

Pre-treatment processes should ensure:
- the removal of foreign materials from the fibres in order to improve their hydrophilic characteristics and their affinity for dyestuffs and finishing treatments
- the improvement of the ability to absorb dyes (which is the case in mercerising)
- the relaxation of tensions in synthetic fibres (without this relaxation of tension, unevenness and dimension instabilities can occur).

The position of pre-treatment within the production scheme is closely related to the position of dyeing in the sequence. The point is that pre-treatment comes immediately before dyeing (and printing).

Pre-treatment processes and techniques depend:
- on the kind of fibre to be treated: for raw goods made of natural fibres such as cotton, wool, flax and silk the technical task is more difficult than for those made of synthetic and artificial fibres. Natural fibres in fact are accompanied by a higher amount of substances that can interfere with later processing. Man-made fibres, in turn, usually contain only preparation agents, water-soluble synthetic size and soil which simple washing processes can remove.
- on the form of the fibre (flock, yarn, woven or knitted fabrics)
- on the amount of material to be treated (for example, continuous methods are more efficient, but are economically viable only for large production capacities).

Pre-treatment operations are often carried out in the equipment in which the material is subsequently dyed. For ease of reading of this part of the document, machines that are not specific to a given treatment are described in a separate annex (see Section 10).

2.6.1 Pretreatment of cotton & cellulose fibres

2.6.1.1 Principal manufacturing processes

Cotton pretreatment includes various wet operations, namely:
- singeing
- desizing
- scouring (alkaline extraction)
- mercerising (and caustification)
- bleaching.

Some of these treatments are obligatory steps only for certain make-ups (e.g. desizing is carried out only on woven fabric).

Moreover some of these treatments are often combined together in one single step in order to respond to the need to reduce production time and space as much as possible. Nevertheless, for practical reasons they will be described as separate treatments, leaving the discussion about specific make-ups to the following sections.

Singeing

Singeing can be carried out both on yarns and fabrics, but it is more common on fabrics, especially on cotton, cotton/PES and cotton /PA substrates.

Protruding fibre ends at the fabric surface disturb the surface appearance and produce an effect known as "frosting" when dyed. It is therefore necessary to remove the surface fibres by passing the fabric through a gas flame.

The fabric is passed over a row of gas flames and then immediately into a quench bath to extinguish the sparks and cool the fabric. The quench bath often contains a desizing solution, in which case the final step in singeing becomes a combined singeing and desizing operation.

Singeing has no effect on the effluents because only cooling water is necessary. As far as air emissions are concerned, relatively strong odours and dust emissions are observed. [EURATEX]

Desizing

Desizing is used for removing from woven fabric sizing compounds previously applied to warp (see Section 2.5.1.2) and is usually the first wet finishing operation performed on woven fabric.

Desizing techniques are different depending on the kind of sizing agent to be removed.

Currently applied techniques can be categorised as follows:
1. techniques for the removal of starch-based sizing agents (water-insoluble sizes)
2. techniques for the removal of water-soluble sizes.

1. Techniques for the removal of starch-based sizes

Starch-based sizes are difficult to remove and require either bacterial action of an enzyme or other chemical treatment in order to be converted into a washable form. This chemical degradation is mainly achieved by:
*   enzymatic desizing
*   oxidative desizing.

Enzymatic desizing is the most widely used method for the removal of starch, amylases being particularly suitable. The advantage in the use of enzymes is that starches are decomposed without damaging cellulose fibre.

In order to reduce the number of steps in the pre-treatment process, it is common practice to combine desizing with cold bleaching in a single step. In this case the process is also called *"oxidative desizing"*. The fabric is impregnated in a bath containing hydrogen peroxide and caustic soda, together with hydrogen peroxide stabilisers and complexing agents. Persulphate is also usually added to the solution.

Due to the action of NaOH, this treatment, beside a desizing/bleaching effect, also serves as pre-scouring treatment. Furthermore, oxidative desizing is particularly useful when the textile contains enzyme poisons (fungicides) or when sizes are present that are difficult to degrade. However, because starch scarcely differs from cellulose in the cross-linking of the cellulose rings, chemical oxidation, if not well controlled, can damage the fibre.

Desizing is usually carried out in pad-batch. The fabric is impregnated in a padder with the desizing solution. It is then rolled-up on a beam and kept in slow rotation for some hours. Sometimes (only for big lots and with enzymes that are stable under steaming conditions) a pad-steam process can be applied. After the reaction time, the fabric is thoroughly washed in hot water (95 ºC).

2. Techniques for the removal of water soluble sizes

For the removal of water-soluble sizes such as PVA, CMC and polyacrylates, theoretically, only washing with hot water and sodium carbonate is needed for desizing. However, the washing efficiency can be increased by:
- adding suitable auxiliaries (wetting agents) to the desizing liquor (with some restrictions in case of size recovery)
- allowing adequate time for immersion in the desizing liquor (this ensures maximum liquor pick-up and adequate time for the size to swell)
- washing thoroughly with hot water in order to remove the solubilised size.

In this case is the process carried out in normal washing machines (?)

Mercerising

Mercerising is carried out in order to improve tensile strength, dimensional stability and lustre of cotton. Moreover an improvement in dye uptake is obtained (a reduction of 30 – 50 % of dyestuff consumption can be achieved thanks to the increased level of exhaustion).

Mercerising can be carried out on yarn, woven and knitted fabric through one of the following different treatments:
- mercerising with tension
- caustisizing (without tension)
- ammonia mercerising.

Mercerising with tension

Caustic soda mercerising is the most commonly applied mercerising technique (it is not applied to flax). Cotton is treated under tension in a solution of concentrated caustic soda (270 – 300g NaOH/l, which means also 170 – 350 g NaOH/kg) [UBA] for approximately 40 - 50 seconds.

During mercerising the temperature is adjusted at low values (5 - 18 ºC) when the lustre is the priority and at slightly higher levels when the improvement of the other characteristics is preferred. Because the reaction between caustic soda and cellulose is exothermic, cooling systems are applied to keep down the temperature of the bath.

Beside the conventional cold treatment, a hot mercerising process is also now commonly applied (is it used only for fabric(?). The material is soaked in a solution of caustic soda close to boiling point. After hot stretching, the fabric is cooled down to ambient temperature and washed under tension.

In order to ensure a homogeneous penetration of the liquor, especially when operating at ambient temperature, wetting agents are employed. Sulphonates mixed with non-ionic surfactants and phosphoric esters are the most commonly used.

Caustisizing

In the caustisizing process, the material is treated at 20 – 30 ºC with caustic soda at lower concentration (145 – 190 g/l) without applying tension. The material is allowed to shrink, thus improving the dye absorption.

Ammonia mercerising

Cotton yarn and fabric can be treated with anhydrous liquid ammonia as an alternative to caustic soda. Effects similar to mercerising are obtained, although the lustre grade is inferior to caustic

soda mercerising. Traces of ammonia have to be removed, preferably with dry heat treatment followed by steaming.

Is this method used in practice (?)

Two examples of mercerising machines respectively for woven fabric (Figure 2.1) and for knitted fabric in tubular form (Figure 2.11) are reported below.
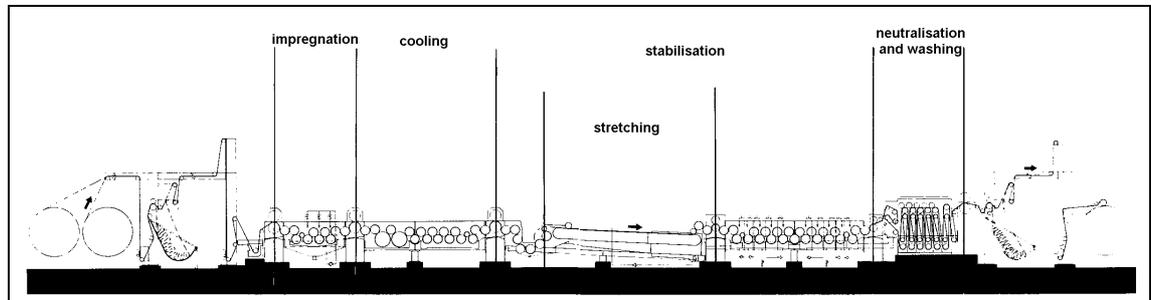
Figure 2.10: Example of Mercerising equipment for woven fabric
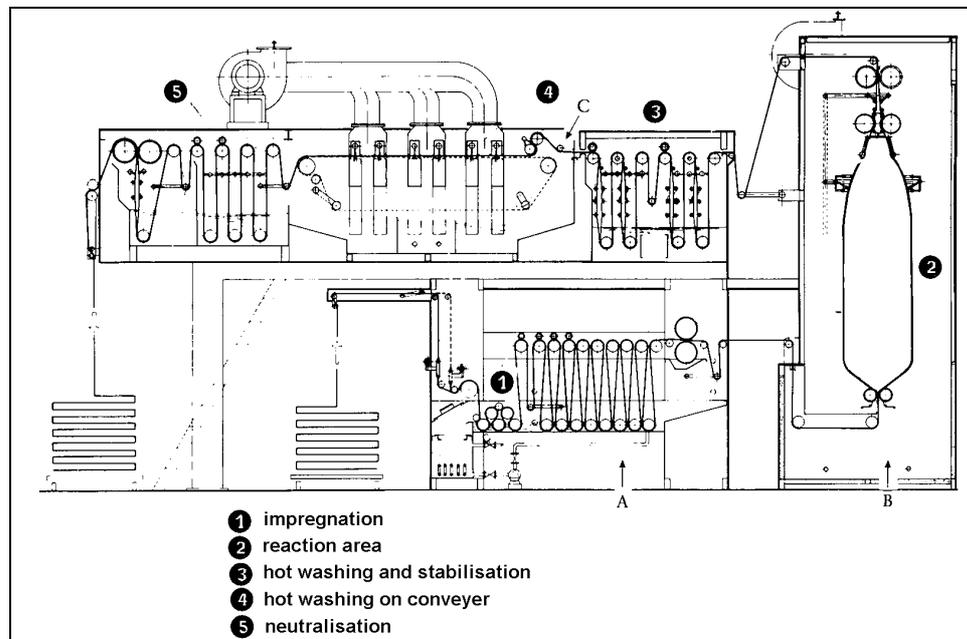
Figure 2.11: Example of Mercerising equipment for knitted fabric in tubular form

Scouring (alkaline extraction)

Scouring (also known as boiling-off or kier boiling) is aimed at the extraction of impurities present on the raw fibre or picked up at a later stage such as:

- pectins
- fat and waxes
- proteins
- inorganic substances, such as alkali metal salts, calcium and magnesium phosphates, aluminium and iron oxides
- sizes (when scouring is carried out on woven fabric before desizing)
- residual sizes and sizing degradation products (when scouring is carried out on woven fabric after desizing).

Scouring can be carried out as a separate step of the process or in combination with other treatments (usually bleaching or desizing) on all kind of substrates: woven fabric (sized or desized), knitted fabric and yarn.

For yarn and knitted fabric, scouring is a batch process which is carried out in the same equipment that will subsequently be used for dyeing (mainly autoclaves or hank dyeing machines for yarn and overflows, jets, etc. for knitted fabric). Woven fabric is scoured in continuous mode using the pad-steam process.

The action of scouring is performed by the alkali (sodium hydroxide or sodium carbonate) together with auxiliaries, which include:
- non-ionic (alcohol ethoxylates, alkyl phenol ethoxylates) and anionic (alkyl sulphonates, phosphates, carboxylates) surfactants
- NTA, EDTA, DTPA, gluconic acid, phosphonic acids as complexing agents, which are used to remove metal ions (and, in particular, iron oxides, which catalyse the degradation reaction of cellulose when bleaching with hydrogen peroxide)
- polyacrylates and phosphonates as special surfactant-free dispersing agents
- sulphite and hydrosulphite as reducing agents (to avoid the risk of formation of oxycellulose when bleaching with hydrogen peroxide).

Bleaching

After scouring, cotton becomes more hydrophilic. However, the original colour stays unchanged due to coloured matter that cannot be completely removed by washing and alkaline extraction.

When the material has to be dyed in dark colours it can be directly dyed without need of bleaching. When it has to be dyed in pastel colours or it needs to be subsequently printed, however, bleaching is an obligatory step in the pre-treatment process.

Bleaching can be performed on all kinds of make-ups (yarn, woven and knitted fabric).

The most frequently used bleaching agents are the following:
- hydrogen peroxide (H_2O_2)
- sodium hypochlorite (NaClO)
- sodium chlorite ($NaClO_2$).

Apart from these, peracetic acid is also applicable. [UBA, 1994]

Bleaching with hydrogen peroxide

Bleaching can be carried out as a single treatment or in combination with other treatments (e.g. bleaching/scouring or bleaching/scouring/desizing can be carried out as single operations).

The textile is treated in a solution containing hydrogen peroxide, caustic soda and hydrogen peroxide stabilisers at pH 12 - 12.5. Sodium silicate together with Mg salts ($MgCl_2$ or $MgSO_4$) and sequestering/complexing agents (EDTA, DTPA, NTA, gluconates, phosphonates and polyacrylates) are commonly used as stabilisers. Operating temperatures can vary in a wide range from ambient to high temperature. Nonetheless, a good bleaching action occurs when operating at around 60 – 80 ºC.

Other auxiliaries used in hydrogen peroxide bleaching are surfactants with emulsifying, dispersing and wetting properties. Employed surfactants are usually mixtures of anionic compounds (alkyl sulphonates and alkyl aryl sulphonates) with non-ionic compounds such as alkylphenol ethoxylates or the biologically degradable fatty alcohol ethoxylates [ULLMANN'S].

Bleaching with hydrogen peroxide in weakly acidic conditions (pH range of 6.5 – 8) is also possible in some cases (e.g. when treating cotton in blends with alkali-sensitive fibres such as wool). At these pH conditions' activators are required to give bleaching activity.

A wide range of bleaching processes can be used, including cold pad-batch, bleaching under steaming conditions and bleaching processes in long bath.

Bleaching with sodium hypochlorite

The high reactivity of this bleaching agent imposes softer operative conditions than hydrogen peroxide (pH 9 - 11 and temperatures not above 30 ºC). Otherwise there is a risk of damage to the cellulose fibre.

The bleaching stage is followed by an anti-chlorine treatment in order to eliminate completely the hypochlorite and decompose the chloroamines generated during bleaching.

The use of hypochlorite as bleaching agent is in decline for ecological reasons. It can still be found in particular cases for yarn and knitted fabric when a high degree of whiteness is required.

When the textile material is bleached with hypochlorite a two-stage process is applied in which hypochlorite is used in the first step and hydrogen peroxide is used in the second one.

What processes are used when bleaching with sodium hypochlorite (?)

Bleaching with sodium chlorite

Chlorite bleaching can be applied to cotton, flax and other cellulosic fibres, often in combination with hydrogen peroxide. The material is bleached by padding or in long bath processes. The chlorite method is still found for knitted fabric (in continuous processes where the fabric is processed in rope form), but its importance is also in decline for ecological reasons.

Bleaching with peracetic acid

Is peracetic acid used in practice (?)

2.6.1.2 Environmental issues

The main environmental issues associated with cotton pretreatment arise from emissions to water.

The characteristics of the emissions vary according to a number of factors: the make-up, the sequence adopted, the fact that some treatments are often combined in a single step, etc.

The most relevant issues are highlighted below for the various operations involved in pretreatment.

Desizing and scouring

In a typical mill processing cotton or cotton-blend woven fabric, desizing represents the main emission source in the overall process. As already stated in Section 2.5.1.2, the washing water from desizing may contain up to 70 % of the total COD load in the final effluent, especially in the case of native sizing agents. Neither enzymatic nor oxidative desizing allows size recovery, while for some synthetic sizing agents size recovery is technically feasible, but difficult to apply for commission companies.

Compared to woven cotton fabric, the removal of contaminants from yarn and knitted fabric is less significant in terms of pollution load. Nevertheless, consideration must be given to the COD load associated with the removal of knitting oils (for knitted fabric), spinning oils and preparation agents (when cotton is in blend with synthetic fibres) and the biodegradability of these compounds. Substances such as synthetic ester oils are readily emulsified or soluble in water and easily biodegraded. More problems are posed by the presence of substances that are difficult to emulsify and poorly biodegradable such as silicone oils, which are found in cotton blends with elastan.

Mercerising

Mercerising is responsible for a large amount of strong alkali that is discharged in wastewater and needs to be neutralised. The corresponding salt is formed after neutralisation. In this respect, the cold process involves higher emission loads than the hot one. In order to allow the required retention time and make possible the cooling of the bath in continuous mode, a portion of the bath needs to be taken out and cooled down in continuous mode. This means that higher volumes of bath are necessary in cold mercerising, which result also in higher emissions if the caustic soda is not recovered.

Bleaching with hydrogen peroxide

The decomposition of hydrogen peroxide, which takes place during the bleaching reaction, forms only water and oxygen. However, environmental concerns associated with the use of stabilisers have to be taken into account. These products may contain complexing agents such as EDTA, DTPA and phosphonates with poor bio-eliminability, which may pass undegraded through the wastewater treatment systems. Their ability to form very stable complexes with metal makes the problem even more serious because they can mobilise heavy metals present in the effluent and release them in the receiving water.

It has been reported ([EURATEX]) that, depending on concentration, pH, time and temperature, effluents containing inorganic chlorides (e.g. NaCl from dyeing and printing, $MgCl_2$ from finishing) can be oxidised to their chlorites/ hypochlorites when they are mixed with hydrogen peroxide bleach wastewater. In this way AOX may be found in wastewater even if bleaching is carried out without chlorine-based bleaching agents. However, experimental measurements have shown that this does not play an important role, if any. [UBA, 1994].

The residual hydrogen peroxide in the effluent, which, due to its oxygen-reducing effect, contributes to increasing chemical oxygen demand of the final effluent, needs also to be taken into consideration [EURATEX].

Bleaching with sodium hypochlorite

For ecological reasons the use of sodium hypochlorite is now limited in Europe to just a few particular cases, connected with knitted fabric and, in some cases, bleaching of yarn when a high degree of whiteness is required. Bleaching with sodium hypochlorite leads, in fact, to secondary reactions that form organic halogen compounds, commonly quantified as AOX. Trichloromethane (which is suspected of being carcinogenic) accounts for the bulk of the compounds formed, but other chlorinating subsidiary reactions might occur, besides haloform reaction.

Bleaching with sodium chlorite

Sodium chlorite bleaching is also responsible for AOX generation in the wastewater. However, compared to sodium hypochlorite, the amount of AOX formed during chlorite bleaching is much lower (on average only 10 % to a maximum of 20 % of the amount of AOX generated by hypochlorite).

Handling and storage of sodium chloride need particular attention because of toxicity and corrosion risks. Mixtures of sodium chlorite with combustible substances or reducing agents can create problems, especially when they are subject to heat, friction or impact. Sodium chlorite forms chlorine dioxide when put in contact with acids. Moreover, sodium chloride decomposition produces oxygen, which supports combustion. Sodium chlorite is also very corrosive and spillages need to be washed away with large amounts of water.

2.6.2 Wool preparation before colouring

Typical preparation wet treatments applied on wool fibre before dyeing are:
- carbonising
- washing (scouring)
- fulling
- bleaching.

Other possible treatments are those that go under the definition of anti-felt and stabilisation treatments. Although they are often carried out before dyeing, they are not obligatory preparation steps. For this reason they have been described under finishing operations (Section 2.9.2.8).

2.6.2.1 Principal manufacturing processes

Carbonising

Sometimes scoured wool contains vegetable impurities that cannot always be completely removed through mechanical operations. Sulphuric acid is the chemical substance used for destroying these vegetable particles and the process is called carbonising.

Carbonising can be carried out on floc/loose fibre or on fabric (this operation is not applied in the carpet sector).

Loose fibre carbonising is performed only on fibres that are later used to produce fine fabric for garments (worsted fabrics) and usually takes place at the scouring mill.

In typical equipment for carbonisation of loose fibre, the still damp scoured wool is soaked in a solution containing 6 – 9 % of mineral acid (generally sulphuric acid). Excess acid and water are removed by pressing or by centrifugation until on average 5 – 7.5 % of sulphuric acid and 50 – 65 % of water remain. The fibres are then dried at 65 – 90 ºC to concentrate the acid and baked at 105 – 130 ºC (carbonising).

As soon as the wool is dried, it is fed into a machine, which consists of two counter-rotating rolls. These rolls crush the carbonised particles into very small fragments, which are then easily removed. The addition of small quantities of detergent to the sulphuric acid improves the yield and reduces the attack on the wool. In order to prevent the fibre from being gradually degraded, the pH is finally set to 6 by neutralisation with sodium acetate or ammonia.

Sulphuric acid can be replaced by gaseous HCl or by aluminium chloride. The latter releases HCl when it is heated: this method is useful for the carbonisation of wool/synthetic fibres mixtures such as wool/PES, that are too sensitive to sulphuric acid.

After carbonising, the fibre can be carded and then spun before being dyed or it can be dyed directly in floc form.

Fabric carbonising is typical of woollen fabrics. The operation can be carried out by either the traditional or the more modern "Carbosol" system.

The conventional procedure is substantially similar to that used for loose fibre. The fabric can be previously soaked in a water or solvent bath and squeezed, but this step is optional. Then it is impregnated in a concentrated sulphuric acid solution (acidification) and squeezed (hydro-extraction) before passing through the carbonising chamber. The carbonised particles are then removed by mechanical action and subsequent washing. In modern carbonising plants all these steps are carried out in continuous mode.

The "Carbosol" process, licensed by SPEROTTO RIMAR, uses an organic solvent instead of water. The equipment consists of three units. In the first one the fabric is impregnated with perchloroethylene, in the second the material is soaked in the sulphuric acid solution and in the third, carbonising and solvent evaporation take place. At this stage the perchloroethylene is recovered by distillation in a closed loop.

The "Carbosol" system is reported to have several technical advantages over the traditional process. The level of acidity of the fabric after carbonising is much lower and the risk of damage to the wool fibre is reduced. Thanks to full recovery of the organic solvent, the process can also be considered more efficient from the environmental point of view.

1) impregnation in sulphuric acid solution
2) squeeze press
3) dryer
4) carbonising chamber
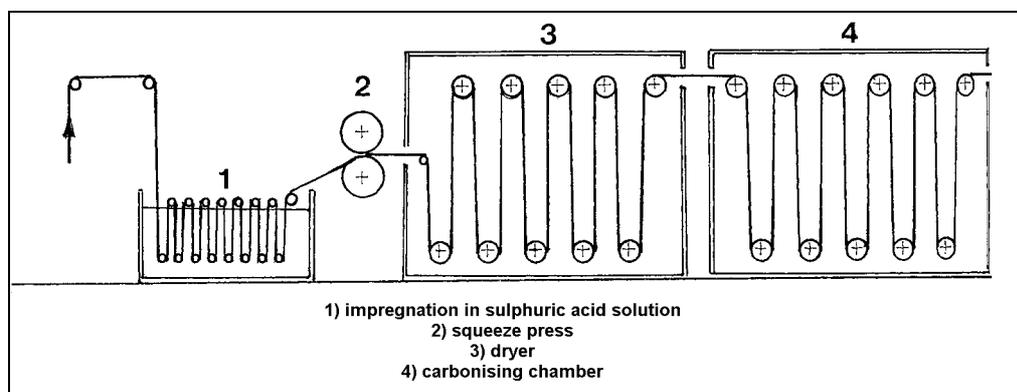
Figure 2.12: Representation of a conventional carbonising installation

1) solvent impregnation unit
2) sulphuric acid impregnation unit
3) carbonising unit
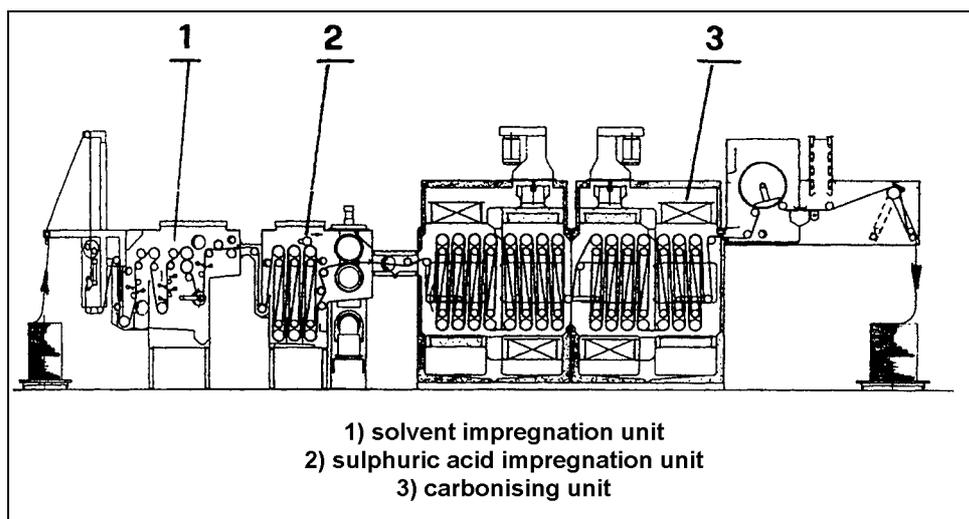
Figure 2.13: "Carbosol" system

Scouring

Both *yarn* and *fabric* contain, besides accidental impurities, a certain amount of spinning oils and in some cases also sizing agents such as CMC and PVA. All these substances need to be removed before dyeing in order to make the fibre more hydrophilic and allow the penetration of the fibre by dyestuffs.

As pointed out in Section 2.4.1, the percentage of spinning oils on woollen wool is quite relevant and it is always above 5 %, while on worsted wool it never reaches 2 %.

Typical substances that have to be removed by scouring can be classified as:
- soluble in water
- insoluble in water, but emulsifiable thanks to the action of surfactants
- insoluble in water and non-emulsifiable (or difficult to emulsify) with surfactants. These substances can be removed only by using organic solvents (in general, halogenated solvents like perchloroethylene).

As a result the material can be washed (scoured):
- with water or
- with solvent (dry cleaning)

Water washing is carried out in neutral or weakly alkaline conditions (by sodium carbonate or bicarbonate) in the presence of detergents. Commonly used detergents are mixtures of anionic and non ionic surfactants such as alkyl sulphates, fatty alcohols and alkylphenol ethoxylates. In wool carpet yarn production the scouring process can include simultaneous chemical setting of yarn twist with reductive agents (sodium metabisulphite) and/or application of insect-resist agents.

Water scouring is normally a batch operation which is carried out in the equipment in which the textile material will be subsequently dyed. This means that an autoclave is the commonly used equipment for yarn, while jets and overflows are the machines typically applied for fabric. In this respect, the carpet sector is an exception. Wool yarn for carpet is scoured on continuous or semi-continuous basis in tape scouring machines (hanks) or in package-to-package scouring machines (package yarn), where the yarn is passed through a series of interconnected bowls (see Section 2.13.5.1.2).

Dry cleaning is less common and is applied when the fabric is heavily soiled and stained with oils from the weaving or knitting process. The most widely used solvent is perchloroethylene. In some cases water and surfactants are added to the solvent to provide a softening effect.

Solvent washing can be carried out either in discontinuous mode in a tumbler (generally for knitted fabric) or in continuous mode in open-width (for woven and knitted fabric). Impurities are carried away by the solvent, which is continuously purified and recycled in a closed loop.

Fulling

This treatment takes advantage of the felting tendency typical of wool fibre when it is submitted to friction under hot humid conditions and is a typical pre-treatment for woollen fabric.

It is usually carried out after carbonising, but in some cases (e.g. heavy woollen fabrics) it can be done directly on raw fabric. The material is kept in circulation in a bath containing fulling auxiliaries. Both acids (pH <4.5) and alkali (pH >8) speed up the fulling process. Fulling auxiliaries available on the market, however, also produce excellent results under neutral conditions. As a result, fulling either in acid or alkaline conditions is becoming less common. After fulling, the fabric is washed.

Machines specially designed for this process are still in use. However, today they have been largely replaced by multifunctional machines, where both fulling and washing can be carried out, simply adjusting the set-up of the equipment.

Bleaching

Wool is bleached with hydrogen peroxide (sodium hypochlorite may discolour and damage the wool). An additional reductive bleaching is, however, indispensable for achieving high levels of whiteness (full bleach). A typical reductive bleaching agent is sodium dithionite (hydrosulfite), which is often used in combination with optical brightners to enhance its effect.

In the oxidative bleaching step, hydrogen peroxide is applied in the presence of alkali and stabilisers, which slow down the decomposition of the hydrogen peroxide.

When wool has been previously submitted to an anti-felt treatment it is preferable to use hydrogen peroxide in weakly acid conditions.

2.6.2.2 Environmental issues

Wool pretreatment gives rise mainly to water emissions, although there are also specific operations (e.g. carbonising with the Carbosol system and dry cleaning) where halogenated (mainly perchloroethylene) solvents are employed. The use of these solvents can produce not only emissions to air, but also contamination of soil and groundwater if their handling and storage is not done using the necessary precautions. The process also involves the generation of exhausted active carbon from the solvent recovery system. This solid waste has to be handled separately from other waste material and disposed of as hazardous waste or sent to specialised companies for regeneration.

Due to the predominantly batch nature of wool pretreatment operations for all types of make-ups, the resulting emissions will be discontinuous and with concentration levels largely influenced by the liquor ratios used.

The pollutants that can be found in the wastewater, originate in part from the impurities that are already present on the fibre when it enters the process sequence and in part from the chemicals and auxiliaries used in the process.

Pollutants originating from impurities present on the raw material

Residues of pesticides used to prevent the sheep becoming infested with external parasites can still be found on scoured wool in amounts which depend on the efficiency of the scouring process. These are mainly organophosphates (OPs) and synthetic pyrethroid (SPs) insecticides and insect growth regulators (IGRs), but detectable residues of organochlorine pesticides (OCs) can be observed. They partition between the fibre and the water according to their stronger or weaker lipophylic character and, as a consequence, traces of these compounds are released in the wastewater. More information about ectoparasiticides can be found in Sections 2.1.1.9 and 2.3.1.2.

Spinning oils and glues (only for woven fabric) also represent an important issue in wool pretreatment: they are removed during the scouring process, contributing to the COD load in the final effluent.

Pollutants originating from chemicals and auxiliaries used in the process

Considerable amounts of surfactants are used in pretreatment as detergents, wetting agents, etc. Surfactants with good biodegradability with acceptable performance are now available. Nevertheless, the use of alkylphenol ethoxylates is still common in some companies due to their

low cost. Alkylphenol ethoxylates (APEOs) and in particular nonylphenol ethoxylates (NPEs) are under pressure due to the reported negative effects of their metabolites on the reproduction system of aquatic species. The environmental issues arising from surfactants in common use are discussed in Section 8.1.

Other pollutants of concern that may be found in water effluent from pretreatment activities are:
- reductive bleaching agents (contribute to oxygen demand in the wastewater)
- poorly bio-eliminable complexing agents (e.g. EDTA, DTPA, phosphonates) from hydrogen peroxide stabilisers, etc.
- AOX from sodium hypochlorite bleaching.

More details regarding environmental issues associated with the above mentioned substances are given elsewhere in this document, in particular in Section 2.6.1.2 (AOX from sodium hypochlorite bleaching) and Section 8.5 (Products containing complexing agents).

2.6.3 Pre-treatment of silk

(?)

2.6.4 Pre-treatment of synthetic material

2.6.4.1 Principal manufacturing processes

Typical operations before colouring are washing and thermofixing (heat-setting).

Washing is necessary to remove from the yarn the preparation agents that have been applied to its surface in the previous treatments (2 – 3 % on the weight of the fibre). Most preparation agents (about 95 %) are removed at this stage (ethoxylated fatty alcohols are commonly used as emulsifying agents). Elastomeric fibres (elastan) are an exception because they contain up to 6 % of preparation agents mainly made up of silicone oils. Silicones are more difficult to remove and partly still remain on the fibre (40 % of the initial add-on) after washing. To improve their removal it is common practice to use ethoxylated nonylphenols.

When pre-treating woven fabric the removal of sizing agents is a crucial step. The extraction of these substances is achieved thanks to the synergistic action of:
- surfactants (non-ionic or mixtures of non-ionic and anionic): they act as wetting and emulsifying agents and promote the solubilisation of the size
- complexing agents (e.g. phosphonates): they are used when there is a risk of re-precipitation of the components of the sizing agents. An increase in hardness level can occur, particularly, in continuous lines when processing synthetic blends with cellulose fibres (characterised by the presence of Ca and Mg salts as natural impurities)
- alkali (caustic soda or sodium carbonate): the alkali is chosen according to the sizing agent employed (for example for the removal of sizing agents based on polyacrylates ammonium salts the use of caustic soda is obligatory, while a polyester sizing agent would precipitate in the same pH conditions).

Thermofixation is also another important operation in synthetic fibres pre-treatment. Its position within the process can be different, depending on the make-up and the fibre. As a result the following possible sequences are possible:
1. thermofixation – washing – dyeing
2. washing – thermofixation – dyeing
3. washing - dyeing - thermofixation.

2.6.4.2 Environmental issues

Synthetic fibres contain several types of impurities that are imparted to the fibres before they reach the textile-finishing mill. These impurities encompass:

- polymer synthesis by products such as unreacted monomers (for example caprolactame, which is the monomer used for the production of PA 6, is emitted to air during thermal treatments) low-molecular-weight oligomers, and residual catalysts
- preparation agents
- sizing agents added before weaving.

Since all these substances are removed before dyeing and finishing, they are ultimately found in pre-treatment wastewater or in air emissions from high-temperature processes such as drying, and thermofixation.

The main environmental concerns associated with the discharge of these organic substances in water are high COD and BOD loads and aquatic toxicity. In particular, the COD:BOD ratio is often high, indicating the potential for pass-through during treatment and subsequent discharge to the environment.

2.7   Dyeing

In the following sections the general principles of dyeing and the most commonly used dyeing techniques for the different fibres are described.

For practical reasons, detailed information concerning dyeing auxiliaries, dyestuffs and dyeing equipment is given in specific annexes (namely, Sections 8.6, 9 and 10).

2.7.1 General principles of dyeing

Dyeing is a method for colouring a textile material in which a dye is applied to the substrate in a uniform manner to obtain an even shade. A dye is an organic molecule which contains a chromophoric group (conjugated system) capable of interacting with light, thus giving the impression of colour.

Textile dyeing involves the use of a number of different chemicals and auxiliaries to assist the dyeing process. Some of them are process-specific, while others are also used in other operations. Some auxiliaries (e.g. dispersing agents) are already contained in the dyestuff formulation, but more commonly auxiliary agents are added at a later stage to the dye liquor. Since auxiliaries in general do not remain on the substrate after dyeing, they are ultimately found in the emissions.

Various dyeing techniques exist:

- mass dyeing, in which a dye is incorporated in the synthetic fibre during its production (this technique will not be described in this document)
- pigment dyeing, in which an insoluble pigment, without affinity for the fibre, is deposited onto the textile substrate and then fixed with a binder
- dyeing processes which involve the diffusion of a dissolved (or at least partially dissolved) dye into the fibre.

This last group of processes is the one that will be discussed in more detail in the following sections. From a molecular point of view four different steps are involved:

1. first, the dye, previously dissolved or dispersed in the dye liquor, diffuses from the liquor to the substrate

2. the second step consists in the accumulation of the dye on the surface of the textile material. This process is controlled by the affinity (substantivity) of the colourant for the fibre

3. the dye diffuses/migrates into the interior of the fibre until this is uniformly dyed. This step is much slower than the transport of the dye within the dye bath. The penetration of the dye into the fibre requires that the fibre itself is accessible. In the case of hydrophilic fibres the dye penetrates through the available micro-pores, while in hydrophobic fibres, whose molecular structure does not allow a continuous water phase, cavities need to be developed in order to make the penetration of the dye possible. In general, access to the fibre is enhanced by temperature. Hydrophobic fibres can only be penetrated by the dye above the glass transition temperature, which sometimes lies above 100 ºC. During the diffusion into the micro-pores an electrostatic barrier, which develops on the surface of the fibre, still has to be overcome. In some cases large amounts of salt have to be added to the dyeing bath in order to reduce the electrostatic forces on the surface of the fibre and promote an even penetration of the dye.

4. the dye must be anchored (fixation) to suitable places within the substrate. Different mechanisms of fixation are known, ranging from chemical reaction of the dye with the fibre to form a covalent bond (reactive dyes) to formation of Van der Waals and other short range forces between the fibre and the dye (direct dyes). This is more fully explained in Annex II.

2.7.2 Dyeing processes

Textiles can be coloured at any of several stages of the manufacturing process so that the following colouring processes are possible:
- flock or stock dyeing
- top dyeing: fibres are shaped in lightly twisted roving before dyeing
- tow dyeing: it consists in dyeing the mono-filament material (called tow) produced during the manufacture of synthetic fibres
- yarn dyeing
- piece (e.g. woven, knitted and tufted cloths) dyeing.

Dyeing can be carried out in batch or in continuous. The choice between the two processes depends on the type of make-up, the chosen class of dye, equipment available and cost involved. Both continuous and discontinuous dyeing involve the following steps:
- preparation of the dye
- dyeing
- fixation
- washing and drying.

Batch- dyeing

In batch dyeing (also called exhaustion dyeing) a certain amount of textile material is loaded into a dyeing machine and brought to equilibrium with a solution containing the dye and the auxiliaries over a period of minutes to hours.

The dyeing process starts with the absorption of the colourant onto the external surface of the fibre, then the diffusion and migration of the colourant through the fibre takes place. The use of chemicals and controlled temperatures accelerates and optimises exhaustion and fixation of the dye. When the dyeing is judged to be on shade, the spent dyebath is drained and the textile material is washed to remove unfixed dyes and chemicals. Washing is usually carried out in the same equipment. However, separate washing machines can also be used in the case of fabric.

An important parameter in discontinuous dyeing is the liquor ratio of the equipment. This is the weight ratio between the total dry material and the total liquor. So, for example, a liquor ratio of 1:10 means that we have 10 litres of water on 1 kg textile material.

This parameter is very important because it influences the environmental impact of discontinuous dyeing processes.

Dyeing machines vary greatly in their liquor ratios, as shown in Table 2.2, and each type of machine has its own limitations and range of applicability to particular substrates.

Make-up		Process	Equipment	Liquor ratio
Loose/stock fibre (also card sliver and tow)		Loose stock dyeing	Autoclave (loose stock dyeing machines)	
Yarn	Bobbins/ cones	Yarn dyeing	Autoclave (package dyeing machines)	1:10 [2]
	Hank	Hank dyeing	Hank dyeing machines	1:17 [2]
Woven and knitted fabric, tufted carpet	Rope	Piece dyeing in rope form	Winch beck	1:10 - 1:30 [1]
			Overflow	
			Jet	1:5 - 1:15 [1]
			Air-flow	
	Open-width	Piece dyeing in open-width form	Winch (for carpet)	
			Beam + washing machine	1:8 - 1:10 [1]
			Jigger + washing machine	1:3 - 1:6 [1]
Source: [1] [RIZA] [2] [EPA]				

Table 2.2: Discontinuous dyeing equipment and liquor ratios

Continuous and semi-continuous dyeing

In continuous and semi-continuous dyeing processes, the textile is impregnated with the dyestuff by means of foulards. Most commonly textiles are fed continuously in open width through a dip trough filled with dye liquor. The substrate absorbs an amount of dye solution and leaves the dip trough through two rollers that control the pick-up of the dye. The surplus of stripped dye flows back into the dye bath. In the carpet industry, thickening agents are added to the pad liquor to prevent dye migration. Moreover, special application systems are also encountered, where the dyestuff is poured, jet-sprayed or applied in the form of foamed liquor.

Dye fixation is usually achieved in a subsequent stage using chemicals or heat (steam or dry heat). The final operation is washing, which is usually carried out in washing machines in the same line.

The only difference between continuous and semi-continuous processes consists in the fact that in semi-continuous dyeing the application of the dye is performed continuously by padding, while fixation and washing are discontinuous.

In general, dyes with low affinity are favoured in continuous dyeing to prevent tailing attributable to undesirable exhaustion of the padding solution and to make washing-off of the unfixed dye easier.

In these processes the factor to be taken into account is the pick-up % (grams of liquor picked up by 100 grams of substrate), while the liquor ratio is unimportant and it is not used.

An overview of the most common techniques and machinery in continuous and semi-continuous processes is given in Table 2.3.

Make-up		Process		Equipment
Woven and knitted fabric, tufted carpet	Rope	Continuous		Padding machine for piece in rope form + (?)
	Open-width	Semi-continuous	Pad-batch	Padding machine + washing machine
			Pad-roll	Padding machine + washing machine
			Pad-jig	Padding machine + jigger + washing machine
		Continuous	Pad-steam	Padding machine + steamer + washing machine
			Pad-dry	Padding machine + stenter frame + washing machine
			Thermosol	

Table 2.3: Semi-continuous and continuous dyeing processes and equipment

2.7.3 Cellulose fibres dyeing

Cellulose does not contain ionic groups and it is therefore unable to absorb dyestuffs that form ionic bonds with the fibre. On the contrary, it shows good affinity for dyes that are able to establish secondary or covalent bonds with the fibre.

Cellulose fibres can be dyed with a wide range of dyestuffs, namely:
- reactive
- direct
- vat
- sulphur
- naphtol.

Reactive dyes

One third of dyes used for cellulose fibres today are reactive dyes. They are mostly applied according to the pad-batch process for woven fabric, while batch processes are the most common for knitted fabric, loose stock and yarn.

In *batch dyeing,* dye, alkali (sodium hydroxide or sodium bicarbonate) and salt are added to the dyebath in one step, at the start of the process, or stepwise. In the stepwise process the alkali is added only after the dye has absorbed to the fibre. Its amount is determined by the reactivity of the system and the desired depth of shade (cold dyers are applied at lower pH compared to warm and hot dyers). Salt is added to improve bath exhaustion: the concentration employed depends on the substantivity of the dye and on the intensity of the shade. Higher concentrations are required for deep shades and low-affinity dyes, as shown in the table below.

Shade	High-affinity dyes	Low-affinity dyes
<0.5 %	10 - 30 g/l NaCl	Up to 50 g/l NaCl
>4 %	~50 g/l NaCl	Up to 80 g/l NaCl
Source [ULLMANN'S]		

Table 2.4: Salt concentration required for reactive dyes

After dyeing, the liquor is drained off and the material is rinsed and then washed off with the addition of auxiliaries.

In *pad dyeing processes* dye and alkali can be added together or separately to the dye bath. When all the chemicals are applied in one step, the stability of the pad liquor is important. In fact with increasing reactivity of the dye there is a risk that the dye, after a long dwell time in the pad box, is hydrolysed by the alkali, before reacting with the fibre. For this reason dye and alkali are commonly metered separately into the padder. In addition, pad boxes are now constructed so that the liquor volume is as low as possible so that it is replaced on average within 5 minutes. [ULLMANN'S]

Among *semi-continuous processes* the cold pad-batch is by far the most important one for reactive dyes. After the textile has been padded with dye and alkali, it is rolled up into batches. Fixing takes place during storage.

In *continuous processes*, padding, fixing, washing off and drying are carried out in the same process line. Fixation is commonly achieved either by dry-heating or by steaming. The following processes are commonly used:
- Pad-steam process (dye application by padding - intermediate drying - alkali application by padding - dye fixation with saturated steam - washing - drying)
- Pad-dry process (dye and alkali are padded at the same time; then the material can be dried and fixed in a single step or it can be thermofixed after an intermediate drying stage).

In all cases, after fixation the material is always carefully washed off in open width or in a rope washing machine to remove completely the hydrolysed colorant and is then dried.

In continuous processes urea is usually added to the padding liquor to increase the solubility of the dye and to act as a solvent for the dye during fixation.

Direct dyes

Direct dyes are also quite important in cellulose fibres dyeing: 75 % of the total consumption of these colorants is used, in fact, to dye pure cotton or viscose substrates [ULLMANN'S].

Direct dyes are applied directly from the dye bath together with salt (sodium chloride or sodium sulphate) and auxiliary agents, which ensure a thorough wetting and dispersing effect. Mixtures of nonionic and anionic surfactants are used for this purpose.

In the *batch process* the dye is made into paste, then dissolved in hot water and added to the dye bath. The electrolyte is then added to the dyebath. After the dyebath has been drained, the fabric is washed with cold water and generally subjected to after-treatment.

Pad processes encompass the following techniques:
- pad-steam
- pad-roll
- cold pad-batch
- pad-jig process (the material is padded with the dye and then passed through a salt liquor in a jigger).

In all processes the material is rinsed at the end with cold water.

With increasing depth of colour the wet fastness decreases to such an extent that after-treatment must generally be carried out. [ULLMANN'S] Two methods exist:
1. removing the unfixed dye by: a) washing with complexing agents or surfactants with a dispersing effect, b) reductive decomposition or c) extraction with an organic solvent

2. reducing the solubility of the dye by blocking the hydrophilic groups and/or enlarging the dyestuff molecules.

Various techniques can be applied to achieve this enlargement of the molecule. Namely, the dyed textile can be treated with:
- fixative cationic agents: these are complex substances that form with the anionic dye a salt-like compound less soluble than the original dye. Quaternary ammonium compounds with long hydrocarbon chains, polyamines and polyethyleneimine derivatives can be used for this purpose
- metal salts: copper sulphate and potassium dichromate can form with certain azo dyes metal-complex with higher light fastness
- agents based on formaldehyde condensation products with amines, polynuclear aromatic phenols, cyanamide or dicyandiamide (the use of these condensation products leads to the formation of sparingly soluble adducts with the dye molecules)
- diazotised bases: after dyeing, the material is submitted to diazotisation and is then coupled with aromatic amines or phenols that must not contain hydrosolubilising groups [ULLMANN'S].

Environmental concerns arise when after-treating with formaldehyde condensation products or metal salts. The method using fixative cationic agents is, therefore, the most frequently applied (?).

Vat dyes

Vat dyes have excellent fastness properties when properly selected and are often used for fabrics that will be subjected to severe washing and bleaching conditions (towelling, industrial and military uniforms, etc.).

Vat dyes are normally insoluble in water, but they become water-soluble and substantive for the fibre after reduction in alkaline conditions (vatting). They are then converted again to the original insoluble form by oxidation and in this way they remain fixed into the fibre.

When applying vat dyes in batch processes the textile is dyed very rapidly and unevenly due to the high affinity of the dye. Nevertheless, level dyeing can be achieved by:
- adding levelling agents
- increase of the temperature under a controlled profile ("High Temperature" process and "Semi-pigmention" method)
- impregnation of the textile with the dye as water-insoluble dispersion, followed by addition of the reductive agent in a subsequent step (pre-pigmentation process).

In all cases, oxidation and after-treatment follow. After-treatment consists in washing the material in a weakly alkaline bath with a detergent at boiling temperature.

Continuous processes are used almost exclusively for dyeing woven fabrics and to only a small extent for knitwear. The most commonly applied continuous process is the pad-steam process. The textile is padded with the aqueous dye dispersion in the presence of anti-migrant (polyacrylates, alginates, etc.) and dispersing/wetting agents, if required. After drying, the fabric is passed through a chemical padder, which contains the required amount of alkali and reducing agent and is fed immediately to a steamer. The material is finally rinsed, oxidised and soaped in an open-width washing machine.

Voluminous open fabrics can be dyed according to a wet-steam process. Unlike the pad-steam process, this process does not require intermediate drying before steaming.

The following chemicals and auxiliaries are applied in vat dyeing:

- reducing agents: mainly sodium dithionite (hydrosulphite) and sulphoxylic acid derivatives (the latter, in particular, are used when the pad-steam process is applied). Sulphur-free organic reducing agents such as hydroxyacetone are also now available for some applications.
- oxidising agents, such as hydrogen peroxide, perborate, or 3-nitrobenzenesulphonic acid
- alkali (caustic soda)
- salt
- dispersing agents: they are already present in the dye formulation and they are further added in the subsequent steps of the dyeing process
- levelling agents: they form adducts with the dye, thus retarding its absorption onto the fibre.

Sulphur dyes

Sulphur dyes are used in piece dyeing (cellulose-polyester blends), yarn dyeing (sewing thread, warp yarn for denim fabric, yarn for coloured woven goods), dyeing of flock, card sliver (wool-man-made fibres blends) [ULLMANN'S].

Like vat dyes, sulphur dyes are insoluble in water, but after reduction under alkaline conditions they are converted into the leuco-form, which is water-soluble and has high affinity for the fibre. After adsorption into the fibre the colorant is oxidised and converted to the original insoluble state. The reducing agent, salts, alkali and unfixed dye are finally removed from the fibre by rinsing and washing.

Mostly continuous dyeing methods are applied, although batch dyeing (in jigger, jet, and winch beck) is also possible.

In *continuous processes* the material is impregnated with dye, reducing agent and wetting agent through a one-bath or a two-bath procedure. With the one-bath procedure (pad-steam process) the reducing agent and the dye are added at the same time. With the two-bath procedure (pad-dry/pad-steam) the material is padded in the liquor containing the dye and the wetting agent, while the reducing agent is applied, if necessary, in a second step, after intermediate drying. The material is then submitted to air-free steaming. After that, rinsing, oxidation and re-rinsing are carried out.

Chemicals and auxiliaries applied to the substrate during the dyeing process are:

- reducing agents: sodium sulphide and sodium hydrogensulphide are the most commonly employed, although binary systems made of glucose and sodium dithionite or thiourea dioxide are also used as alternative reducing agents for water-soluble dyes. Sulphur dyes can also be available in the ready-for-use form, in which case the reducing agent is already contained in the formulation.
- alkali (caustic soda)
- salt
- dispersing agents (they are necessary in the process steps in which the pigment has not yet been reduced or has been re-formed by oxidation)
- complexing agents: EDTA or polyphosphates are used in some cases, especially in circulating-liquor dyeing to avoid the negative effects of alkaline-earth ions on dyeing
- oxidising agents: mainly hydrogen peroxide and halogenated organic compounds such as bromate, iodate and chlorite.

Naphtol dyes

Naphtol AS dyes allow colours with outstanding fastness, but their popularity has declined because of application costs and the possible presence of arylamines on the fabric and in the effluent [EURATEX].

Dyeing with azoic colorants is a complex process which involves a number of delicate steps:

- preparation of the naphtolate solution by the hot solution process (the naphtol is dissolved by boiling with caustic soda) or by the cold solution process (the naphtol is solubilised with alcohol or cellosolve, caustic soda and cold water). For certain naphtols the addition of formaldehyde is also necessary to prevent the formation of free naphtol
- application of the naphtolate to the fibre by batch or padding techniques
- preparation of the diazotized base by reaction with sodium nitrite and hydrochloric acid (this step can be avoided when using fast colour salts)
- formation of the azoic dye into the fibre, by passing the textile, previously impregnated with the naphtolate solution, through a bath containing the diazotized base or the fast colour salt (addition of buffering agents is necessary to control the pH, in order to increase the coupling capacity)
- after-treatment by rinsing the material to remove the excess of naphtol from the fibre.

Dyestuff	Chemicals and auxiliaries/ typical application conditions	Technique
Reactive	- pH 9.5 - 11.5 by addition of sodium carbonate and/or sodium hydroxide - Salt is used to increase dye bath exhaustion: higher concentrations are used for low-affinity dyes and for deep shades - Application temperatures vary from 40 ºC to 80 ºC depending on the class of the dyestuff - In padding processes urea or cyanoguanidine is usually added to the pad liquor - After dyeing, the material is soaped at 100 ºC and then washed off with addition of surfactants to remove unfixed dye	Batch Pad-batch Pad-steam Pad-dry
Direct	- Salt is used to increase bath exhaustion - Mixtures of nonionic and anionic surfactants are used as wetting/dispersing agents - After-treatment is usually necessary to improve wet-fastness (possible use of fixative cationic agents, formaldehyde condensation products)	Batch Pad-batch Pad-jig Pad-steam
Vat	- Alkali and reducing agents (sodium dithionite, sulphoxylic acid derivatives, thiourea dioxide, organic reducing agents) are applied to convert the dye to the sodium leuco form - Poorly degradable dispersants are present in the dye formulation and are further added in other steps of the process - Levelling agents are sometimes necessary - Temperature and the amount of salt and alkali required vary according to the nature of the dye (IK, IW, IN) - Dye is fixed to the fibre by oxidation, generally using hydrogen peroxide, but halogen-containing oxidising agents can also be used - After-treatment takes place in a weakly alkaline detergent liquor at boiling temperature - In continuous processes, anti-migration and wetting agents are used	Batch Pad-steam
Sulphur	- Reducing agents (Na_2S, NaHS, glucose-based combination of reducing agents) and alkali are applied to convert the dye into soluble form, unless ready-for-use dyes are used - Dispersants and complexing agents are used in batch dyeing - In batch dyeing, the dye generally absorbs at 60 - 110 ºC, while in the pad-steam process the material is padded at 20 - 30 ºC and then subjected to steaming at 102 - 105 ºC - Oxidation is carried out mainly with hydrogen peroxide, bromate and iodate	Batch Pad-steam Pad-dry/ pad-steam
Naphtol	- Preparation of the naphtholate (caustic soda and, in some cases, addition of formaldehyde is required to stabilise the naphthol on the fibre) - Impregnation of the naphtholate by exhaustion or padding processes - Preparation of the diazotised base (with $NaNO_2$ and HCl) - Developing stage (the textile is passed through the cold developing bath or the developing solution is circulated through the stationary textile in the dyeing machine)	Batch Padding methods

Table 2.5: Summary of the most common dyestuffs and dyeing techniques applied for cellulose fibres

2.7.4 Wool dyeing

Wool can be dyed with the following dyestuffs:
* acid
* chrome
* 1:1 and 1:2 metal complex
* reactive.

Acid dyes

Acid dyes are typically applied in acidic conditions, but the pH range used varies depending on the type of acid dye. The greater the affinity of the dyestuff for the fibre, the more the ionic bonds must be repressed by applying the dye at higher pH.

Therefore *level-dyeing colorants* are applied under strongly acidic conditions (1 – 3 % formic acid) in the presence of sulphate ions (5 – 10 % sodium sulphate) to assist migration and levelling. Levelling agents are not generally required and the rate of dye uptake is controlled initially by increasing the temperature of the dyebath slowly (1 ºC/min.) and then extending the time at the boil to allow the dye to migrate from areas of high initial uptake.

Fast acid dyes (also known as half-milling dyes or perspiration-fast dyes) exhibit superior fastness properties to level-dyeing acid dyes, while retaining some of the migration properties. Application is from a moderately acidic dyebath (1 – 3 % acetic acid) in the presence of sodium sulphate (5 – 10 %) and levelling agent to assist migration.

Acid milling dyes have good affinity for the fibre and do not migrate well at the boil. They are therefore applied at more neutral pH (5 - 7.5 with acetic acid) in the presence of sodium acetate (2g/l) or ammonium sulphate (4 %) and levelling agent (1 – 2 %). Sodium sulphate is usually avoided as it has little effect on migration and can promote uneven dye adsorption.

Levelling agents play an important role in acid dyeing. A number of non-ionic, cationic, anionic and amphoteric surfactants belong to this category.

Chrome dyes

A number of techniques have been developed for the application of chrome dyes. The chrome mordant process relies on chroming the fibre prior to dyeing with a chromable dye; the *Metachrome* process applies both dye and chromium salt simultaneously. Both processes have been largely superseded by the *Afterchrome* process in which the dye is applied first and the fibre is then chromed in a separate step, utilising the exhausted dyebath and thus conserving water.

Application of the dyestuff takes place fin a moderately acid dyebath (1 % acetic acid) often with an addition of formic acid towards the end of the boiling period to promote exhaustion of the dye. The dyebath is then cooled back from the boil to approx. 80 ºC, the pH is lowered to approx. 3.5 with formic acid and the pre-dissolved chromium salt added. The dyebath is then returned to the boil and boiling continued for 20 - 30 minutes. Chromium is added to the dyebath as either sodium or potassium dichromate. In solution the chroming species present vary according to pH, with the dichromate anion $Cr_2O_7^{2-}$ predominating at pH between 3 and 7. Although it is the chromium (VI) anion which is initially adsorbed by the wool, the dye complex is formed with chromium (III), formed by the action of reducing groups in the fibre itself. Strong acids have an activating effect on this process; organic acids (tartaric, lactic, formic acid) or thiosulfate can also be used to enhance the degree of conversion of Cr VI.

Metal-complex dyes

Application of *1:1 metal-complex dyes* is carried out from a strongly acidic dyebath (sulphuric or formic acid to pH 3 - 4.5) in the presence of sodium sulphate (5 %) and levelling agent. Owing to these particular operative conditions, this class of dyestuffs is particularly suitable for piece-dyeing of carbonised wool.

1:2 metal-complex dyes form the most important group in this class and may be divided into two sub-groups: weakly polar and strongly polar 1:2 complexes. Application is usually carried out in moderately acidic conditions:
- pH range between 4 and 7 (acetic acid) in the presence of ammonium acetate, for weakly polar complexes
- pH range 5 - 6 (acetic acid) in the presence of ammonium sulphate, for strongly polar complexes.

The use of levelling agents is very common when dyeing with metal-complex dyes. The groups of substances used for acid dyes apply also in this case.

Reactive dyes

Reactive dyes are generally applied at pH values of between 5 and 6, depending on the depth of shade, in the presence of ammonium sulphate and the specialised levelling agents (amphoteric substances, which form complexes with the dye at low dyebath temperatures and then break down as the dyeing temperature increases).

The dyeing method may include a temperature hold step at 65 – 70 ºC, during which the dyebath is maintained at this temperature for 30 minutes in order to allow the dye to migrate without fibre reaction. Where dyeing of the very highest fastness is required, the fibre is rinsed under alkali conditions (pH 8–9 with ammonia) to remove un-reacted dyestuff.

Dyestuff	Chemicals and auxiliaries/ typical application conditions	Technique
Acid dyes	- Strongly acidic conditions for equalising dyes (by formic acid) - Moderately acidic conditions for half-milling dyes (by acetic acid) - More neutral conditions for milling dyes (by acetic acid and sodium acetate or ammonium sulphate) - Salt: sodium sulphate or ammonium sulphate - Levelling agents (not necessary for equalising dyes)	Batch dyeing
Chrome dyes (mordant)	- pH 3 to 4.5 - sodium sulphate - organic acids: acetic and formic acid (tartaric and lactic acids can also be used) - reducing agent: sodium thiosulphate - after-chrome with Na or K dichromate	Batch dyeing (After-chrome method)
1:1 metal-complex dyes	- pH 1.8 to 2.5 (pH 2.5 in the presence of auxiliary agents such as alkanolethoxylates) - sulphuric or formic acid - salt: sodium sulphate - ammonia or sodium acetate can be added to the last rinsing bath	Batch dyeing
1:2 metal-complex dyes	- pH 5 to 7 - ammonium sulphate or acetate - levelling agents (non-ionic, ionic and amphoteric surfactants)	Batch dyeing
Reactive dyes	pH 5.5 to 6.5 formic or acetic acid levelling agent after-treatment with ammonia for highest fastness	Batch dyeing

Table 2.6: Summary of the most common dyestuffs and dyeing techniques for wool fibre

2.7.5 Silk dyeing

(?)

2.7.6 Synthetic fibres dyeing

2.7.6.1 Polyamide fibres

Polyamide fibres (PA 6 and PA 6,6) are easily dyed with various types of dyes. Due to their hydrophobic characteristics, they can be dyed with disperse dyes, whereas thanks to the presence of the groups NH-CO- and NH_2- in the chain of the polymer, acid, reactive and 1:2 metal-complex dyes can also be used.

Before dyeing, fabrics must generally be pre-fixed to compensate for material-related differences in affinity and to reduce the sensitivity to creasing during the dyeing process. Pre-fixing can be performed in a stenter frame (15 – 20 seconds at 190 ºC for PA 6 or at 200 – 230 ºC for PA 66) or in hot water (45 min at 130 ºC). [ULLMANN´S]

Disperse dyes

Disperse dyes used for polyamide fibres are mainly azo compounds and anthraquinones. They are applied especially for lighter shades.

The material is dyed in acidic conditions (pH 5) by acetic acid. A dispersing agent is always added to the liquor.

Acid dyes

As with acid dyeing of wool, with increasing dye affinity, the ionic interaction in the initial phase must be repressed to achieve uniform absorption. This means that for high-affinity dyes the liquor must be neutral at the start and the slowly increased to optimise exhaustion. The level of acidity of the bath is regulated either by means of pH-controlling instruments or by adding retarding agents (acid donors, such as ammonium sulphate, sodium pyrophosphate or special auxiliaries based on esters of organic acids, which release acid during the dyeing process).

Optimal exhaustion and uniform dyeing can also be achieved by controlling the temperature profile.

Auxiliary agents (anionic, cationic, non-ionic surfactants) are normally used to improve the levelling effect.

The wet-fastness of dyeing with acid dyes on polyamide fibres is often unsatisfactory. After-treatment with synthanes (synthetic tanning agents) is often necessary. The synthanes are added to the exhausted bath or to fresh liquor at pH 4.5 by formic acid. The material is treated at 70 - 80 ºC and is then rinsed.

Metal-complex dyes

Among 1:2 metal-complex dyes, molecules containing sulphonic groups are the most suitable for polyamide fibres.

The absorption of the dyes increases with decreasing pH. Dyeing conditions vary from weakly acidic by addition of ammonium sulphate and acetic acid to neutral or moderately alkaline for high-affinity dyes. For high-affinity dyes the addition of amphoteric or no-nionic levelling agents is also necessary.

Reactive

In principle, the reactive dyes used for wool are also suitable for polyamide. The dyeing process is carried out in weakly acidic conditions (pH 4.5 - 5). The process is started at 20 – 45 ºC and then temperature is increased near to boiling. Non-ionic surfactants and sodium bicarbonate or ammonia are used in the after-treatment step.

Dyestuff	Chemicals and auxiliaries/ typical application conditions	Technique
Disperse	- pH=5 by acetic acid - dispersing agents (sulphoaromatic condensation products or non-ionic surfactants) - dyeing is conducted at near-boiling temperature	Batch
Acid dyes	- pH conditions from acid to neutral depending on the affinity of the dye - optimal bath exhaustion and level dyeing are achieved by either pH or temperature control methods (levelling agents are also used) - in the acidic range, electrolytes retard the exhaustion - with levelling dyes, wet-fastness is often unsatisfactory and after-treatment with synthanes can be necessary	Batch
1:2 metal-complex dyes	- dyes containing sulphonic groups are preferred because they are more water-soluble and produce better wet-fastness - to improve absorption of low-affinity dyes (especially for disulphonic) dyeing is carried out in weakly acidic conditions using acetic acid - high-affinity dyes are applied in neutral or weakly alkaline medium using amphoteric or non-ionic levelling agents	Batch
Reactive dyes	- in principle the reactive dyes used for wool are also suitable for PA - dyeing is conducted at near-boiling temperature in weakly acidic conditions - after-treatment is performed at 95 ºC using a non-ionic surfactant and sodium bicarbonate or ammonia	Batch

Table 2.7: Summary of the most common dyestuffs and dyeing techniques for polyamide fibres

2.7.6.2 Polyester fibres

Articles made of pure PES are dyed almost exclusively using batch dyeing techniques and among these, dyeing under high-temperature conditions is the most commonly applied.

Dyeing polyester fibres under atmospheric conditions (below 100 ºC) was also frequently used in the past with the aid of carriers. Since these substances are ecologically harmful, dyeing below 100 ºC is no longer in use today for pure PES fibres, unless the modified polyester fibres known as NCD (*Non-Carrier Dyeable*) fibres are employed. Thanks to physical and chemical alterations provided to the structure of the fibre during the manufacturing process, these new fibres show a lower crystallinity and as a result are easier to dye without need for carriers. Moreover, the use of sulphated aromatic polycarboxilic acid as co-monomers leads to an increase in the number of anionic sites, granting a better exhaustion of cationic dyestuffs.

Concerning high-temperature dyeing, the process is usually carried out in acidic conditions (pH 4 - 5) with addition of acetic acid under pressure at 125 – 135 ºC. In these conditions levelling agents are necessary to prevent excessively rapid absorption.

Provided that alkali-stable dyes are used, dyeing in alkaline medium (pH 9 - 9.5) is also possible. This technique has been developed in order to counteract the migration of oligomers typical of PES fibres (see Section 2.1.1.1). In fact, oligomeric components (cyclic trimers of ethylene terephthalate are especially harmful) tend to migrate out of the fibre during dyeing,

thus forming with the dye agglomerates that can deposit on the textile or on the dyeing equipment. To achieve level effects, ethoxylated products are used as levelling agents also in this case.

The thermosol process is another applied technique, although it is primarily used for PES/cellulose blends. The dye is padded on the textile together with a thickening agent. A drying step at 100 – 140 ºC is carried out. Then the dye is fixed (200 – 225 ºC for 12 – 25 seconds). An alkaline reductive after-treatment is normally carried out. Non-ionic surfactants are usually added as dispersants to the final washing bath.

Dyestuff	Chemicals and auxiliaries/ typical application conditions	Technique
Disperse	- pH 4 - 5 by acetic acid - levelling agents (aliphatic carboxylic esters, ethoxylated products, combinations of alcohols, esters or ketones with emulsifying agents) - possible addition of complexing agents (EDTA) for dyes sensitive to heavy metals	Batch dyeing at 125 - 135 ºC under pressure (HT)
	- this techniques requires the use of carriers unless modified polyester fibres are employed	Batch dyeing below 100 ºC
	- pH 4 - 5 by acetic acid - thickeners such as polyacrylates and alginates are added to the padding liquor in order to prevent migration of the dye during drying - after-treatment with a solution containing sodium hydrosulphite and sodium hydroxide (dispersing agents are added to the last washing bath)	Thermosol process

Table 2.8: Summary of the most common dyestuffs and dyeing techniques for polyester fibres

2.7.6.3 Polyacrylic fibres

So called PAC fibres are hydrophobic and contain anionic groups in the molecule. As a result, they can be dyed with disperse and cationic dyes. With the introduction of cationic co-monomers in the polymer, the fibre can also be dyed with acid dyes.

Batch dyeing is commonly applied for cable or stock (package dyeing), yarn in hank form or packages and for fabric. Piece dyeing can be performed on beam, overflow, paddle (for knitwear), or drum (socks).

Stock, cable and top can be also dyed on special machine, using the pad-steam process, preferably with pressurised steam to obtain short fixing times. Piece goods, especially upholstery material (velour), are also dyed according to the pad-steam process, but in this case fixing is carried out with saturated steam. This implies longer fixing times, which means that rapidly diffusing cationic dyes and dye solvents are required.

Disperse dyes

Disperse dyes are used to produce light to medium-deep shades. The dyeing techniques correspond to those used on polyester fibres. However, dyeing can be performed at temperatures <100 ºC without carriers. Furthermore, due to the good migration properties of disperse dyes, levelling agents are not required.

Cationic dyes

Typical recipes used in *batch dyeing* include an electrolyte (sodium acetate or sodium sulphate), acetic acid, a non-ionic dispersant and a retarding agent. Dyeing is conducted by controlling the

temperature in the optimum range for the treated fibre. Finally the bath is cooled down and the material is rinsed and submitted to after-treatment.

Continuous processes commonly applied are:
- pad-steam process (fixation with pressurised steam at more than 100 ºC) - this process has the advantage of reducing fixing time. Pad liquor typically contains a steam-resistant cationic dye, acetic acid and a dye solvent
- pad-steam process (fixation with saturated steam at 100 - 102 ºC) - this process requires a longer fixing time. Rapidly diffusing cationic dyes and dye solvents, which exhibit a carrier effect, are required.

- When dyeing with basic dyes, special levelling agents (also called retarding agents) are widely used to control the absorption rate of the colorant on the fibre, thus improving level dyeing.

Dyestuff	Chemicals and auxiliaries/ typical application conditions	Technique
Disperse	- dyeing conditions correspond to those used for polyester - addition of carriers is not required	
Cationic	- Acetic acid (pH 3.6 - 4.5) - Salt (sodium sulphate or sodium acetate) - Retardant auxiliaries (usually cationic agents) - Nonionic dispersing agents	Batch
	- Acetic acid (pH 4.5) - Dye solvent - Steam-resistant, readily-soluble dyes (usually liquid) are required	Pad-steam process with pressurised steam
	- Dye solvent - Rapidly diffusing dyes are required	Pad-steam process with saturated steam

Table 2.9: Summary of the most common dyestuffs and dyeing techniques for polyacrylic fibres

2.7.6.4 Cellulose acetate (AC) and cellulose triacetate (CT)

In contrast to the other regenerated cellulose fibres, CA and CT are hydrophobic and therefore they can be dyed with disperse dyes under conditions which are very similar to those applying to PES fibres.

Cellulose acetate is dyed by the exhaustion method with disperse dyes in the presence of non-ionic or anionic dispersing agents in weakly acidic conditions (pH 5 - 6). Dyeing is normally done at 80 – 85 ºC. However, a series of less wetfast dyes already absorb onto the fibre at 50 - 60 ºC, whereas more wetfast dyes require temperatures up to 90 ºC.

Compared to CA, CT dyeing and finishing characteristics are more similar to purely synthetic fibres. CT, like CA, is dyed with disperse dyes in a weakly acidic medium in the presence of levelling auxiliaries. Applied dyeing techniques for CT are:
- Batch dyeing process, usually at 120 ºC, but if these conditions are not possible a dyeing accelerant (based on butyl benzoate or butyl salicylate) is required
- Thermosol process.

2.7.7 Fibre blends dyeing

Natural/synthetic fibre blends are becoming more and more important in the textile industry because this allows combining the favourable technological properties of synthetic fibres with the pleasant feel of natural fibres.

Of the worldwide consumption of PES fibres, 55 – 60 % is used in blends with cellulose fibres or wool. About 40 % of polyamide is used in blends, while 50 % of polyacrylic fibres is used especially in blends with wool for knitwear. [ULLMANN'S]

Fibre blends can be produced according to three different methods:
- fibres of different types in the form of staple fibres are mixed at the yarn manufacturing stage, during spinning
- fibres of different types are separately spun and the resulting yarns are wounded together to give a mixed yarn
- fibres of different types are separately spun and blended together only at the weaving stage where one fibre is used as warp and the other one as weft.

Dyeing of blend fibres is always longer and more difficult as an operation compared to pure fibre dyeing. Despite these disadvantages, dyeing tends to be placed as close as possible towards the end of the finishing process. In fact this enables the dyer to satisfy the requests of the market without the need to store large amounts of material already dyed in flock or yarn form in all available shades.

When dyeing blend fibres, the following methods can be applied:
- the two fibres are dyed in the same tone ("tone on tone") or in two different shades using the same dyes
- only one fibre is dyed (the colorant is not absorbed by the other ones)
- the different fibres are dyed in different tones.

For "tone on tone" dyeing, it is sometimes possible to use the same dye for the different fibres. When dyes of different classes have to be employed, the dyeing process is easier to control when the selected colorants have affinity only for one fibre and not for the other one. In reality, however, this situation is exceptional and the dyeing of fibre blends remains a complex operation.

Blend fibres dyeing can be done in batch, semi-continuous and continuous processes. Batch processes include:
- dyeing in one bath and one step (all dyes are added in the same bath in one single step)
- dyeing in one bath and in two steps (dyes are added to the same bath in subsequent steps)
- dyeing in two baths (dyes are applied in two steps in two different baths).

The most common fibre blends will be discussed in the following sections.

Polyester-cellulose blends

A large part of the entire production of PES (ca. 45 %) is used to make this mixture. Polyester-cellulose blends are used for all types of clothing and for bed linen. The cellulose component is usually cotton, but viscose staple fibres and occasionally linen are also used. The preferred mixing ratio is 67:33 PES: cellulose (for textiles worn close to the skin), 50:50 and 20:80. [ULLMANN'S]

In dyeing PES-cellulose mixtures, disperse dyes are used for the polyester component, while the cellulose portion is usually dyed with reactive, vat and direct dyes. Pigment dyeing is also commonly used for light shades.

Disperse dyes stain cellulose fibres only slightly and they can easily be removed by subsequent washing or, if necessary, by alkaline reduction treatment. Most of the dyes used for cellulose stain PES only slightly or not at all.

PES-cellulose blends are commonly dyed in continuous processes. Nevertheless, for yarn and knitwear, batch dyeing is of major importance.

In *batch dyeing,* the application of dyes can be done in one or two steps in one bath or in two different baths in subsequent stages. The disperse dye is general applied at high-temperature (HT) conditions without use of carriers. The one-bath/ one-step procedures are generally preferred, being more economic. In this case special auxiliaries, so-called acid donors, are used, which lower the pH when the temperature is increased. In this way it is possible to fix the reactive dyes in alkaline conditions and then reach the optimal dyeing conditions (pH 5 - 6) for disperse dyes by increasing the temperature.

In *continuous processes* the dyes are usually applied in one bath. The fabric is subsequently dried and disperse dye is fixed to the PES component by the thermosol process. Afterwards, the second dye is developed according to the procedure typical of each class, using in general pad-steam, pad-jig or pad-batch processes.

Table 2.10 presents a summary of the most frequently applied processes is presented. Dyes are applied according to application conditions typical of their class. For more details regarding a given class of colorant, see the specific section.

Technique			Disperse /vat	Disperse/ reactive	Disperse /direct	Pigment
Batch	One-bath process				Y K	W [(1)]
	Two-bath process			Y K?		
	One-bath two-step process		Y K?	Y K?	Y K	
Continuous	I stage	II stage				
	Application of all dyes in one bath by padding + drying followed by	Thermosol + pad-jig	W			
		Thermosol + pad-batch		W		
		Thermosol +pad-steam	W	W	W	
Y = yarn W = woven fabric K = knitted fabric [(1)] Pigment dyeing includes padding with the pigment, a binder and auxiliaries, drying and polymerisation at 140 ºC for 5 min.						

Table 2.10: Summary of dyestuff and dyeing techniques for polyester-cellulose blends

Polyester-wool blends

Polyester-wool blends are widely used, especially for woven goods and knitwear. The most frequently found ratio is 55:45 PES: wool.

Wool cannot be dyed at the high temperatures typical of the HT dyeing process for PES fibres and PES-cellulose blends. The dyeing time should also be as short as possible so that the wool is not damaged. For large productions it is therefore preferable to dye wool and PES separately in top, blending the two fibres at the yarn manufacturing stage. However, quick changes in fashion and short-term planning frequently do not allow separate dyeing.

When dyeing polyester-wool blends, disperse dyes are used for polyester and anionic (acid and metal-complex dyes) for wool.

Only disperse dyes that stain wool as slightly as possible or are easily removed by washing can be used for dyeing wool-cellulose blends. Disperse dyes, in fact, tend to stain wool and a reductive after-treatment is not always possible (appropriately stable dyes are required).

PES-wool blends are typically dyed according to the following batch processes:
- at boiling temperature with carriers
- at 103 – 106 ºC with little carrier
- at 110 – 115 ºC with the addition of formaldehyde as a wool protective agent and without carrier (HT conditions).

Because of the environmental concerns associated with the use of carriers (see Section 8.6.7) the first dyeing technique is avoided when possible. To this respect, modified PES fibres can also be used, which can be dye at boiling temperature without use of carriers (see Section 2.1.1.1)

The one-bath process method is preferred in practice; the two-bath process is applied when deep shades and high fastness are required. The material is first dyed with disperse dyes. Then a reductive intermediate treatment is applied before dyeing the wool part. After dyeing, an after-treatment is applied to remove disperse dye attached to the wool, if the dye used for wool can withstand it. The material is treated with ethoxylated fatty amine in weakly acid liquor at 60 ºC.

Polyamide-cellulose blends

Since PA fibres have affinity for almost all dyes used for cellulose, different possibilities are available for dyeing this blend:
- direct and disperse dyes (pH 8)
- acid or 1:2 metal-complex dyes (pH 5 - 8)
- vat dyes (exhaust and pad-steam process are used)
- reactive dyes.

Application conditions are those typical of each class of dye. They have already been described in the specific sections.

Polyamide-wool blends

Blends with polyamide/ wool ratios varying from 20:80 to 60:40 are used. This blend is particularly important in the carpet sector. More detailed information is therefore reported in the specific section dedicated to this sector (see Section 2.13.5).

As general information about the dyeing processes suitable for this type of blend, both fibres have affinity for acid and 1:2 metal-complex dyes. However, since PA is more accessible to the dye than wool, it is dyed more deeply, particularly in the case of light colours. To counteract this effect, special levelling agents (also called PA reserving/ blocking agents) are used (mainly aromatic sulphonates). These auxiliaries have a relatively high affinity for the PA fibre and retard the absorption of the colorant on this part of the blend.

Dyeing is performed in the presence of acetic acid and sodium sulphate. Due to limited affinity of the material for acid dyes, 1:2 metal-complex dyes are required for dark shades. [ULLMANN'S]

Polyacrylonitrile-cellulose blends

PAC-cellulose blends are used for household textiles (drapery and table linen) and imitation fur ("peluche" in which the pile consists of PAC fibres and the back is made of cotton). The percentage of PAC in the mixtures varies between 30 and 80 %.

PAC can be dyed with cationic or disperse dyes, while direct, vat or reactive dyes can be used for the cellulose component.

The following methods are the most commonly used for dyeing this blend:
- *Continuous dyeing* with cationic and direct dyes according to the pad-steam process (to avoid precipitation of cationic and anionic dyes present in the pad liquor at relatively high concentration, combination of anionic and non ionic surfactants are added to the solution)
- *Batch dyeing* (usually according to the one-bath, two-steps method) with cationic and vat dyes or with cationic and reactive dyes.

Polyacrylonitrile-wool blends

Among synthetic fibres, PAC fibres are the most suitable for obtaining blends with wool that keep a wool-like character. This makes this blend widely used, especially for knitwear and household textiles. The blending ratio of PAC to wool varies from 20:80 to 80:20.

Metal-complex, chrome and acid dyes are the dyestuffs typically used for the wool part, while PAC is dyed with cationic dyes.

Cationic dyes stain wool fibre. As a matter of fact cationic dyes attach first to wool and then migrate to PAC fibre at higher temperature. Even if well-reserving dyes are selected, dyeing must be conducted for a sufficiently long time (from 60 to 90 minutes) in order to obtain good wool reserve [ULLMANN'S].

PAC-wool blends can be dyed using the following exhaustion methods:
- one-bath one-step
- one-bath two-step
- two-bath.

The first one allows shorter dyeing times and lower consumption of water. However, it is not always applicable because the simultaneous presence in the dye bath of anionic and cationic compounds can produce the precipitation of the formed adducts on the fibre. Precipitation can be prevented using dispersing agents and selecting adequate dyes.

When dyeing with the one-bath, two-step method the use of reserve agents is not necessary. In fact, wool absorbs the cationic dye and slowly releases it, acting as a retarding agent (exerting a retardant effect on PAC).

2.7.8 Environmental issues

Potential sources and types of emissions associated with dyeing processes are summarised in the following table.

Operations	Emission sources	Type of emission
Colour kitchen operations	Dye preparation	TO BE COMPLETED
	Auxiliaries preparation	?
	Dispensing of dyes and auxiliaries (automatic)	?
	Dispensing of dyes and auxiliaries (manual)	?
Batch dyeing	Dyeing	Discontinuous, low-concentration water emission at the end of each cycle
	Washing and rinsing operations after dyeing	Discontinuous, low-concentration water emission at the end of each cycle
	Cleaning of equipment	Discontinuous, low concentration emission
Semi-continuous and continuous dyeing	Application of the colorant	No emission from the process
	Fixation by steam or dry-heat	Continuous emission to air (not relevant emission)
	Washing and rinsing operations after dyeing	Continuous, low concentration water emission
	Discharging of leftovers in the chassis and feed storage container	Discontinuous, concentrated emission at the end of each lot
	Cleaning of equipment	Discontinuous, low concentration emission

Table 2.11: Overview of the typical emissions generated in dyeing processes

As the table shows, most of the emissions are emissions to water. Due to the low vapour pressure of the substances in the dyebath, emissions to air are generally not relevant and can be regarded more as problems related to the workplace atmosphere. A few exceptions are pigment dyeing and those dyeing processes where carriers are employed. In pigment dyeing the substrate is not washed after pigment application and therefore the pollutants are quantitatively released to air during drying. Emissions from carriers are to air and water. These particular auxiliaries and the environmental concerns associated with their use are described in Section 8.6.7.

In the first part of the following discussion the environmental issues related to the substances employed will be described, while in the second part the environmental issues related to the process will be mentioned.

2.7.8.1 Environmental issues related to the substances employed

Water-polluting substances in the above mentioned emissions may originate from:
*   the dyes themselves (e.g. toxicity, metals, colour)
*   auxiliaries contained in the dyes' formulations
*   basic chemicals (e.g. alkali, salts, reducing and oxidising agents) and auxiliaries used in dyeing processes
*   contaminants present on the fibre when it enters the process sequence (residues of pesticides on wool are encountered in loose fibre and yarn dyeing and the same occurs with spin finishes present on synthetic fibres).

Dyes

Spent dyebaths (discontinuous dyeing, residual dyeliquors and water from washing operations always contain a percentage of un-fixed dyes. The rates of fixations vary considerably among the different classes of dyes, being especially low for reactive and sulphur dyes. Moreover, large variations are found even within a given class of colorants. This is particularly significant in the case of reactive dyes. Fixing rates above 60 % cannot be achieved, for example, in the case of turquoise-green reactive dyes (where the chromophore is a phthalocyanine). In contrast, the so-called double anchor reactive dyes can achieve extremely high rates of fixation.

The degree of fixation of an individual dye varies according to type of fibre, shade and dyeing parameters. Therefore fixation rate values can be given only as approximations. However they are useful to give an idea of the amount of unfixed dyes that can be found in wastewater. Information from different authors is given in the table below.

Dyestuffs	EPA	OECD	ATV	Bayer	EURATEX
Acid dyes - for wool - for polyamide	10 20	}7 - 20	}7 - 20	-	}5 - 15
Basic dyes	10	2 - 3	2 - 3	2	?
Direct dyes	30	5 - 20	5 - 30	10	5 - 35
Disperse dyes - for acetate - for polyester 1 bar - for polyester HT	25 15 5	}8 - 20	}8 - 20	}5	}1 - 15
Naphtol dyes	25	5 - 10	5 - 10	-	10 - 25
Reactive dyes	50 - 60	20 - 50	5 - 50	30	20 - 45
Metal-complex	10	2 - 5	2 - 5	5	2 - 15
Chrome dyes	-	-	1 - 2	-	?
Vat dyes	25	5 - 20	5 - 20	-	5 - 30
Sulphur dyes	25	30 - 40	30 - 40	-	10 - 40
Source: [UBA, 1994], [EURATEX] EPA: US Environmental Protection Agency OECD: Organisation for Economic Co-operation and Development ATV: Abwasser Technishe Vereinigung (Waste Water Technical Association)					

Table 2.12: Percentage of non-fixed dye that may be discharged in the effluent for the principal classes of dyes

As a result of low fixation, dyestuffs which are poorly bio-eliminable pass through the wastewater treatment plant and are ultimately found in the effluent. The first undesiderable effect in the receiving water is colour. High doses of colour not only cause aesthetic impact, but can also interrupt photosynthesis, thus affecting aquatic life. Other effects are related to organic content of the colorant (expressed as COD and BOD), its aquatic toxicity and the presence in the molecule of metals or halogens that can give rise to AOX emissions.

These issues are discussed in more detail for each class of dyestuff in Section 9. Only some general key issues are considered in this section.

AOX emissions

Vat and reactive dyes are more likely to contain organic halogens in their molecule. The content of organically bound halogen can be up to 12 % on weight for some vat dyes. Vat dyes, however, show a very high degree of fixation. In addition, they are insoluble in water and the amount that reaches the effluent can be eliminated with high efficiency in the wastewater treatment plant through absorption on the activated sludge.

Reactive dyes, on the contrary, may have very low fixation degrees (the lowest level of fixation is observed with phthlocyanine in batch dyeing) and their removal from wastewater is difficult because of the low biodegradability and/or low level of absorption of the dye onto activated sludge during treatment. Reactive dyes very often contain halogen atoms (e.g. monochlorotriazines). However, these halogens act as so-called "leaving groups". In this case, if the fixation reaction takes place, the halogen enters the effluent as an ion, rather then organically bound halogen.

For the other classes of colorants the AOX issue is not relevant because, with few exceptions, halogen content is usually below 0.1 %.

Heavy metals emissions

Metals can be present in dyes for two reasons. First, metals are used as catalysts during the manufacture of some dyes and can be present as a impurities. Second, in some dyes the metal is chelated with the dye molecule, forming an integral structural element.

Dye manufacturers are now putting more effort into reducing the amount of metals present as impurities. This can be done by selection of starting products, removal of heavy metal and substitution of the solvent where the reaction takes place.

ETAD has established limits in the content of heavy metal in dyestuffs. The values have been set to ensure that emission levels from a 2 % dyeing and a total dilution of the dye of 1:2500, will meet the known wastewater requirements [BASF].

Examples of dyes containing bound metals are copper and nickel in phthalocyanine groups, copper in blue copper-azo-complex reactive dyes and chromium in metal-complex dyes used for wool. The presence of the metal in these dyes can be regarded as a less relevant problem provided that the dye is fixed on the textile good and not discharged in wastewater. However, not all the dye in the dyebath is exhausted and dye wastes can also result from handling, weighing, drum cleaning and spills. [EPA]

Toxicity

Dyestuffs showing aquatic toxicity and/ or allergenic effects are highlighted in Section 9. Here it is also important to mention that about 60 % to 70 % of the dyes used nowadays are azo dyes. Under reductive conditions, these dyes may produce amines and some of them are carcinogenic. A list of carcinogenic amines that can be formed by cleavage of certain azo dyes is shown in the Table 2.13.

1	4-aminodiphenyl
2	Benzidine
3	4-chloro-o-toluidine
4	2-naphthylamine
5	p-chloroaniline
6	2,4-diaminoanisol
7	4,4´-diaminodiphenylmethane
8	3,3´-dichlorobenzidine
9	3,3´-dimethoxybenzidine
10	3,3´-dimethylbenzidine
11	3,3´-dimethyl-4,4´-diaminodiphenylmethane
12	2-methoxy-5-methylaniline
13	4,4´-methylene-bis-(2-chloraniline)
14	4,4´-oxydianiline
15	4,4´-thiodianiline
16	o-toluidine
17	2,4-toluylenediamine
18	2,4,5-trimethylaniline
19	o-aminoazotoluene
20	2-amino-e-nitrotoluene

Table 2.13: List of carcinogenic amines

In Germany, the sale of textiles dyed with dyes that can cleave and form carcinogenic amines has been forbidden since January 1996. According to [EURATEX], more than 100 dyes with the potential to form carcinogenic amines are still available on the market.

Auxiliaries contained in dye formulations

Depending on the dye class and the application method employed (e.g. batch or continuous dyeing, printing) different additives are present in the dye formulations. Since these substances are not absorbed by the fibres, they are completely discharged in the wastewater. Typical additives are listed in the table below.

Additive	Chemical composition	COD mg O_2/l	BOD$_5$ mg O_2/l	TOC elimination [1]
Dispersants	- Lignin sulphonates - Naphthalene sulphonates condensation products with formaldehyde - Ethylene oxide/ propylene oxide copolymers	1200 650	50 50	15 % 15 %
Salts	Sodium sulphate, sodium chloride			
Powder binding agents	Mineral- or paraffin oils (+ additives)			
Anti-foaming agents	Acetyl glycols			
Anti-freeze agents	- Glycerine - Glycol	1200 1600	780 10	90 % 95 %
Thickening agents	- Carboxymethyl cellulose - Polyacrylates	1000	0	30 %
Buffer systems	Phosphate, Acetate			
Source [VITO] [1] Statistical elimination test (Zahn-Wellens Test)				

Table 2.14: Ecological properties of dye formulations additives

While these additives are not toxic to aquatic life, they are in general not readily eliminable and are poorly biodegradable. This applies in particular to the dispersants present in the formulations of vat, disperse and sulphur dyes, which are water-insoluble and need these special auxiliaries in order to be applied to the textile in the form of aqueous dispersions. These dispersants consist mainly of naphthalene sulphonate-formaldehyde condensation products and lignin sulphonates, but sulphomethylation products derived from the condensation of phenols with formaldahyde and sodium sulphite can also be found. Other not readily eliminable additives are acrylate and CMC-based thickeners and anti-foam agents

The difference between liquid and powder formulations should also be mentioned. Dyes supplied in liquid form contain only one third of the amount of dispersing agent normally contained in powder dyes (see Table 2.15). The reason for this difference stems from the manufacturing process of powder dyes: the very small particles generated during grinding must be protected during the subsequent drying process and this is possible only by adding high proportions of dispersing agents.

Formulation component	Powder formulation	Liquid formulation
Dye	30 - 50 %	20 - 40 %
Dispersing agent	40 - 60 %	10 - 20 %
Salts	0 - 20 %	-
Powder binding agents	0 - 5 %	-
Anti-foaming agents	0 - 5 %	0 - 5 %
Anti-freeze agent	-	10 - 15 %
Thickening agent	-	0 - 5 %
Water	5 - 10 %	40 - 60 %
Source [VITO]		

Table 2.15: Proportion of additives and dye in powder and liquid dyes

Basic chemicals and auxiliaries used in the dyeing process

Regarding the environmental concerns associated with the chemicals and auxiliaries used in dyeing processes it is worth mentioning the following key issues.

Sulphur-containing reducing agents

Wastewater from sulphur dyeing contains sulphides used in the process as reducing agents. In some cases the sulphide is already contained in the dye formulation and in some other cases it is added to the dye bath before dyeing. In the end, however, the excess of sulphide ends up in the wastewater. Sulphides are toxic to aquatic organisms and contribute to increasing COD load. In addition, sulphide anions are converted into hydrogen sulphide under acidic conditions, thereby giving rise to problems of odour and corrosivity.

Sulphur-containing reducing agents, namely sodium hydrosulphite (also called sodium dithionite) are also used in vat dyeing processes. During the dyeing process sodium dithionite is converted into sulphite, which is toxic to fish and bacteria, and in some cases it is converted to sulphate. In the wastewater treatment plant sulphite is normally oxidised into sulphate, but this can still cause problems. Sulphate, in fact, may cause corrosion of concrete pipes or may be reduced under anaerobic conditions into hydrogen sulphide. Hydroxyacetone, although it produces an increase in COD load, is recommended to lower the sulphur content in wastewater, but it cannot replace hydrosulphite in all applications. Newly developed organic reducing agents with improved reducing effects are currently being tested.

Oxidising agents

Dichromate is no longer used in Europe as an oxidising agent when dyeing with vat and sulphur dyes, but it is still widely used for the fixation of chrome dyes in wool dyeing. Chromium III exhibits low acute toxicity, while chromium VI is acutely toxic and has been shown to be carcinogenic towards animals. During the dyeing processes with chrome dyes, Cr VI is reduced to Cr III if the process is under control. Nevertheless emissions of trivalent chromium in the wastewater have to be taken into account in this process.

It is also worth mentioning the AOX emissions that may arise from the use of bromate, iodate and chlorite as oxidising agents in vat and sulphur dyeing processes.

Salt

Salts of various types are used in dyeing processes for different purposes (e.g. to promote level dyeing or increase dye exhaustion). In particular, large amounts of salt are used in cotton batch dyeing processes with reactive dyes. The amount of salt employed is quite significant compared to other classes of dyestuffs, for example direct dyes (Table 2.16).

Shade	Dye o.w.f	Direct	Reactive
Paste/light	<1.5 %	2.5 - 7.5 g/l	30 - 60 g/l
Medium	1.0 - 2.5 %	7.5 - 12.5 g/l	70 - 80 g/l
Dark	>2.5 %	12.5 - 20 g/l	80 - 100 g/l
Source [EPA]			

Table 2.16: Amount of salt employed in cotton batch dyeing processes with reactive and direct dyes

In addition to the use of salt as a raw material, neutralisation of commonly employed acids and alkali produces salt as a by-product.

Salts are not effectively removed in conventional wastewater treatment systems and they are therefore ultimately discharged in the receiving water. Although the mammalian and aquatic toxicities of the commonly employed salts are very low, in arid or semi-arid regions their large-scale use can produce concentrations above the toxic limit and increase the salinity of the groundwater.

Carriers

The use of these auxiliaries, which were widely employed in the past, has now been reduced due to ecological and health problems. They are still an issue in dyeing of polyester in blend in wool. Carriers include a wide group of organic compounds, many of them steam volatile, poorly biodegradable and toxic to humans and aquatic life. However, as the active substances usually have high affinity for the fibre (hydrophobic types), 75 – 90 % are absorbed by the textile and only the emulsifiers and the hydrophilic types such as phenols and benzoates derivatives are found in the wastewater. The carriers that remain on the fibre are partially volatilised during drying and fixing operations and can give rise to air emissions.

Dyestuffs manufacturers may mix the carriers with the dyes. In this case textile finishers will have little knowledge of the loads discharged. [TEBODIN]

Other auxiliaries of environmental interest

Other substances that may be encountered in the dyeing auxiliaries and that may give rise to water pollution are:
- fatty amine ethoxylates
- alkylphenol ethoxylates (APEO)
- quaternary ammonium compounds
- polyvinylpyrrolidones
- cyanamide-ammonia salt condensation products
- acrylic acid-maleic acid copolymers
- ethylenediamine tetraacetate (EDTA)
- diethylenetriaminepentaacetate (DTPA)
- ethylenediaminetetra(methylenephosphonic acid) (EDTMP)
- diethylenetriaminepenta(methylenphosphonic acid) (DTPMP).

These are water-soluble hard-to-biodegrade compounds which can pass untransformed or only partially degraded, through wastewater treatment systems.

In addition, some of them are toxic (e.g. quaternary amines) or can give rise to metabolites which may affect reproduction in the aquatic environment (APEO).

2.7.8.2 Environmental issues related to the process

Water and energy consumption in dyeing processes are a function of the dyeing technique and machinery employed.

Batch dyeing processes generally require higher water and energy consumption levels than continuous processes, due to the higher liquor ratios involved. The liquor ratio may also play an important role in the level of exhaustion of the dye. This parameter is related to the exhaustion level of the bath through the equation: $E = K/(K+L)$, where:

K (affinity) = 50 to 1000 for various dye/fibre combinations
L (liquor ratio) = 5 to 50 for various machines
E (exhaustion) = 0.5 to 1 (50 to 100 % exhaustion)

From this equation it can be inferred that when L increases, E decreases and a lower amount of dye is absorbed onto the fibre when the equilibrium is reached. The effect is more pronounced on low-affinity dyes.

The liquor ratio also has an influence on the consumption levels of chemicals and auxiliaries. Most of them are dosed on the basis of the amount of bath (o.w.b) rather than the weight of the fibre (o.w.f). For example, in a 1:5 bath ratio, 50 g/l of salt is 250g/kg of fibre, but at 1:40 liquor ratio, the same 50 g/l of salt correspond to 2 kg/kg of fibre.

Continuous and semi-continuous dyeing processes consume less water, but this also means a higher dyestuff concentration in the dye liquor. In discontinuous dyeing the dye concentration varies from 0.1 to 1 g/l, while in continuous processes this value is in the range of 10 to 100 g/l. The residual padding liquor in the pads, pumps and pipes must be discarded when a new colour is started. The discharge of this concentrated effluent can result in a higher pollution load compared with discontinuous dyeing, when short lots of material are processed. Modern continuous dyeing ranges, however, have steadily improved in recent years. Small pipes and pumps and small pad-bath troughs reduce the amount of concentrated liquor to be discarded. In addition, it is possible to minimise the discard of leftovers, thanks to automated dosing systems, which meter the dye solution ingredients in the exact needed amount.

In both continuous and batch dyeing processes final washing and rinsing operations are water-intensive steps to take into consideration.

2.8 Printing

2.8.1 Printing processes

Printing, like dyeing, is a process for applying colour to a substrate. However, instead of colouring the whole substrate (cloth, carpet or yarn) as in dyeing, print colour is applied only to defined areas to obtain the desired pattern. This involves different techniques and different machinery with respect to dyeing, but the physical and chemical processes that take place between the dye and the fibre are analogous to dyeing.

The printing process involves the following steps:
* colour paste preparation: when printing textiles, the dye or pigment is not in an aqueous liquor, instead, it is usually finely dispersed in a printing paste, in high concentration
* printing: the dye or pigment paste is applied to the substrate using different techniques, which are discussed below
* fixation: immediately after printing, the fabric is dried and then the prints are fixed mainly with steam or hot air (for pigments)
* after-treatment: this final operation consists in washing and drying the fabric (it is not necessary when printing with pigments or with other particular techniques such as transfer printing).

When describing the different printing techniques, a distinction should be made between printing with pigments, which have no affinity for the fibre, and printing with dyes (reactive, vat, disperse, etc.) capable of diffusing into the fibre.

2.8.1.1 Printing with pigments

Pigment printing has gained much importance today and for some fibres (e.g. cellulose fibres) is by far the most commonly applied technique. Pigments can be used on almost all types of textile substrates and, thanks to increased performance of modern auxiliaries, it is now possible to obtain high-quality printing using this technique.

Pigment printing pastes contain a thickening agent, a binder and, if necessary, other auxiliaries such as fixing agents, plasticizers, defoamers, etc.

White spirit-based emulsions, used in the past as thickening systems, are used only occasionally today (mainly half-emulsion thickeners). More information regarding the characteristics of the auxiliaries used can be found in Section 8.7.

After applying the printing paste, the fabric is dried and then the pigment is fixed with hot air. The advantage of pigment printing is that the process can be done without subsequent washing (which, in turn, is needed for all other printing techniques).

2.8.1.2 Printing with *diffusing* dyes

Printing paste preparation

The process starts with the preparation of the paste. Compared to pigment printing, the composition of the pastes is more complex and variable, being determined not by the dye used, but by the printing technique, the substrate, the application and the fixation methods applied.

Apart from the dye, printing pastes contain a thickening agent and various other auxiliaries, which can be classified according to their function as follows:

- oxidising agents (e.g. m-nitrobenzenesulphonate, sodium chlorate, hydrogen peroxide)
- reducing agents (e.g. sodium dithionite, formaldehyde sulphoxylates, thiourea dioxide, tin(II) chloride)
- discharging agents for discharge printing (e.g. anthraquinone)
- substances with a hydrotropic effect, like urea
- dye solubilisers, which are polar organic solvents like glycerine, ethylen glycol, butyl glycol, thiodiglycol etc.
- resists for reactive resist printing (e.g. sulphonated alkanes)
- defoamers, (e.g. silicon oils, organic and inorganic esters, aliphatic esters, etc.).

More information about the characteristics of the above mentioned auxiliaries can be found in Section 8.7.

All the necessary ingredients are metered (dosed) and mixed together in a mixing station. Since between 5 and 10 different printing pastes are usually necessary to print a single pattern (in some cases up to 20 different pastes are applied), in order to reduce losses due to incorrect measurement, the preparation of the pastes is done in automatic stations. In modern plants, with the help of special devices, the exact amount of printing paste required is determined and prepared in continuous mode for each printing position, thus reducing leftovers at the end of the run.

It is common practice in many printing houses to filter the printing pastes before application, using for example a filter cloth. This operation is especially important for thickeners to prevent free particles from blocking the openings of the screens.

Printing (paste application)

After preparation, the paste is applied to specific areas of the textile using one of the following techniques:
- direct printing
- discharge printing
- resist printing
- transfer printing.

In the case of *direct printing* the dye is applied to specific areas of a pre-treated textile substrate, which can be white or pre-dyed (in light colours).

We can speak of *discharge printing*, if in the fixation process that follows the application of the printing paste there is local destruction of a dye applied previously. If the etched (discharge), previously dyed area becomes white, then the process is called *white discharge*. If, on the contrary, a coloured pattern has to be obtained in the etched area after the destruction of the previously applied dye, then the process is called *coloured discharge*. In this case the printing paste must contain a reduction-resistant dye along with the chemicals needed to destroy the previous one. As a result the pre-dyed background is destroyed according to a pattern and the dye, which is resistant to reduction, takes its place.
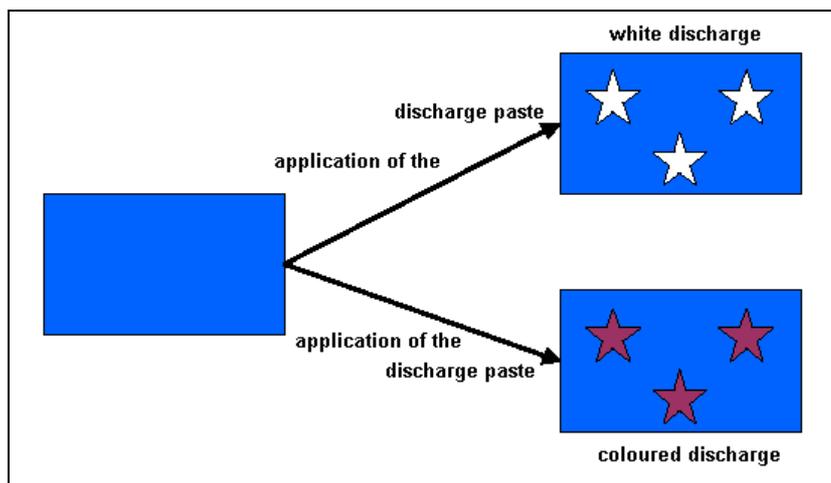
Figure 2.14: Schematic representation of discharge printing

In the case of *resist printing*, a special printing paste (called "resist") is printed onto certain areas of the fabric to prevent dye fixation. In the case of *physical resist* the material is printed with a difficult-to-wet resin that inhibits the penetration of a dye applied in a second stage. On the other hand, with a *chemical resist*, dye fixation is prevented by a chemical reaction. Depending on the way the process is carried out, one can speak of pre-printing, intermediate or over-printing resists. In the first case, which is also the most common, the resist paste is initially printed and dried, then the material is dyed in continuous mode, for example by padding. Over-printing resists can be applied only if the dye, already present in the previously dyed and dried fabric, is still in its unfixed form, as in the case of developing dyes.
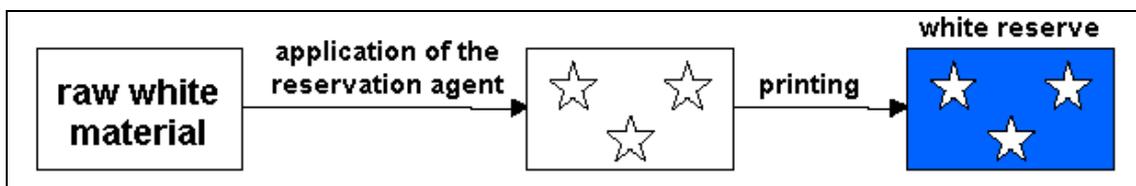
Figure 2.15: Schematic representation of resist printing

The difference between *transfer printing* and the techniques described earlier is that with this technique the surface of the fabric is not directly printed. Instead, the pattern is first created on an intermediate carrier (e.g. paper) using selected disperse dyes and then it is transferred from there to the fabric. The dye is usually fixed by placing the printed paper in contact with the fabric into a thermal pressure system. Under the influence of the heat the dye sublimates and diffuses from the carrier into the fibre of the textile substrate. There is no need for further treatment such as steaming, washing, etc. This technique is applied for polyester, polyamide and some acrylonitrile fibres.

Fixation

After printing, the fabric is dried. Water evaporation leads to an increase in dye concentration and at the same time prevents the colours from smearing when the fabric is transported over the guide rollers. At this stage the dye is not yet fixed.

The aim of the subsequent fixation step is to transport as much as possible of the dye, which is retained by the thickener, into the fibres. This is especially important with dyes, such as vat dyes, for example, that are printed in the insoluble form and are converted into the correspond soluble state only after reaction with the reducing agents during the fixation process.

Fixation is usually carried out with steam. Water vapour condenses on the printed material, swells up the thickener, heats the print and provides the necessary transport medium for the diffusion of the dye. The distribution of the dye between fibre and thickener is an important factor in determining the fixation degree of the dye, which is called "retaining power" of the thickener. The thickener, in fact, is often composed of polysaccharides and therefore competes with cellulose in retaining the dye. This is the main reason why the fixation rate of a given dye is 10 % lower in printing than in dyeing.

After-treatment

The last step of the printing process consists in washing and drying the fabric. When printing with insoluble dyes such as vat dyes this operation also serves as a means to re-convert the dye to the original oxidised state. In this case, after an initial rinsing with cold water, the printed material is treated with hydrogen peroxide. The process is completed with a soap treatment with sodium carbonate at the boiling point.

As already explained, after-treatment is not necessary with pigment printing and transfer printing.

Ancillary operations

At the end of each batch and at each colour change various cleaning operations are carried out:
- the rubber belt, to which the fabric is glued during printing (see description below), is cleaned in continuous mode with water to remove excess adhesive and printing paste. Some machines are equipped with water re-circulation systems
- the printing gears (all systems responsible for feeding and applying the paste to the substrate) are cleaned by first removing as much as possible of the paste residues and then rinsing with water. In some companies the paste residues are directed back to the appropriate printing paste batch containers for re-use
- the remaining paste in the containers, in which the paste is prepared (paste vats), are in general previously cleaned up by means of sucking systems before being washed out with water. The residual printing paste collected in this manner is then disposed of.

2.8.2 Printing technology

A variety of different machines can be used for printing fabrics. The most commonly used are described below.

Flat-screen printing

Flat-screen and rotary-screen printing are both characterised by the fact that the printing paste is transferred to the fabric through openings in specially designed screens. The openings on each screen correspond to a pattern and when the printing paste is forced through by means of a squeegee, the desired pattern is reproduced on the fabric. A separate screen is made for each colour in the pattern.
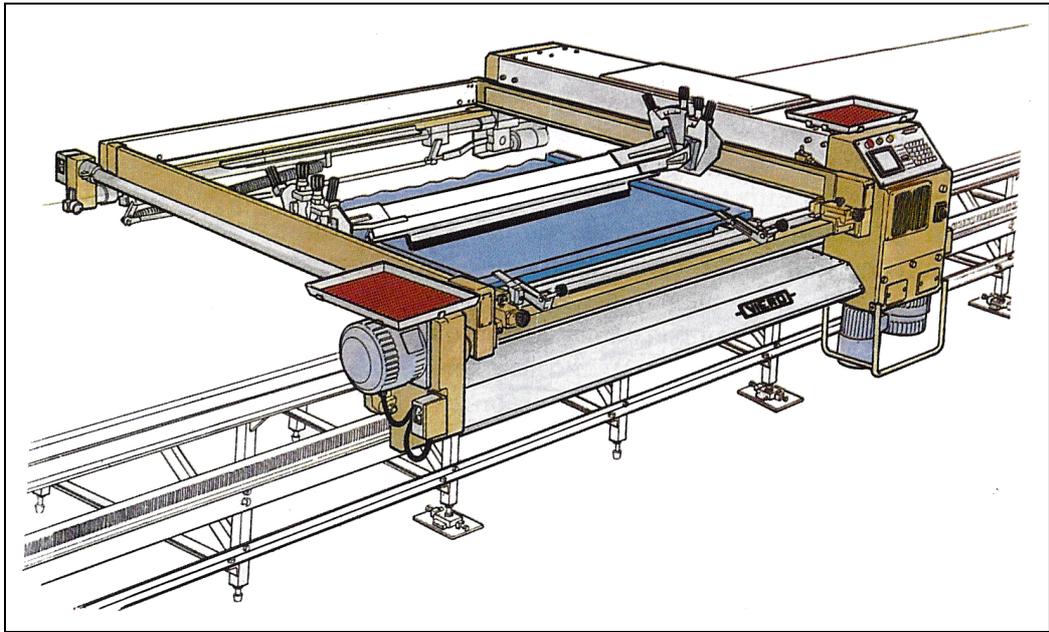
Figure 2.16: Screen printing with automatic squeegee system

Flat-screen printing machines can be manual, semi-automatic or completely automatic. One type of machine, which is still commonly found in printing houses, can be described as follows. The fabric is first glued to a moving endless belt. A stationary screen at the front of the machine, is lowered onto the area that has to be printed and the printing paste is wiped with a squeegee. Afterwards the belt, with the fabric glued on it, is advanced to the pattern-repeat point and the screen is lowered again. The printed fabric moves forward step by step and passes through a dryer. The machine prints only one colour at a time. When the first colour is printed on the whole length of the fabric, the dried fabric is ready for the second cycle and so on until the pattern is completed.
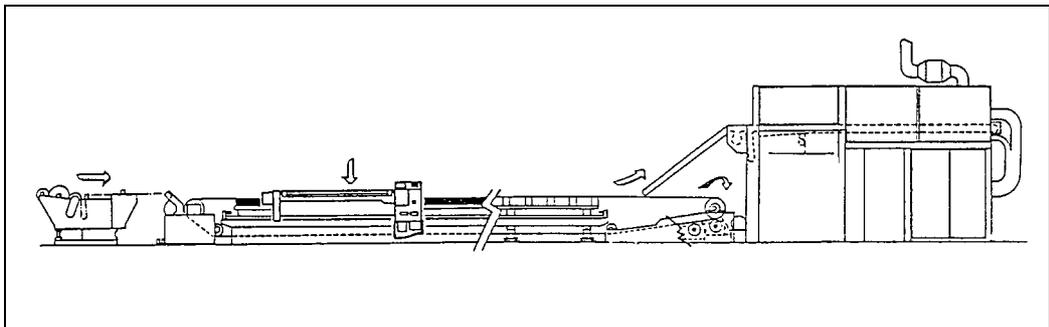
Figure 2.17: Schematic representation of a flat-screen printing machine

In other fully mechanised machines all the colours are printed at the same time. A number of stationary screens (from 8 to 12, but some machines are equipped with up to 24 different screens) is placed along the printing machine. The screens are simultaneously lifted, while the textile, which is glued to a moving endless rubber belt, is advanced to the pattern-repeat point. Then the screens are lowered again and the paste is squeezed through the screens onto the fabric. The printed material moves forward one frame at each application and as it leaves the last frame it is finally dried and it is ready for fixation.
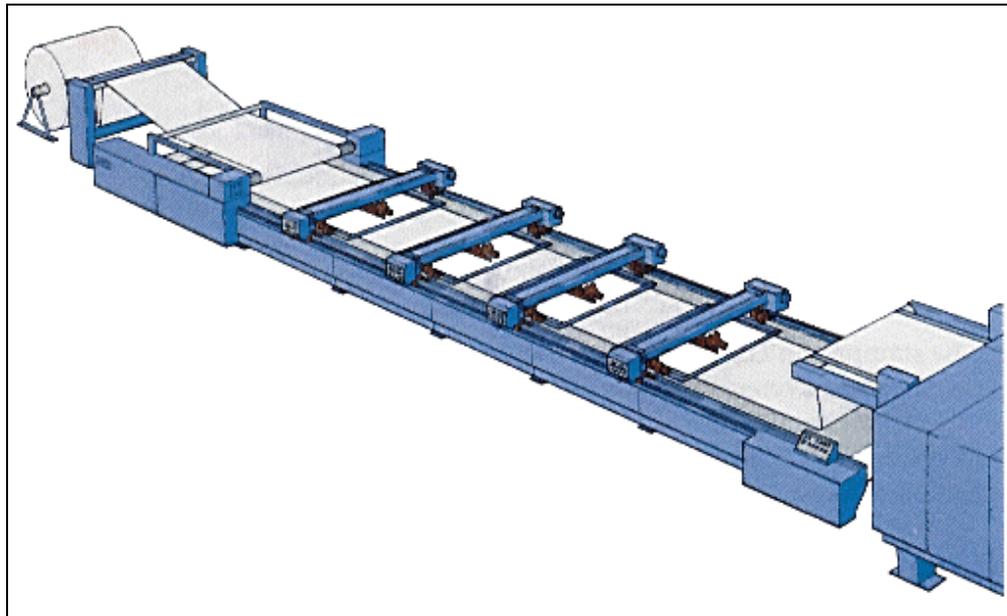
Figure 2.18: Schematic representation of "Mechanised screen printing machine with stationary screens mounted in a frame"

In both machines the endless rubber belt, after pulling away the fabric, is moved downward in continuous mode over a guide roller and washed with water and rotating brushes to remove the printing paste residues and the glue, if necessary. After this, the belt is sent back to the gluing device. In some cases the glue is applied in liquid form by a squeegee, while in other machines the belts are pre-coated with thermoplastic glues. In this case the textile is heated and then it is squeezed by a roller or simply pressed against the rubber-coated belt, causing the glue to soften and instantly adhere.

After printing, the screens and the application system are washed out. It is common practice to squeeze the screens back into the printing paste mixing containers before washing them.

Rotary-screen printing

Rotary-screen printing machines use the same principle described earlier, but instead of flat screens, the colour is transferred to the fabric through lightweight metal foil screens, which are made in the form of cylinder rollers. The fabric moves along in continuous mode under a set of the cylinder screens while at each position the print paste is automatically fed to the inside of the screen from a tank and is then pressed through onto the fabric. A separate cylinder roller is required for each colour in the design.
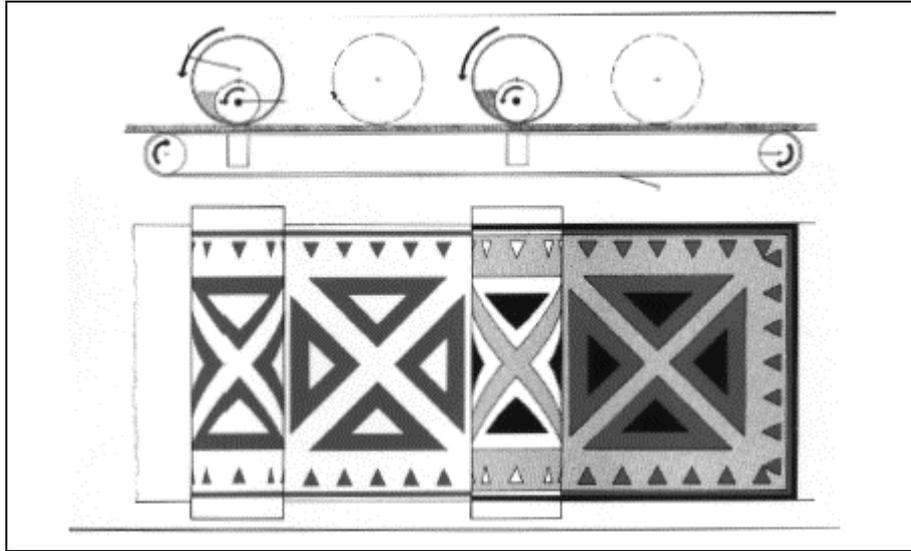
Figure 2.19: Schematic representation of the rotary-screen printing process
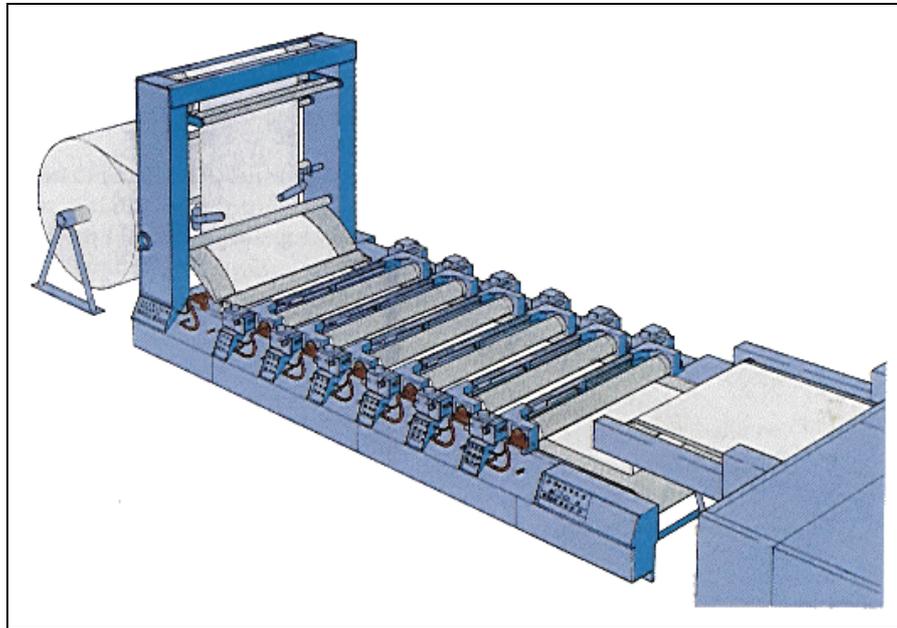
Figure 2.20: Schematic representation of a rotary-screen printing machine

A conventional paste feeding system for rotary-screen printing machines is represented in Figure 2.21. A suction pipe leads from the paste vat to a pump, from where a printing hose leads to the squeegee (dye pipe with squeegee). From here the paste is directed inside the cylinder roller. The fill volume of this so-called printing paste input system is quite high and as a consequence the amount of paste residue that has to be removed at each colour change is also fairly relevant. Various systems have been introduced in order to lower the volume configuration of this equipment, which also reduces the amount of such wastes. Another possibility, which has also already been implemented in some companies, is to recover and re-use these residues for making up new recipes.
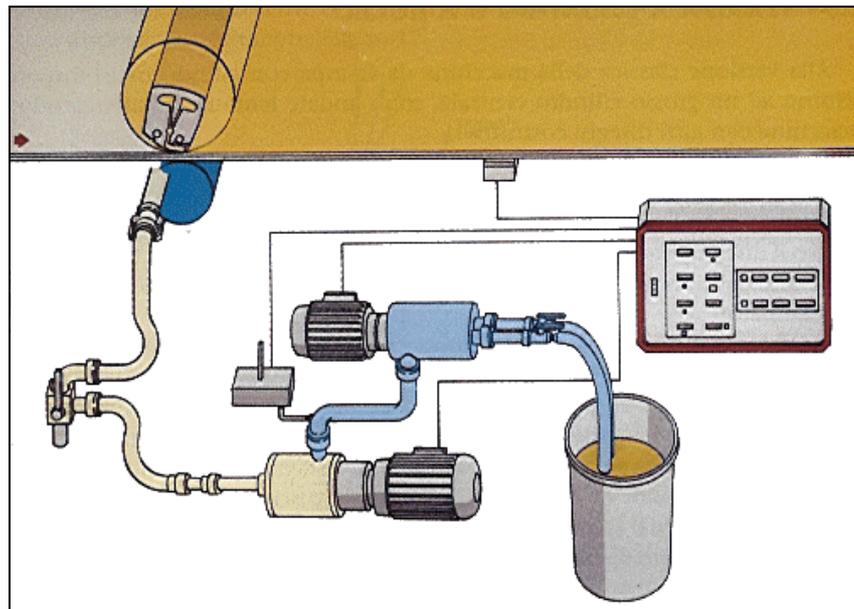
Figure 2.21 Printing-paste feeding system for a rotary-screen printing machine

Rotary-screen printing machines are equipped with both gluing and washing devices analogous to those described earlier for flat-screen printing. The belt is washed in order to remove the residues of paste and adhesive. Not only the belt, but also the screens and the paste input systems (hoses, pipes, pumps, squeegees, etc.) have to be cleaned up at each colour change.

Roller printing

In roller printing the print paste is supplied from reservoirs to rotating copper rollers, which are engraved with the desired design. These rollers contact a main cylinder roller that transports the fabric. By contacting the rollers and the fabric the design is transferred to the fabric. As many as 16 rollers can be available per print machine, each roller imprints one repeat of the design. As the roller spins, a doctor blade in continuous mode scrapes the excess of paste back to the colour trough. At the end of each batch the paste reservoirs are manually emptied into appropriate printing paste batch containers and squeezed out. The belt and the printing gear (roller brushes or doctor blades, squeegees and ladles) are cleaned up with water.
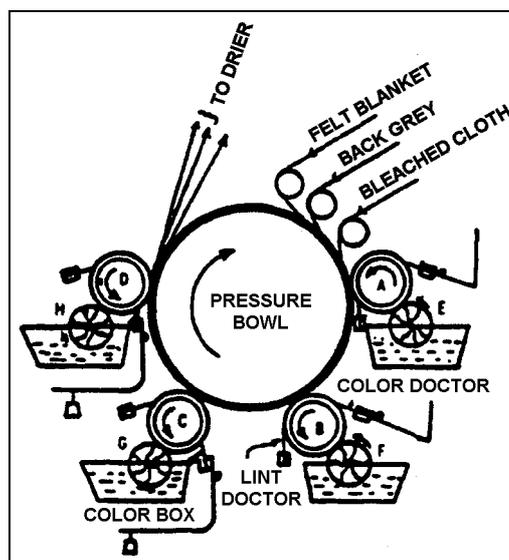
Figure 2.22: Roller printing machine
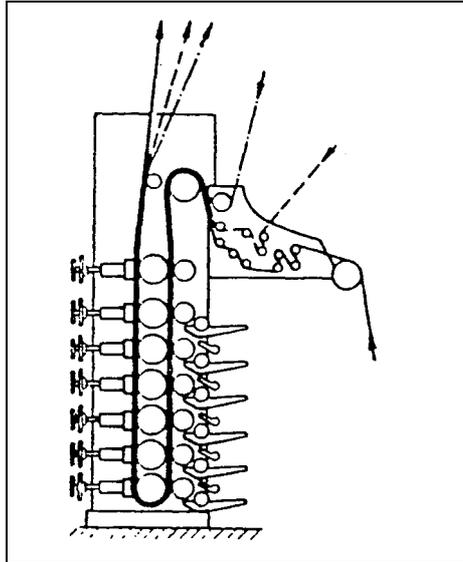
Figure 2.23: More recent example of roller printing machine

Ink-jet printing

Jet printing techniques are employed for printing carpets. Two techniques are now available: the "Millitron" and the "Chromojet" systems. The advantages of these techniques are:
- contact with the substrate is avoided
- a good pile penetration effect is achieved, thanks to the high kinetic energy of the air borne dye
- it is possible to use low viscosity printing pastes that are easy to fix and wash out
- the cost associated with the production of the screens is eliminated, which is a considerable advantage if we think of the size of the screens that are necessary in the case of carpets.

In the *Millitron printing system* the injection of the dye into the substrate is accomplished by switching on and off a dye jet by means of a controlled air stream. The carpet moves along without any parts of the machine being in contact with the face of the substrate. Air streams hold continuously flowing dye jets, deflected into a catcher or drain tray. This dye is drained back to the surge tank, filtered and re-circulated. When a jet is requested to fire, the air jet is momentarily switched off, allowing the correct amount of dye to be injected into the textile substrate. The dye is supplied in continuous mode from the main storage tank to compensate for the amount of dye consumed.
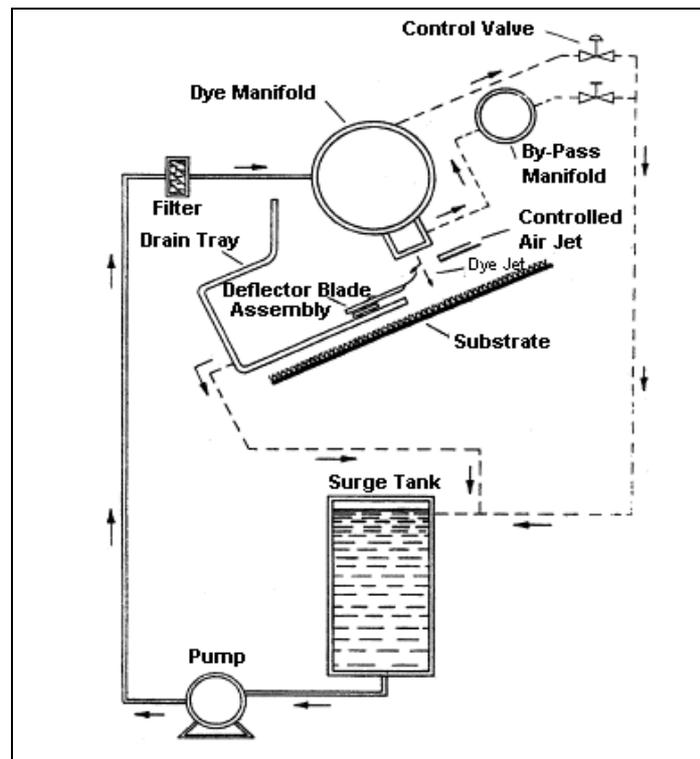
Figure 2.24: Schematic representation of the Millitron system

In the *Chromojet system* the printing dyestuff is sprayed onto the face of the carpet in a given pattern by means of high-speed valves (nozzles). The material is accumulated into a J-box, and is then steamed and brushed. When it reaches the printing table it is stopped. The jets are mounted on a sliding frame that can itself be moved in the direction of the warp while the carpet remains stationary during the printing process. The printing head is equipped with 512 nozzles, which are magnetically controlled and can open and close up to 400 times a second. This system was developed by Messrs Zimmer in Kufstein, Austria.

The TAK system is another printing system that can be found in the carpet industry. With this technique irregular patterns can be produced. The carpet, previously dyed with a ground shade, is provided with coloured spots through dripping. The size and the frequency of the coloured spots can be varied by adjusting the overflow groove placed along the carpet width.
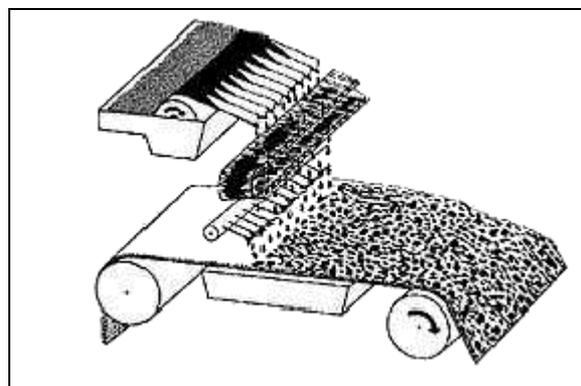
Figure 2.25: Schematic representation of the TAK system

2.8.3 Environmental issues

The table below shows the emissions that can be identified in printing processes.

Operation	Origin of the emission	Type of emission
TO BE COMPLETED?	?	?
?	?	?

Table 2.17: Overview of typical emissions associated with printing processes

Printing paste residues

Printing paste residues are produced for different reasons during the printing process and the amount can be particularly relevant.

Wasted paste results, for example, from incorrect measurements, or more frequently from the common practice of calculating an extra amount of printing paste to prevent a shortfall.

Moreover, at each colour change, printing equipment and containers (dippers, mixers, homogenizers, drums, screens, stirrers, squeegees, etc.) have to be cleaned up. Print pastes adhere to every implement due to their high viscosity and it is common practice to use dry capture systems to remove them before rinsing with water. In this way these residues can at least be disposed of in segregated form, thus minimising water contamination.

Another potential source of printing paste comes from the preparation of sample patterns. Sometimes they are produced on series production machines, which means high specific amounts of residues produced.

Wastewater from wash-off and cleaning operations

Wastewater in printing processes is generated primarily from final washing of the fabric after fixation, cleaning of application systems in the printing machines, cleaning of colour kitchen equipment and cleaning of belts.

Wastewater from cleaning-up operations accounts for a large share of the total pollution load, even more than water from wash-off operations.

Emission loads to water are mainly attributable to dyestuff printing processes because in the case of pigment printing, apart from small amounts coming from cleaning operations, pigments are completely fixed on the fibre without need for washing-off.

Pollutants that are likely to be encountered in wastewater are listed in the table below.

Pollutant	Source	Remarks
Organic dyestuff	Un-fixed dye (the degree of fixation of dyes in printing is in general 10 % lower than when dyeing with the same dye)	The related environmental problems depend on the type of dyestuff concerned (these have already been discussed in Section 9)
Urea	Hydrotropic agent	High levels of nitrogen contribute to eutrophication
Sulphates and sulphites	Reducing agents by-products	
Polysaccharides	Thickeners	High COD, but easily biodegradable
CMC derivatives	Thickeners	Hardly biodegradable and hardly bioeliminable
Polyacrylates	Thickners Binder in pigment printing	Hardly biodegradable and hardly bioeliminable
Glycerin and polyols	Anti-freeze additives in dye formulation Solubilising agents in printing pastes	
m-nitrobenzene sulphonate and its corresponding amino derivative	In discharge printing of vat dyes as oxidising agent In direct printing with reactive dyes inhibits chemical reduction of the dyes	Hardly biodegradable
Polyvinyl alcohol	Blanket adhesive	Hardly biodegradable and hardly bioeliminable
Multiple-substituted aromatic amines	Reductive cleavage of azo dyestuff in discharge printing	Hardly biodegradable and hardly bioeliminable
Mineral oils / aliphatic hydrocarbons	Pigment printing thickeners Pigment printing pastes (half emulsion) still occasionally used	Haliphatic alcohols and hydrocarbons are readily biodegradable Aromatic hydrocarbons are hardly biodegradable and hardly bioeliminable

Table 2.18: Pollutants that are more likely to be encountered in wastewater from printing processes

Volatile organic compounds from drying and fixing

Drying and fixing are another important emission source in printing processes. The following pollutants my be encountered in the exhaust air:
- aliphatic hydrocarbons (C_{10}-C_{20})
- monomers such as acrylates, vinylacetates, styrene, acrylonitrile, acrylamide, butadiene
- alcohols, esters, polyglycols
- formaldehyde
- phosphoric acid esters
- ammonia (from urea decomposition).

2.9 Finishing

2.9.1 Finishing processes

The term "finishing" covers all those treatments that serve to impart to the textile the desired end-use properties. These can include properties relating to visual effect, handle and special characteristics such as waterproofing and non-flammability.

Finishing may involve mechanical/physical and chemical treatments. Moreover, among chemical treatments we can further distinguish between treatments that involve a chemical

reaction of the finishing agent with the fibre and chemical treatments where this is not necessary (e.g. softening treatments).

Some finishing treatments are more typical for certain types of fibre (for example, easy-care finishes for cotton, antistatic treatment for synthetic fibres and mothproofing and anti-felt treatments for wool). Other finishes have more general application (e.g. softening).

Figure 2.26 gives an overview of some common finishing treatments. In this document particular attention is given to chemical finishes because these are the processes with the most significant polluting potential.

Overview finishing treatments. TO BE INSERTED.

Figure 2.26: Overview of most common finishing treatments

In the case of fabric (including carpets in piece form), the finishing treatment usually takes place as a separate operation after dyeing. Only in pigment dyeing it is possible to combine resin finishing and pigment dyeing in the same step by applying the pigment and the film-forming polymer in the dyeing liquor.

In more than 80 % of cases, the finishing liquor, in the form of an aqueous solution/dispersion, is applied by means of padding techniques. The dry fabric is passed through the finishing bath containing all the required ingredients, and is then passed between rollers to squeeze out as much as possible of the treating solution before being dried and finally cured. Washing as final step, tends to be avoided if not absolutely necessary.

In order to reduce the pick-up, other so-called minimum application techniques are gaining importance. These are topical application methods like:
- kiss-roll (or slop-padding) application (the textile is wetted by means of a roller, which is immersed in a trough and which applies a controlled amount of liquor on only one side of the textile)
- spray application
- foam application.

In the case of foulard application the pick-up is approximately 70 %, while with minimum application systems this can be about 30 %. In the minimum application techniques, however, the liquors are more concentrated by a factor of 2 to 3 in order to allow the same amount of active ingredient to be applied.

In the wool yarn carpet sector the functional finishes are applied to the yarn or to the loose fibre either during the dyeing process or in the subsequent rinsing bath.

Apart from particular cases where there are problems of incompatibility between the different auxiliaries, both with padding and long liquor application techniques (batch processes), all the finishing agents necessary to give the textile material the desired properties are applied in a single bath rather than in different steps.

2.9.2 Chemical finishing treatments

2.9.2.1 Easy-care treatments

Easy-care finishings are applied to cellulose-containing fibres to impart characteristics such as easy-to-wash, creasing resistance during wash and wear, no ironing or minimum ironing. These

properties are now required for cellulose fibres to allow them to compete with synthetic fibres such as polyamide and polyester.

Easy-care recipes consist of various ingredients:
- cross-linking agent
- catalyst
- additives (softeners, hand builder most commonly, but also water-repellents, hydrophilizing agents, etc.)
- surfactants as wetting agent.

Information about the typical substances used can be found in Section 8.8.1. In the easy-care process the fabric, after being padded, is dried in open-width in a stenter frame and is finally cured. The most common curing method is the dry cross-linking process, in which the fabric is cured in a dry state in a curing apparatus or on the stenter immediately after drying.

2.9.2.2 Water-repellent treatments (hydrophobic treatments)

Water-repellent treatments are applied to fabrics for which waterproofing properties are required but which also need air and water-vapour permeability.

This may be obtained by:
- precipitation of hydrophobic substances such as paraffin emulsions together with aluminium salts (e.g. wax-based repellents)
- chemical transformation of the surface of the fibre by addition of polymers that form a cross-linked water-repellent film (e.g. silicone repellents, resin-based repellents, fluorochemical repellents).

The characteristics of the substances used as water-repellents are described in Section 8.8.5.

2.9.2.3 Softening treatments

Softeners are used not only in finishing processes, but also in batch dyeing processes, where they are applied in the dyeing baths or in the subsequent washing baths.

The application of softening agents does not involve curing processes. In continuous or semi-continuous processes the impregnated fabric is dried in the stenter frame.

The substances used as softening agents are described in Section 8.8.6.

2.9.2.4 Flame-retardant treatments

Flame-retardant finishing has become more and more important and it is compulsory for some articles. Flame-retardant treatments should protect the fibre from burning, without modifying the handle, the colour or the look of the fabric.

They are generally applied for cotton and synthetic fibres, but in some specific cases, in particular in the carpet sector, they can also be required for wool.

The substances that are usually used as flame-retardant finishing treatments are described in Section 8.8.4.

Two other different approaches exist to producing textile products with flame-retardant properties:
- addition of specific chemicals in the spinning solution during fibre manufacturing
- development of modified fibres with inherent flame-retardant properties.

2.9.2.5 Antistatic treatments

The process consists in treating the fabric with hygroscopic substances (antistatic agents) which increase the electrical conductivity of the fibre, thus avoid the accumulation of electrostatic charge.

These finishing treatments are very common for synthetic fibres, but they are also applied to wool in the carpet sector for floorcoverings that have to be used in static-sensitive environments.

The substances commonly used as antistatic agents are described in Section 8.8.3.

2.9.2.6 Mothproofing treatments

The mothproofing of wool and wool-blends is restricted to the production of textile floorcoverings. Thy are normally applied during the dyeing process.

The biocides used in the mothproofing treatments are described in Section 8.8.2.

2.9.2.7 Bactericidal and fungicidal treatments

These finishes are used mainly for fabrics or apparel for hospitals or for socks/ hosiery (odour suppressants).

The products used are biocides: they are mentioned in Section 8.8.2.

2.9.2.8 Anti-felt treatments

Anti-felt finishing is applied with the purpose of conferring anti-felt characteristics to the wool good. It is required when the good needs to be repetitively washed in a laundry machine without shrinking.

Two treatments, which are also complementary, are applied:
* oxidising treatment (subtractive treatment)
* treatment with resins (additive treatment).

These treatments can be applied at any stage of the process and on all different make-ups. They are most commonly applied on combed tops for specific end-products (e.g. underwear).

Oxidising treatments

In the oxidising treatment the specific chemicals used attack the scales of the cuticles and chemically change the external structure of the fibre.

This treatment has traditionally been carried out using one of the following chlorine-releasing agents:
* sodium hypochlorite
* sodium salt dichloroisocyanurate
* active chlorine (no longer used).

The oldest process is the one using sodium hypochlorite. However, since the development of active chlorine is difficult to control, wool fibre characteristics can be deeply changed, also giving irregular results. Dichloroisocyanurate is more advantageous here because it has the ability to release chlorine gradually, thereby reducing the risk of fibre damage.

The process with dichloroisocyanurate (Basolan process licensed by BASF) consists in impregnating the material in a bath (35˚C) containing the oxidant, sodium sulphate and an auxiliary (surfactant). After 20 - 30 min the material is rinsed, then it is submitted to an anti-chlorine treatment with 2 – 3 % of sodium bisulphite and rinsed again.

All these chlorine-based agents have recently encountered restrictions because they react with components and impurities (soluble or converted into soluble substances) in the wool, to form absorbable organic chlorine compounds (AOX).

Alternative oxidising treatments have therefore been developed. In particular, peroxysulphate, permanganate, enzymes and corona discharge come into consideration. However, the only alternative to chlorine-based agents readily available today is peroxysulphate.

The process with peroxysulphate compounds is quite similar to the chlorine treatment. The material is treated with the oxidising agent in acid liquor at room temperature until the active oxygen has been largely consumed. Sodium sulphite is then added to the same liquor at slightly alkaline pH (reductive after-treatment to remove active chlorine residues and chloramine). The goods are subsequently rinsed. If necessary, they are treated with a polymer (see treatments with resins below).

Treatments with resins (additive processes)

In additive processes, polymers are applied to the surface of the fibre with the aim of covering the scales with a "film". However, this treatment must be regarded as a pseudo felt-free finishing process, as it is not the felting propensity that is reduced, but merely the effect thereof.

The polymer must have a high substantivity for wool. Cationic polymers are the most suitable for this treatment because, after the previous oxidative and reductive pre-treatment, the wool surface becomes anionic.

The polymer may be, in some case, sufficiently effective on its own to make pre-treatment unnecessary. However, the combination of subtractive and additive processes has the greatest technical effect.

Combined treatments: Hercosett process

The oldest combination process is the so called Hercosett process (by C.S.I.R.O), which consists in chlorine pre-treatment followed by application of a polyamide-epichloridrine resin.

Whilst the Hercosett process can be carried out in batch or continuous mode, the latter is predominant nowadays.

The continuous process consists of the following steps (see Figure 2.27):
1. chlorine treatment in acid medium (using chlorine gas or sodium hypochlorite)
2. reduction of chlorine using sulphite in the same bath
3. rinsing
4. neutralisation with sodium carbonate
5. rinsing
6. resin application
7. softener application
8. drying and polymerisation.

Pre-clorivating	Rinsing	Neutral Antichlor	Rinsing	Resin	Softener	Drying
15 - 20 ℃ pH 15 - 20	20 - 30 ℃	30 - 35 ℃ pH 8.5 - 9.5	25 - 30 ℃	35 - 50 ℃ pH 7.4 - 7.8	40 - 45 ℃ pH 7.5 - 8.0	60 - 80 ℃
Sodium-hypochorite Sulphuric Acid Wetting Agent	Water	Sodium-Carbonate Sodium Sulfite	Water	Bicarbonate of Soda Sodium Carbonate	Softener	
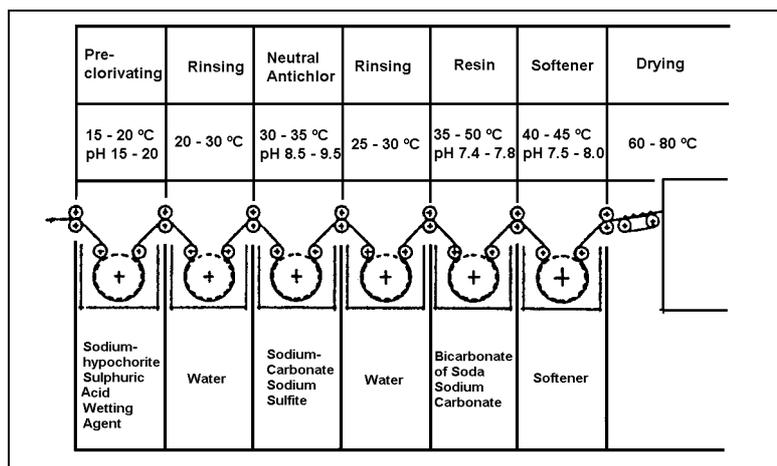
Figure 2.27: Schematic representation of the Hercosett process

The Hercosett process has been widely used for years as anti-felt finishing of wool in different states (loose fibre, combed top, yarn, knitted and woven fabric) due to its low cost and high quality effects. However, the effluent shows high concentrations of COD and AOX. The formation of AOX is attributable not only to the oxidant, but also to the resin. In fact, the typical resin applied in the Hercosett process is a cationic polyamide whose manufacturing process involves the use of epichloridrine, which is another source of the chlorinated hydrocarbons in the effluent.

Alternative resins have been developed, based on polyethers, cationic aminopolysiloxanes, synergic mixtures of polyurethanes and polydimethylsiloxanes, but they all have some limitations concerning their applicability.

New processes have also been developed, but so far the results achieved with the Hercosett process cannot be fully matched by any alternative, which is why it is still the preferred process particularly for treatments such as the anti-felt finishing of combed tops.

2.9.3 Environmental issues

Among textile finishing processes, the chemical ones are those that are more significant from the point of view of the emissions generated. As in dyeing, the emissions are quite different between continuous and discontinuous processes. Therefore this distinction will be used in the discussion of the main environmental issues associated with finishing. Anti-felt treatments represent a peculiar type of finishing both in terms of applied techniques and emissions. The environmental issues related to this process are therefore discussed in Section 2.9.2.8 together with the description of the process.

Environmental issues associated with continuous finishing processes

With some exceptions (e.g. application of phosphor-organic flame-retardant), continuous finishing processes do not require washing operations after curing. This means that the possible emissions of water pollution relevance are restricted to the system losses and to the water used to clean all the equipment. In a conventional foulard, potential system losses at the end of each batch are:
- the residual liquor in the chassis
- the residual liquor in the pipes
- the leftovers in the batch storage container from which the finishing formulation is fed to the chassis.

Normally these losses are in the range of $1 - 5\%$, based on the total amount of liquor consumed; it is also in the finisher's interest not to pour away expensive auxiliaries. However, in some cases, within small commission finishers, losses up to 50 % may be observed. This depends on the application system (e.g. size of foulard chassis) and the size of the lots to be finished. In this respect, system-losses for spraying, foam and slop-padding application techniques are much lower in terms of volume (although more concentrated in terms of active substance).

As a fundamental rule, residues of concentrated liquors should be recycled, if possible, or otherwise disposed of separately in order to avoid contamination of other effluents. However, these liquors are sometimes drained and mixed with other effluents.

Although the volumes involved are quite small when compared with the overall wastewater volume produced by a textile mill, the concentration levels are very high, with active substances contents in the range of $5 - 25\%$ and COD of 10 to 200 gO_2/litre. In the case of commission finishing mills working mainly on short batches, the system losses can make up a considerable amount of the overall COD load. In addition, many substances are difficult to biodegrade or are not bio-degradable at all and sometimes they are also toxic (e.g. biocides).

The pollutants that can be found in the wastewater may vary widely depending on the type of finish applied. The typical pollutants associated with the use of the most common finishing agents are discussed in Section 8.8. In particular, the following substances are worth mentioning because they are water-soluble and hardly biodegradable:
- ethylene urea and melamine derivatives in their not cross-linked form (cross-linking agents in easy-care finishes)
- organo-phosphorous and polybrominated organic compounds (flame retardant agents)
- polysiloxanes and derivatives (softening agents)
- alkyphosphates and alkyletherphosphates (antistatic agents).

In the drying and curing operation air emissions are produced due to the volatility of the active substances themselves as well as that of their constituents (e.g. monomers, oligomers, impurities and decomposition by-products). The emission loads depend on the drying or curing temperature, the quantity of volatile substances in the finishing liquor, the substrate and the potential reagents in the formulation. The range of pollutants is very wide and depends on the active substances present in the formulation and again on the curing and drying parameters. In most cases, however, the emissions produced by the single components of the finishing recipes are additive. As a result, the total amount of organic carbon in the exhaust air can easily be calculated by means of emission factors given for the finishing recipes by the manufacturers.

Another important factor to consider regarding air emissions is that the directly heated (methane, propane, butane) stenters themselves may produce relevant emissions. According to EURATEX, emissions, for example, of formaldehyde up to 300 g/h (2 - 30 mg/m^3) have been observed in some cases, which were attributable to inefficient combustion of the gas in the stenter frame. It is therefore obvious that the environmental benefit obtained with the use of formaldehyde-free finishing recipes is totally lost if the burners in the stenter frames are poorly adjusted and produce high formaldehyde emissions.

The active substances in the most common finishing agents and the possible associated air emissions are discussed in Section 8.8. Moreover a more comprehensive list of pollutants that can be found in the exhaust air from heat treatments in general, is reported in Section (to be inserted).

Environmental issues associated with discontinuous processes

The application of functional finishes in long liquor by means of batch processes is used mainly in yarn finishing and in the wool carpet yarn industry in particular. Since the functional finishes are generally applied either in the dyebaths or in the rinsing baths after dyeing, this operation

does not entail additional water consumption with respect to dyeing. For the resulting water emissions, as with batch dyeing the degree of exhaustion of the active substances is the key factor which influences the emission loads. The maximisation of the exhaustion level is particularly important when biocides are applied in mothproofing finishing. Note here that the finishing agents are dosed based on the weight of the fibre and not on the amount of bath (in g/litre).

The pollutants that may be encountered in wastewater vary depending on the finishing agents applied; Section 8.8 gives more details. The main issues worth mentioning are the application of mothproofing agents (emissions of biocides) and the low level of exhaustion of softeners (emissions of poorly biodegradable substances).

2.10 Washing

2.10.1 Washing with water

Important factors in washing are:
- water characteristics
- choice of soaps and detergents
- mechanical action
- temperature and pH
- rinsing stage.

Washing is normally carried out in hot water (40 – 60 ºC) in the presence of wetting agent and detergent. The detergent emulsifies the mineral oils and disperses the undissolved pigments. The choice of the surfactants may vary also depending on the type of fibre. Mixtures of anionic and non-ionic surfactants are commonly used. An important factor in the selection of a surfactant is its effectiveness in strong alkaline conditions.

Washing always involves a final rinsing step to remove the emulsified impurities.

Washing can be carried out in discontinuous (in rope form or open-width) or in continuous mode, being the latter the most commonly used.

2.10.2 Dry cleaning

Industrial solvent washing is sometimes necessary especially for delicate fabrics. In this case the impurities are carried away by the solvent, which is usually perchloroethylene. In the same step, softening treatments may also be carried out. In this case, water and surfactant-based chemicals are added to the solvent.

Solvent washing may be carried out continuously in full width (for woven or knitted fabric) or discontinuously with yarn or fabrics in rope form (generally for knitted fabric).

Solvent plants have a built-in solvent treatment and recovery system in which the solvent is purified by distillation and re-used for the next washing process. Residual sludge from distillation must be disposed of as hazardous waste in case of high concentration of solvent.

After distillation, the solvent must be cooled before reuse and thus high amounts of cooling water are required. This water is never contaminated by solvent and can therefore be reused. In mills having both solvent and water washing facilities, warm water from the cooling plant may be used for water washing treatments, allowing water and energy savings. In many cases, however, this water is not reused and it is discharged together with the other effluents.

Both closed and open airflow circuits can be used for the removal of solvent from fabric.

In open circuit machines, when the washing cycle is over, large amounts of air are taken from the external environment, warmed up with a steam heat exchanger and introduced into the machine, thus obtaining the evaporation of the organic solvent. This process goes on until the solvent is almost completely eliminated from clean fabrics. Solvent-rich-air is then sent to a centralised activated charcoal filtering system. Filters require regular regeneration to ensure optimal cleaning performance. Most modern filters allow discharge into the atmosphere below 3 – 4 ppm.

In closed circuit machines the volume of air used to carry out the drying process, instead of being filtered and released into the atmosphere, is internally treated. Such treatment consists in recovering the solvent by condensation using a chiller. When the solvent has been removed from air and recovered, solvent-poor-air is heated by a heat exchanger and then sent again inside the machine. Recovered solvent is sent to a centralised plant, where it is distilled and purified. Closed circuit machines do not require an active carbon filter.

Apart from the above mentioned air emissions in open-circuit machines, possible emissions during washing operations may result from machine losses (which can be eliminated or reduced by hermetic sealing of the machinery) and from solvent attached to the dried fabric and ultimately released in the atmosphere. Most modern machines have a built-in control system which makes it impossible to open the machine hatch if the solvent concentration in the machine is greater than values established by national regulations.

Other potential sources of emissions are represented by the solvent contained in the residual sludges and active carbon filters.

Figure 2.28, Figure 2.29 and Figure 2.30 show the solvent and the air circuits in closed and open loop solvent washing machines (the solvent circuit is always closed)
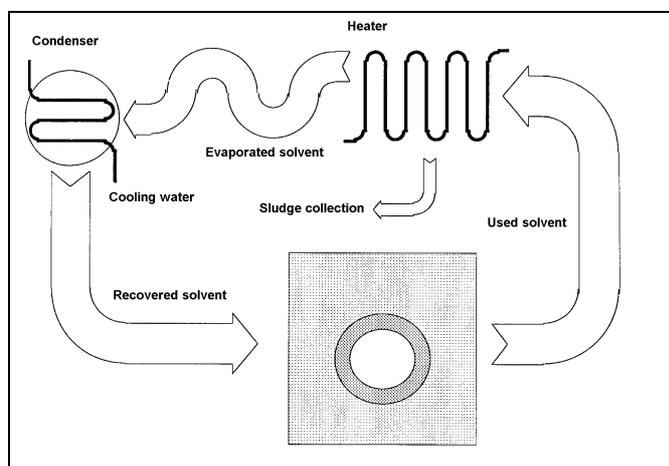
Figure 2.28: Solvent washing: representation of the solvent circuit
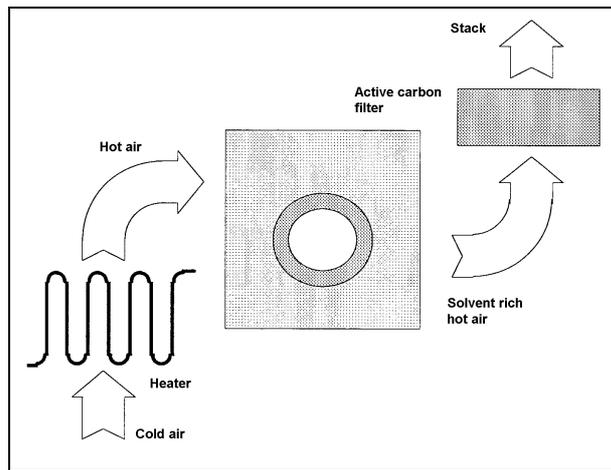
Figure 2.29: Solvent washing: representation of the air circuit in a open-loop washing machine
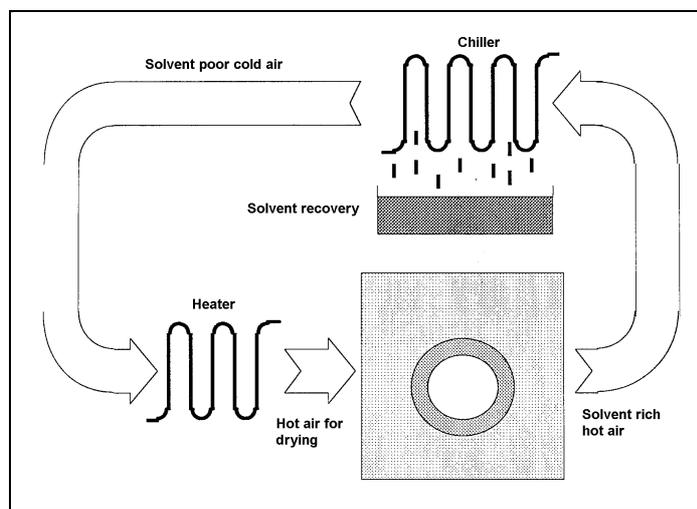
Figure 2.30: Solvent washing: representation of the air circuit in a closed-loop washing machine

2.11 Drying

Drying is necessary to eliminate or reduce the water content of the fibres, yarns and fabrics following wet processes. Drying is a high energy-consuming step.

Drying techniques may be classified as mechanical or thermal. Mechanical processes are used in general to remove the water which is mechanically bound to the fibre. This is aimed at improving the efficiency of the following step. Thermal processes consist, instead, in heating the water and converting it into steam. Heat can be transferred by means of:
* convection
* infrared radiation
* direct contact
* radio-frequency.

In general, drying is never carried out in a single machine. On the contrary, at least two different techniques are adopted.

2.11.1 Loose fibre drying

The water content of the fibre is initially reduced by either centrifugal extraction or by mangling before evaporative drying.

2.11.1.1 Centrifugal extraction

Textile centrifugal extractors (hydroextractors) are essentially a more robust version of the familiar domestic spin dryer, and normally operate on a batch principal, although machines capable of continuous operation may be used in very large installations.

When using conventional batch hydroextractors, fibre is unloaded from the dyeing machine into specially designed fabric bags which allow direct crane loading of the centrifuge. An extraction cycle of 3 - 5 minutes reduces residual moisture content to approximately 1.0 l/kg (dry fibre weight).

2.11.1.2 Mangling

Pneumatically loaded mangles may be used to reduce the water content of dyed loose fibre. Such equipment is often associated with a fibre opening hopper which is designed to break up the dyepack and present the fibre to a continuous dryer as an even mat. Mangling is invariably less efficient than centrifugal extraction.

2.11.1.3 Evaporative drying

All hot air evaporative dryers are of essentially similar design consisting of a number of chambers through which hot air is fan circulated. Consecutive chambers operate at different temperatures, fibre passing from the hottest into progressively cooler chambers. Fibre may be transported on a brattice or conveyer belt or may be carried through the machine on the surface of a series of "suction drums". High efficiency dryers with perforated steel conveyer belts have been developed which even out the air pressure drop across the fibre matt. This design results in more even drying and lower thermal energy requirements.

While the majority of dryers are steam heated, a number of manufactures supply radio frequency dryers. Fibre is conveyed on a perforated polypropylene belt through the radio frequency field and air flow is fan assisted. These machines are reported to be significantly more energy efficient than steam heated chamber dryers, the fibre is not subjected to such high temperatures and the moisture content of the dried material can be controlled within fine limits.

2.11.2 Hanks drying

2.11.2.1 Centrifugal extraction

Drained hanks from the dyeing machine can contain up to 0.75 kg water per kg of dry fibre. Moisture content is normally reduced by centrifugal extraction prior to evaporative drying using equipment identical to that described for loose fibre, above. Yarn is normally unloaded from the dyeing machine into fabric bags held in round carts to facilitate direct crane loading of the centrifuge. Hydroextraction reduces the moisture content to approximately 0.4 litres/kg dry weight.

2.11.2.2 Evaporative drying

Evaporative dryers consist of a number of heated chambers with fan assisted air circulation, through which the hanks pass suspended on hangers or poles or supported on a conveyer. The hank sizes employed in carpet yarn processing require a slow passage through the dryer to ensure an even final moisture content, and a residence time of up to 4 hours is not uncommon. Air temperature is maintained below 120 °C to prevent yellowing. All designs are capable of

continuous operation. Thermal input is normally provided by a steam heated exchanger and many designs incorporate air to air heat exchangers on the dryer exhaust to recover heat.

Less commonly, hanks may be dried by employing a de-humidifying chamber. Moisture is recovered by condensation, using conventional dehumidification equipment. In comparison to evaporative dryers, yarn residence time tends to be longer, but energy consumption is lower.

2.11.3 Yarn packages drying

The moisture content of dyed packages is initially reduced by centrifugal extraction. Specially designed centrifuges, compatible with the design of the dyeing vessel and yarn carriers are employed.

Traditionally packages were oven dried, very long residence times being required to ensure adequate drying of the yarn on the inside of the package. Two methods are currently used, rapid (forced) air drying and radio frequency drying, the latter sometimes being combined with initial vacuum extraction. Forced air dryers generally operate by circulating hot air from the inside of the package to the outside at a temperature of 100 ºC, followed by conditioning, in which remaining residual moisture is redistributed in a stream of air passing from the outside to the inside of the package. Radio frequency dryers operate on the conveyer principal and are perhaps more flexible than the types mentioned above. Lower temperatures can be used and thermal efficiency is said to be high.

2.11.4 Fabric drying

The drying process for fabric usually involves two steps: the first one is aimed at removing water which is mechanically bound to fibres, while the second one is necessary to dry completely the fabric.

2.11.4.1 Hydro-extraction by squeezing

The fabric is squeezed by means of a padding machine through two or three rollers covered with rubber. This process cannot be applied to delicate fabric.

2.11.4.2 Hydro-extraction by suction

The fabric is transported flat over a "suction drum" which is linked to a pump. The external air is sucked through the fabric and thereby removes the excess water. The resulting residual humidity is still about 90 %.

2.11.4.3 Centrifugal hydro-extractor

The design of this machine is similar to the one described earlier for loose fibre and yarn hydro-extraction. With heavy fabric, an horizontal axis machine may be used.

This is the most efficient method for mechanical water removal, but it cannot be applied to delicate fabrics prone to form permanent creases.

2.11.4.4 Stenter

This machine is used for full drying of the fabric. The fabric is conveyed through the machine in open width. A hot current of air is blown across the fabric thereby producing evaporation of the water.

The fabric is sustained and moved by two parallels endless chains. The fabric is hooked undulating and not taut to allow its shrinking during drying.

Various stenter designs exist: horizontal and multi-layer. In the horizontal stenter machine, the fabric enters wet from one side and exits dried from the other. In the multi-layer type it enters and exists from the same side. While in the first one the fabrics moves horizontally without direction changes, in the second it is deviated many times, which makes this equipment unsuitable for delicate fabrics. On the other hand horizontal stenter frames occupy more space and are less efficient (in terms of energy consumption(?)

2.11.4.5 Hot-flue dryer

This machine is composed of a large metallic box in which many rolls deviate the fabric (in full width) so that it runs a long distance (about 250 m) inside the machine. The internal air is heated by means of heat exchangers and ventilated.

2.11.4.6 Contact dryer (heated cylinder)

In this type of machinery the fabric is dried by direct contact with a hot surface. The fabric is longitudinally stretched on the surface of a set of metallic cylinders. The cylinders are heated internally by means of steam or direct flame.

2.11.4.7 Conveyor fabric dryer

The fabric is transported within two blankets through a set of drying modules. Inside each module the fabric is dried by means of a hot air flow.

This equipment is normally used for combined finishing operations on knitted and woven fabrics when, along with drying, a shrinking effect is also required in order to give the fabric a soft hand and good dimensional stability.

2.11.4.8 Airo dryer

This machine can be used for washing, softening and drying operations on woven and knitted fabrics in rope form.

During the drying phase the fabric in rope form is re-circulated in the machine by means of a highly turbulent air flow. Water is thus partly mechanically extracted and partly evaporated.

Thanks to the particular design of this machine it is possible to carry out in the same machine wet treatments such as washing. In this case the bottom of the machine is filled up with water and the required chemicals and the fabric is continuously soaked and squeezed.

The capacity of this machine is determined by the number of channels (from 2 to 4).

2.12 Carpet back-coating

The coating process is an important production step which is applied to improve the stability of textile floor-coverings. Moreover, coating may have a positive influence on properties such as sound-proofing, stepping elasticity and heat insulation.

We can distinguish the following types of coatings:
* pre-coating
* foam coating
* textile backing coating
* heavy coating
* reinforcement
* back finish.

Pre-coating

A common feature of tufted carpets is that they are pre-coated after tufting to permanently anchor the needled pile loops in the carrier layer (Figure 2.31). The pre-coating material used consists of:
- x-SBR latex, which is a dispersion containing a copolymer produced from styrene, butadiene and carbonic acid
- fillers
- water
- additives (e.g. thickeners, anti-foam, foam-stabilisers, etc.).
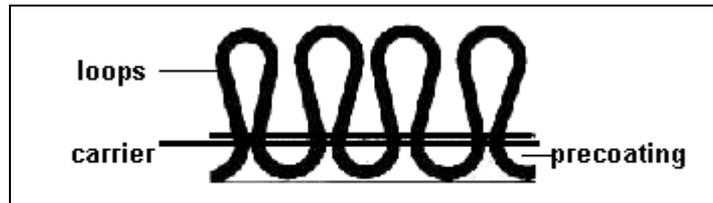
Figure 2.31: Pre-coated tufted carpet

The pre-coating can be applied:
- unfoamed by means of slop-padding (Figure 2.32)
- foamed by means of the doctor-blade technique (Figure 2.33).
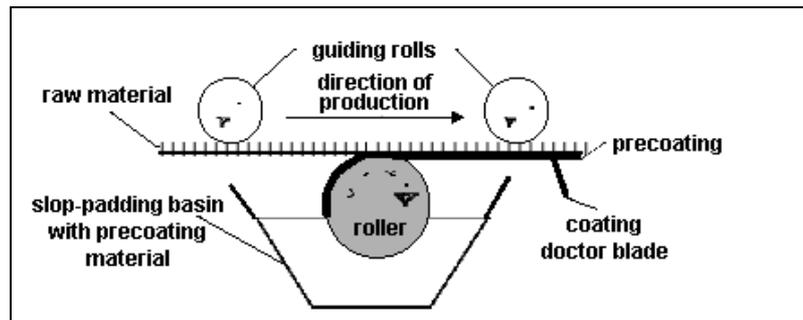
Figure 2.32: Pre-coating application by slop-padding
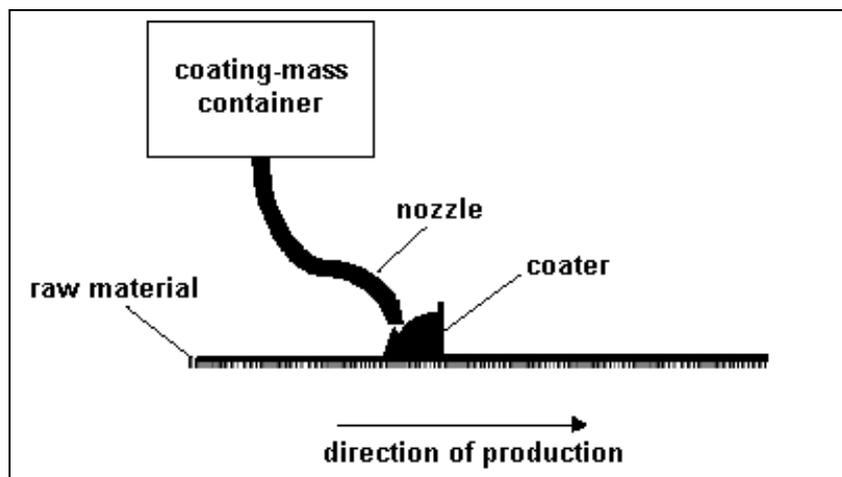
Figure 2.33: Pre-coating application by doctor-blade technique

During the subsequent drying stage, thanks to the formation of hydrogen bonds, the polymer chains are netted into a three-dimensional web and an elastic plastic layer is produced.

SBR foam coating

Foam coating methods consist in the application of a foam layer onto a pre-coated carpet, as the following figure shows.
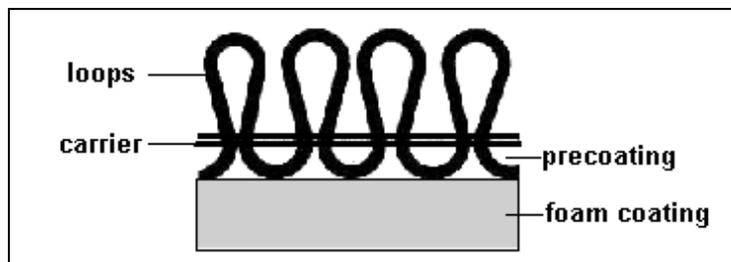
Figure 2.34: Foam-coated tufted carpet

The foam finish is carried out in two steps: foam application and foam solidification through drying. The lattice is foamed with air and then applied by means of a doctor-blade onto the pre-coated carpet.

The SBR foam must be stabilised until it is solidified in the vulcanisation oven. For this stabilisation, two methods are used:
• the non-gel process, which uses surfactants as foam stabilisers
• the gel process, which uses zinc tetra-ammonium acetate (AA gel system) or sodium silicon fluoride (SSF gel system) as gelatinising agents.

The overall process is schematised in Figure 2.35.
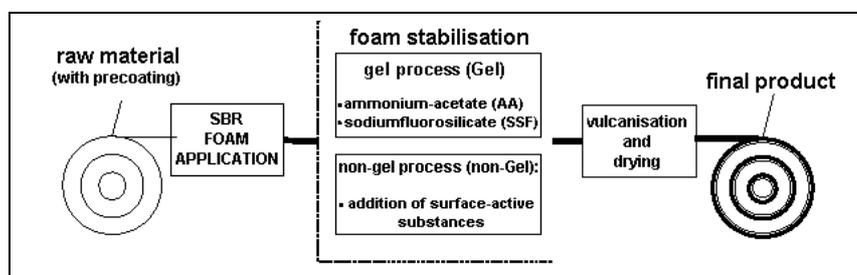
Figure 2.35: Representation of the SBR foam coating process

The foam is composed of:
• the SBR colloidal dispersion
• a paste, which contains a number of active additives
• inactive fillers (mainly chalk, which is added to the ready-compounded paste)
• water
• thickeners (e.g. Polyvinyl alcohol, methyl cellulose, polyacrylates)
• colorants and pigments
• anti-oxidants and ozone stabilisers.

Some of the active components of the paste are responsible for the environmental impact of this coating method. In order to identify better the emission sources they can be divided as follows:

Polymerisation additives:

	Remarks
- Foam stabilisers	
- Cross-linkers	Usually sulphur, but also peroxides
- Vulcanisation accelerators	- Mercaptobenzo thiazoles - Dithiocarbamates (e.g zinc dimethyl dithiocarbamate)
- Activators	Usually combination of ZnO and stearic acid

Processing additives:

	Remarks
- Foaming agents and stabilisers	Surfactants
- Gelatinising agents	e.g. zinc tetra-ammonium acetate (AA gel system) or sodium silicon fluoride (SSF gel system)
- Hydrophobic substances in order to improve the foam surface and the water-repellent properties	Paraffin dispersions and silicon emulsions
- Complexing agents, to chelate metal ions (they behave as catalysts for ageing the foam layer)	e.g. EDTA, DTPA, polyphosphates
- Antioxidants	
- Thickeners	Organic polymers based on polyacrylates and cellulose (e.g.CMC)

Functional additives:

- UV stabilisers
- antistatic agents.

PU foam coating

Polyurethane is another method for foam coating. The ICI polyurethane coating process is the most commonly applied. The carpet is prepared by steaming and then reaches the spray chamber where the components of the polyurethane (diisocyanate and an alcohol) are sprayed. The CO_2 produced during the chemical reaction is embedded into the foam. The coating is reinforced in an infrared heating field and in a subsequent reaction field. The process is schematically represented in the following diagram.
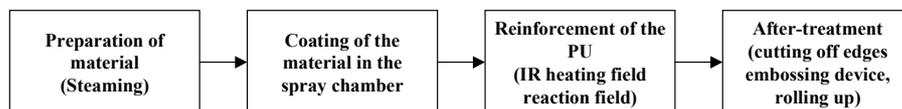
Figure 2.36: PU foam coating

Textile back coating

Textile backing consists in the application of a textile fabric onto the pre-coated carpet. The connection between the carpet and the textile fabric is obtained through the application of a layer of:
- laminating glue
- melting glue.
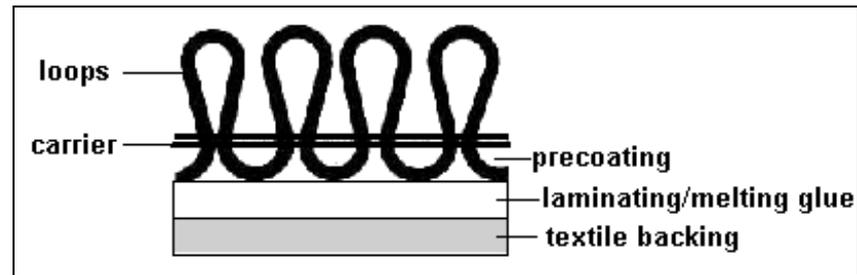
Figure 2.37: Textile backing

Laminating glue

In this process an x-SBR latex is applied to the carpet by slop-padding. After the application of the textile fabric, the final reinforcement of the latex is carried out by means of heat treatment (Figure 2.38). The latex composition is similar to that used for pre-coating, with a higher share of polymer dispersion in order to allow a higher adhesive power.
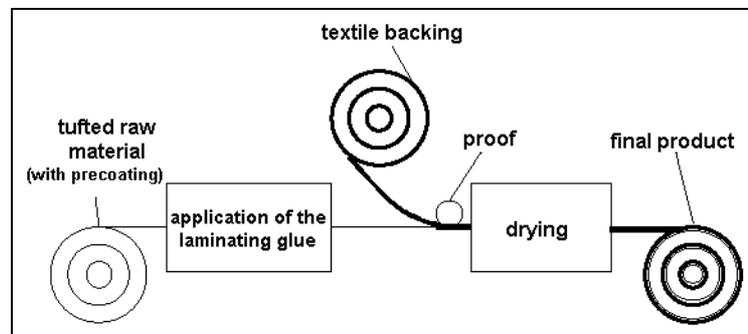
Figure 2.38: Textile backing by means of the laminating glue process

Melting glue

This system uses thermoplastic polymers (mainly polyethylene) which are meltable by means of heat. In powder lamination, polyethylene powder is evenly sprinkled onto the the back of the carpet. Subsequently the polymer is melted in an infrared field. In the next stage the fabric is pressed into the melting glue. Through subsequent cooling off, the melting glue becomes permanently connected between the textile fabric and the bottom side of the carpet. The process is represented in Figure 2.39.
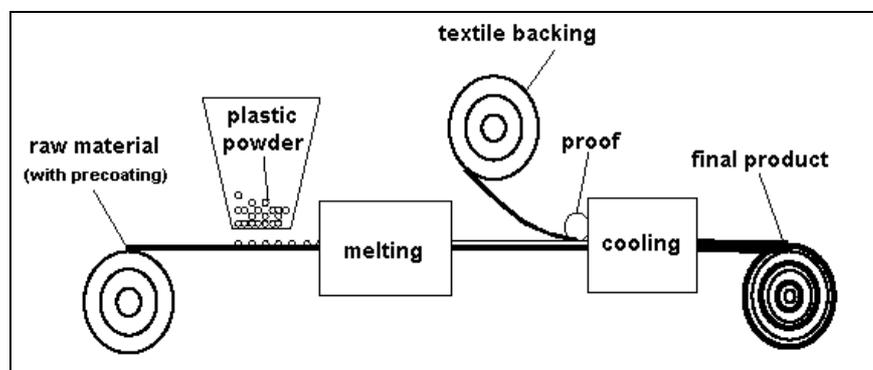
Figure 2.39: Textile backing by means of the powder lamination (melting glue)

Another textile backing process by means of melting glue is the so called AdBac process. In this case the carpet is constructed using a primary cloth (carrier layer) with low melting point additives. In the next stage the secondary cloth (also with a low melting point) is brought into contact with the back of the carpet before this enters the heating zone. The higher temperature melts the cloths, which are then forced together by nip rolls at the exit of the heating zone. The carpet is then cooled off. A scheme of a carpet produced with the AdBac process is reported in Figure 2.40.
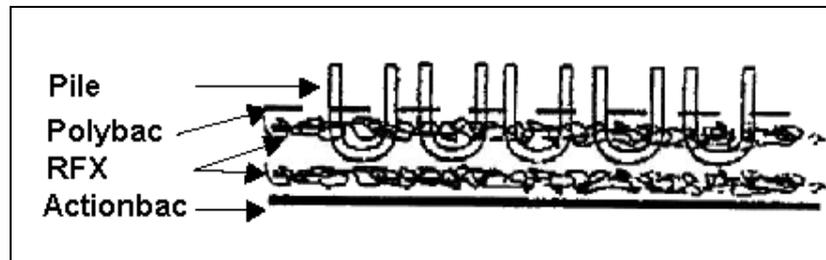
Figure 2.40: Carpet manufactured with the AdBac process

Heavy coating

Heavy coating is mainly used for the coating of self-lying (SL) tiles. The coating process consists in the application of the coating material by means of slop-padding or doctor blade and subsequent reinforcement. In most cases the coating material is applied into layers (two-coat technique). After the first layer, which may also serve as a pre-coating layer, a glass-fibre web may be added. The second coating application follows. The following coating materials are used:
- APO (abbreviation for "atactical polyolefin")
- bitumen (enriched with inorganic and organic additives)
- PVC (polyvinylchloride)
- EVA (ethylen vinyl acetate).

The process principle is schematised in Figure 2.41.
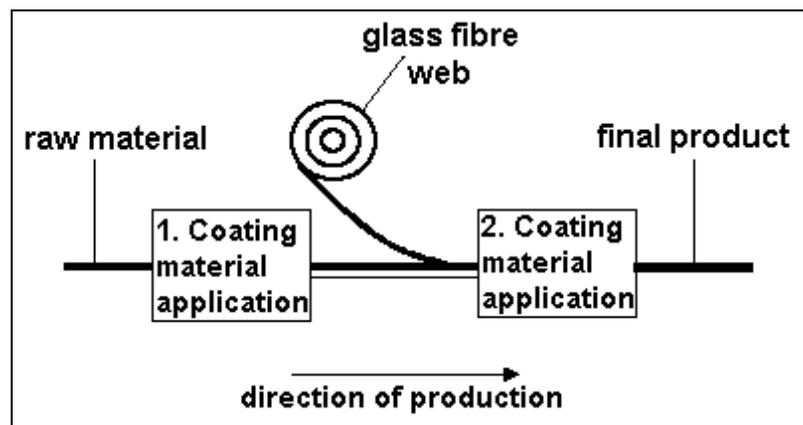
Figure 2.41: Representation of the heavy coating process

2.13   Textiles industry categories

Up to this point, this chapter has described the fundamental unit processes in the textiles industry that are within the scope of this document. The information given there has been

structured by fibre type, which has made it possible to explain those issues that are determined by the physico-chemical behaviour of the fibre. From a practical point of view, however, a subdivision of the textile industry activities into sub-sectors based on the type of the fibre, offers little practical aid.

In practice, there are established patterns of activity, with finishing mills tending to concentrate on particular kinds of make-up or end-product (e.g. yarn, woven fabric, carpet, etc.), because this is defined by the specialist machinery used. This degree of specialisation doesn't apply to the same extent to the fibre. Although in the past the predominance of natural fibres made possible the identification of separate sectors based on the fibre (mainly cotton and wool), nowadays the proliferation of man-made fibres means that finishers almost always process a wide variety of fibres, even if one type is dominant within a particular mill (e.g. wool, cotton, etc.).

As an aid to the application of this BREF, therefore, the rest of this chapter gives practical information on the main categories of mills that are actually found in this sector.

The typical mill categories listed below also prepare the ground for the presentation of the emission and consumption levels in Chapter 3.

- Wool scouring mills

- Mills finishing yarn and/or floc   -   mainly CV, PES, PAC and/or CO floc material
                                       -    mainly WO floc material
                                       -    mainly WO yarn
                                       -    mainly CO yarn
                                       -    mainly PES yarn
                                       -    mainly WO, PAC and/or CV yarn

- Mills finishing knitted fabric   -   mainly CO
                                       -    mainly CO with a relevant proportion of printing
                                       -    mainly synthetic fibres
                                       -    mainly WO

- Mills finishing woven fabric   -   mainly CO and/or CV
                                       -    mainly CO and/or CV with a relevant proportion of printing
                                       -    mainly WO (worsted)
                                       -    mainly WO (woollen)
                                       -    mainly PA

- Carpet industry   -   wool and wool-blend carpet yarn/ loose fibre dyehouses
                                       -    integrated carpet manufacturing companies

The carpet industry is kept in a separate group from the other finishing mills. This is slightly inconsistent with the categorisation system adopted (based on the processing operations), in which a category of mills finishing yarn consisting mainly of wool is already identified in the list under the heading "Mills finishing yarn". However, the peculiarity of carpet as end-product involves such specific requirements that companies tend to specialise in the processing of products that are suitable only for the carpet sector.

2.13.1 Wool Scouring Mills

Wool processed in Europe is mostly imported. Most of the wool produced in Europe is in fact coarse wool which is suitable for the manufacturing of carpets, but not for use in apparel. Merino wool (fine wool) is therefore imported mainly form Australia, New Zealand, South Africa, Argentina, Uruguay and Brazil.

The organisation of the scouring sector reflects the two main systems used to process wool: the woollen and the worsted system. Scourers tend to specialise for one or the other. Woollen system scourers normally only scour the wool (sometimes they may blend it before dispatching it to the customer). Worsted system scourers usually scour, card and comb the wool thus producing a sliver of parallel fibres which is called top. Due to this difference, worsted system scourers are usually referred to in English as combers.

Within Europe, significant quantities of wool are also obtained from skins of slaughtered animals by a process called fellmongering in which the skins are treated chemically or biochemically to loosen the wool roots so that the wool can readily be separated from skins.

The scouring process is the only wet process carried out in scouring mills and it has already been described in detail in Section 2.3.1.1.

Most of the scourers have an on-site wastewater treatment plant to treat their effluent. The majority discharges the treated effluent to sewer, but there are several scourers who discharge directly to surface waters. Those in the latter category should necessarily treat their effluent to higher standards. Of the scourers who discharge to sewer, some treat only the heavily contaminated effluent from the scouring section and discharge the rinse water flowdown without treatment; others mix the two effluent streams before treatment.

Broadly speaking, there are four main types of effluent treatment process used by scourers:
- coagulation/flocculation;
- evaporation;
- membrane filtration;
- anaerobic/aerobic biological treatment.

Some scourers use combinations of the above processes. Neither the heavily contaminated effluent from the scouring section, nor the mixed scouring and rinsing effluents can be treated directly by aerobic digestion because their COD values are too high. It is normal to subject these effluent streams to anaerobic biological treatment or coagulation/flocculation before aerobic biological treatment.

All of the effluent treatment processes employed by scourers produce a sludge or a concentrate which has to be disposed of safely. Sludge disposal routes used include landfill, composting, incineration, pyrolysis/gasification, and brick manufacture.

2.13.2 Mills finishing yarn and/or floc

Mills finishing floc mainly consisting of CV, PES, PAC and/or CO

?

Mills finishing floc mainly consisting of WO

?

Mills finishing yarn mainly consisting of WO

?

Mills finishing yarn mainly consisting of CO

?

Mills finishing yarn mainly consisting of PES

?

Mills finishing yarn mainly consisting of WO, PAC and/or CV

?

2.13.3 Mills finishing knitted fabric

Mills finishing knitted fabric mainly consisting of CO

?

Mills finishing knitted fabric mainly consisting of CO with a relevant proportion of printing

?

Mills finishing knitted fabric mainly consisting of synthetic fibres

?

Mills finishing knitted fabric mainly consisting of WO

?

2.13.4 Mills finishing woven fabric

Mills finishing woven fabric mainly consisting of CO and/or CV

?

Mills finishing woven fabric mainly consisting of CO and/or CV with a relevant proportion of printing

?

Mills finishing woven fabric mainly consisting of WO (worsted)

?

Mills finishing woven fabric mainly consisting of WO (woollen)

?

Mills finishing woven fabric mainly consisting of PA

?

2.13.5 The Carpet industry

Diagram: overview of the wet processes involved in carpet finishing industry. DATA NEEDED TO BE INSERTED.

2.13.5.1 Wool and wool-blend carpet yarn dye-house

The production of spun dyed yarn can be regarded as a specific sector within the carpet manufacturing industry. Mills can be identified as dyehouses processing mainly wool and wool-blend fibres. Different treatments are carried out in order to convert white loose fibre into dyed carpet yarn. Wet processes essentially consist of dyeing and other ancillary operations carried out either in loose fibre or yarn form. Dry processes consist, in turn, in blending, carding, spinning, etc. These processes will not be considered here, since they have already been described in previous sections. Depending on when colouration takes place raw fibre flows through some or all of these processes. As can be seen from Figure 2.42, three basic process sequences are possible.
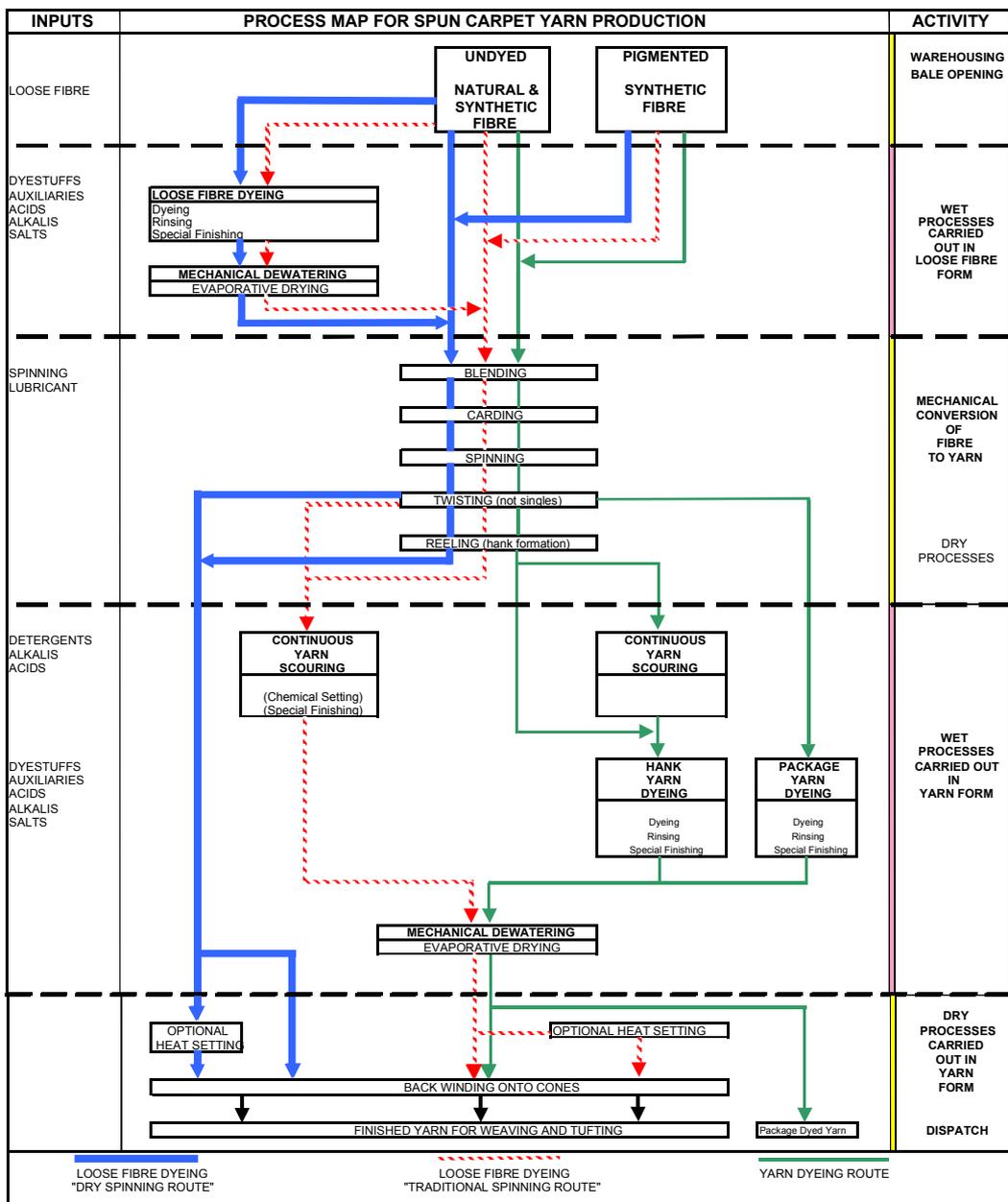
Figure 2.42: General process flow diagram for wool and wool-blend carpet yarn production

The **dry spinning route**, so called because there is no wet processing after yarn formation, begins with colouration at the loose fibre stage. This is followed by yarn formation and finally twist setting. This process sequence is of relatively recent origin and requires the consistent use of wool with a low lanolin content and specialised spinning lubricants which can be left on the yarn without causing subsequent soiling of the carpet. The process is particularly useful in the production of yarn for large volume plain shade carpets and for effect yarns, obtained by blending together fibre dyed to different shades. While this production sequence is the most economical in terms of resource consumption, the selection of clean raw materials and the ongoing maintenance of the mill in a clean condition are essential.

The **traditional loose stock dyeing route** was originally used to produce large batches of yarn to the same shade for plain carpets. Loose fibre is first dyed and then converted to yarn using what is still sometimes referred to as the "oil spinning" process; this terminology arose from the practice of using spinning lubricants based on dispersions of mineral oil. Even small traces of residual mineral oil would lead to a marked propensity for the carpet to soil in service, and so yarns prepared by this route were thoroughly cleaned by scouring (washing) in hank form (see below). While the use of mineral oil-based lubricants has been largely replaced with water-soluble synthetic products, the practice of scouring the yarn is still judged to be essential by many processors in order to avoid potential claims arising from soiling. Unlike the dry spinning process, this route allows greater flexibility in the purchase of raw materials, in that wool with a higher lanolin content can be used.

In the **Yarn Dyeing Route,** clean fibre is first converted into yarn before dyeing. This process is particularly suitable for the production of the small coloured lots required for patterned carpet weaving or the bespoke trade, where white yarn can be held in stock and dyed as required to fill orders. The process is, however, by no means restricted to small batches, and dyeing machines with capacities of up to four tonnes are used to produce plain shades for both tufting and weaving.

In the case of integrated yarn manufacturers, it is common to find two or more of these process streams operating side by side and sharing common wet processing equipment. Since the dyeing and finishing techniques used apply equally to all three sequences, they are discussed in the following sections without further considering the different routes mentioned. Variants are described where they occur, and the relevance of any dry process segments is discussed where they have a significant impact on environmental performance or emissions.

2.13.5.1.1 Carpet loose fibre dye-house

Fibre is conventionally dyed in loose form (loose stock) when a large quantity of yarn is required to be of precisely the same shade, for example in a large solid shade (plain coloured) carpet where subtle variations in colour would be visible in service. Single colour batches may be made up of a number of individual dyeings, the dyer adjusting the dye addition to each dyeing in order to achieve the desired final shade of the yarn. Thorough mixing of the individual dyeings in a batch is achieved in a specific mechanical blending operation and during carding. Loose fibre dyeing, therefore, need not to be as level as, for example, yarn dyeing, where there is no possibility of levelling the colour by further mechanical processing.

Dyed loose fibre is also used to achieve multicoloured effects in some yarns. In this process fibre dyed to different shades is blended together to produce a large range of designs, such as the "heather" styles in fashion at the present time. Such blends may contain dyed and undyed natural fibre and undyed and pigmented synthetic fibre.

Where the final yarn will contain a blend of wool and synthetic fibres (typically 80 % wool and 20 % polyamide) the required weights of the two components are normally dyed separately to optimise application conditions and dyestuff selection for each fibre type.

Loose-fibre dyeing processes

Scoured wool and new synthetic fibre are presented to the dyehouse in a "clean" state and usually require no further treatment to remove contaminants before dyeing. If purchased from outside sources, fibrous raw materials normally arrive on site in the press-packed bales used universally by the textile industry to transport raw fibre.

Within an integrated manufacturing site, for example, one with its own wool scouring facilities, loose fibre may be transferred between the scouring department and blending department or loose fibre dyehouse by pneumatic conveyer or as individual low-density bales from intermediate warehousing.

Special opening machinery is not usually necessary when dealing with previously scoured wool and with new synthetic fibre. Bales are, therefore, often simply weighed and then brought into the dyehouse, opened at the side of the dyeing machine and the required quantity of (dry) fibre loaded manually into the dyeing vessel. Alternatively, fibre may be wet prior to packing in order to facilitate more even machine loading.

Various types of machines are used for dyeing wool and synthetic fibres in loose form. These include conical pan, pear shaped and radial flow machines (see Section 10). Loose fibre is typically packed into these machines manually.

Dyestuffs are dissolved in hot water before being added to the circulating bath. Typical dyestuffs and chemicals for wool and wool-blends are employed.

In the majority of cases all chemical and dyestuff additions are made manually to the open dyeing machine. Less frequently or if "pressure" dyeing machinery is being utilised (for synthetic fibres, because wool is normally dyed at atmospheric pressure), pre-dissolved chemicals and dye are introduced to the circulating dyebath from special addition tanks.

The dyebath is typically run for 10 - 15 minutes to ensure even penetration of the liquor through the fibre pack before commencing the heating cycle, raising the temperature of the dyeliquor to 98 ºC at a rate of $1 - 2$ ºC per minute. On reaching top temperature, dyeing may continue for up to 60 minutes, during which time the dyebath pH may be checked and adjusted by adding further acid to achieve maximum dye uptake. Progress of the dyeing is normally judged by eye and fibre samples are then removed for comparison with a standard.

A dyeing which is judged to be on shade will be terminated and the machine drained. A dyeing which is not of the required colour may have further additions of one or more dyestuffs, the dyebath being returned to the boil after each addition. Because of the blending operation which follows loose fibre dyeing, it is uncommon for there to be more than one shade addition unless the machine load is the only fibre in a batch.

Dyeing is followed by rinsing with cold water, to remove any surface-bound dyestuff and to cool the dyepack before manual unloading. The machine may be filled with cold water and then run for 10 - 15 minutes before draining. The use of "flood rinsing" in which the dyebath is allowed to refill and then run continuously to drain during the rinsing operation is now much less common due to increases in water charges and effluent disposal costs.

Liquor from both the dyeing and rinsing process may be recycled for further use. In this case the machine must be fitted with an external holding tank. The dyebath may be recycled if a number of dyeings of the same shade are being performed to make up a bigger dyelot. In this case the dyebath is pumped to the reserve tank and dropped back to the dyeing vessel when required for the next dyeing. There are, however, severe limitations to the use of this process because dye uptake is temperature-dependent and starting the dyeing at too high a temperature can result in an unacceptable rate of strike and unlevel application. The selection of dyestuffs and dyeing

conditions which promote maximum uptake of dye are required for the successful operation of this process.

In such circumstances it is more usual to recycle the rinse liquor, as the temperature of this liquor is lower and more compatible with dyeing start temperatures. Depending on the design of the machine a reserve tank may not be required for the operation of this process, as the fibre carrier can often be removed with the dyeing vessel full. Both these alternatives conserve water, and to a lesser degree, thermal energy.

Application of functional finishes

A number of functional finishes may be applied to the loose fibre, either during the dyeing process itself or by application from an additional bath following dyeing/rinsing. This is particularly relevant in the "dry spinning" route where there will be no further wet processing after yarn formation. Finishes applied at the loose fibre stage include insect-resist treatments, anti-static treatments, anti-soiling treatments and treatments to counteract yarn/carpet colour change due to light exposure in service.

For expediency these finishes are combined with dyeing whenever possible, after-treatments only being used when the chemistry of the two finishes is incompatible or if they require widely differing conditions of temperature and pH. Co-application with the dyes is simply accomplished by adding the product to the dyebath, usually with the dyeing auxiliaries.

After-treatments may require a fresh bath of clean water, or alternatively the rinse bath may be clean enough for reuse.

Specific techniques have been devised to minimise the concentration of mothproofing agents present in the spent liquors from loose fibre dyeing. The formulated commercial product is added at the beginning of the dyeing cycle and dyeing carried out as normal. At the end of the dyeing cycle the pH of the dyebath is lowered with the addition of formic acid and boiling is continued for a further 20 - 30 minutes. These strongly acidic conditions promote uptake of any active ingredient not adsorbed by the wool fibre under normal dyeing conditions and residual concentration can be reduced by up to 98 %.

Rinsing the fibre at moderate temperatures is known to cause desorption of mothproofer bound on or close to the surface of the wool fibre. Active ingredient concentrations in the spent rinse bath may consequently be significantly higher than those present in the dyebath. Techniques to minimise the impact of rinse desorption have been developed, in which the rinse bath is recycled, forming the next dyebath, thus eliminating all residues from the rinse liquor and reducing overall water consumption by 50 %.

Fibre in a drained carrier will contain up to 2 litres/kg of residual water (dry fibre weight). This is initially reduced by either centrifugal extraction or by mangling before evaporative drying in a hot air dryer.

2.13.5.1.2 Carpet yarn dye-house

On integrated sites the spun un-dyed yarn may be held in a bulk store as either hanks, wound onto cones or wound onto the special centres compatible with package dyeing equipment. Batches of suitable size are drawn from this material to fill individual orders. Commission yarn processors generally receive hanks baled in conventional wool bales.

In hank-based processes the bales are normally brought into the dyehouse and opened at the side of the scouring or dyeing machine ready for manual loading

Yarn scouring

Scouring is generally carried out as a semi-continuous process in which batches of yarn are transported through a series of aqueous baths containing detergent and alkali or rinse water. As shown in
Figure 2.42, scouring can be carried out both on dyed and un-dyed yarn. To prevent cross contamination with dyestuffs, integrated yarn manufacturers may operate two scouring machines, one being reserved for scouring white yarn prior to dyeing and the second for the scouring of coloured yarn.

Yarn may be scoured using either hank scouring or package to package (sometimes referred to as single end) processing machinery.

In *tape scouring machines* (Figure 2.43) hanks are transported through the machine trapped between an upper and lower set of nylon tapes which run in an endless belt through each bowl and mangle set, guided by intermediate rollers in the bottom of each bowl. Bowl working volume is typically between 1200 and 1800 litres. Throughput capacity typically ranges from 500 to 1500 kg/hour. Residence time in each bowl varies between 20 and 45 seconds. Heating is provided by either closed coils in the base of the machine or live steam injection.

A

C

B   B   B

Bowl 1   Bowl 2   Bowl 3   Bowl 4
Scouring   Scouring   Rinse   Rinse

Machine may consist of 3, 4 or 5 bowls and may include an optional low volume final bowl for Insect Resist application

A: Manual hank loading table – hanks trapped between upper and lower tapes
B: Pneumatic squeeze press between bowls
C: Manual hank unloading table – hanks released from tapes
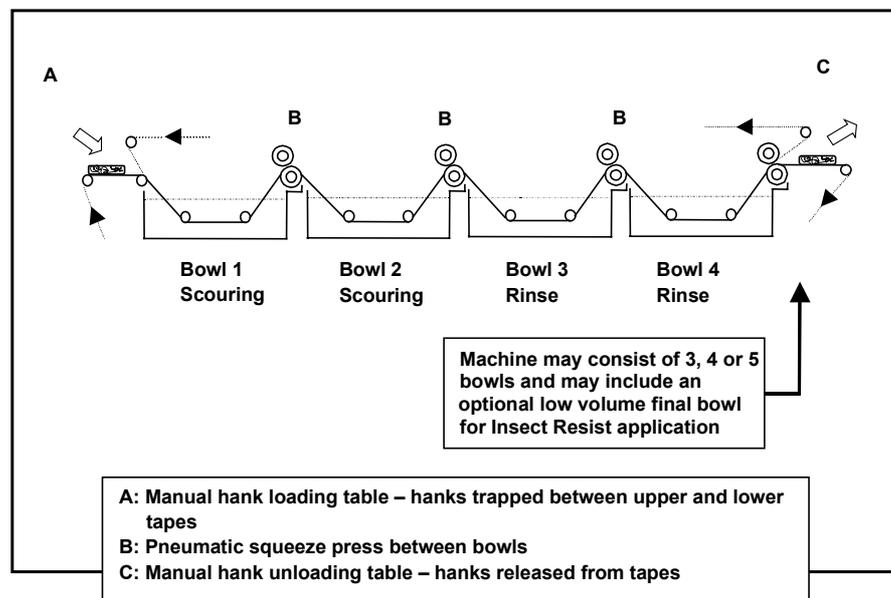
Figure 2.43: Schematic layout of a hank-scouring machine

Each bowl is initially charged with the required chemicals and further additions are made during processing, either manually or with a metering device. In machines used only for scouring, the process liquor may flow from bowl four towards bowl one, thus providing a simple counter-current extraction system. Specific water consumption varies widely, depending on the quantity of yarn processed through the machine before dropping the liquor for cleaning and the extent of any flowdown to drain from the scouring bowls. Values between 2 and 7 litres of water per kg yarn are common.

"Package to package" scouring machines (Figure 2.44) are less common and are of more recent design. With this machinery the whole process may be automated, including drying. Coiling devices take yarn from a number of individual cones and form this into an endless blanket of overlaid coils, laid down automatically onto a moving conveyer belt. The conveyer passes through each of the scouring and rinse bowls. The yarn is transferred to a second conveyer,

which then passes through the dryer. The yarn blanket is then un-coiled and the yarn finally rewound onto cones.
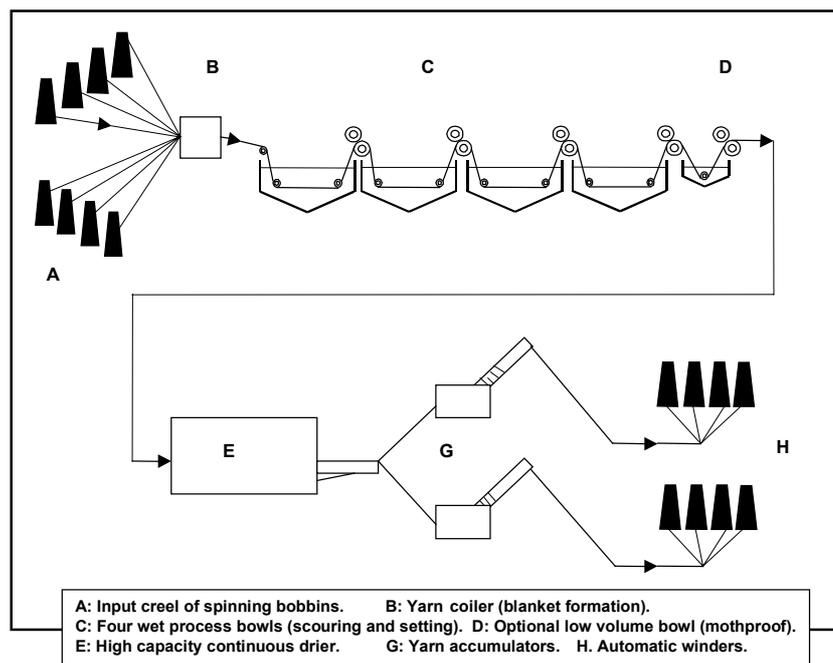
Figure 2.44: Schematic diagram of a "Package to Package" yarn scouring installation

The scouring bowls are of larger volume (3500 litres) than tape scour machines and heating may be by direct gas firing. Most machines are equipped with dual yarn coilers, giving an overall capacity of up to 500 kg/hour.

Both hank and single end machines may be utilised only for scouring or the process may be modified to include simultaneous chemical setting of yarn twist and the application of insect-resist (IR) agents.

Scouring to remove lubricant

When the machines are operated only *to remove lubricant,* the first two bowls are charged with detergent and alkali and operate at 50 – 60 ºC, while the remaining bowls serve to rinse the yarn with clean water at 20 – 30 ºC. Chemical additions are made initially to set the bath concentration at a predetermined level, which is then maintained by further additions during processing.

Scouring and insect-resist treatment

Four-bowl machines are normally used if the scouring process is to incorporate a simultaneous insect-resist (IR) treatment. Bowls 1 & 2 are charged as above for scouring, bowl 3 contains clean water for rinsing, and bowl 4 is adapted for insect-resist application. Bowl 4 may be of the low volume type (100 - 200 litres), designed specifically for the treatment of yarn with insect-resist agent in order to minimise the volume of the process liquor and the resulting emissions.

In these installations, insect-resist agent is applied by a process of "continuous exhaustion" rather than physical impregnation and the active substance is stripped from the bath by the yarn, equilibrium bath concentration being maintained by continuous chemical metering at a rate proportional to yarn throughput.

Application is carried out at 50 – 60 ºC under acidic conditions (approximately pH 4.5 by either formic or acetic acid) to promote rapid uptake of the active substance in the short yarn residence times available.

The insecticide content of the bowl is such that it cannot be discharged to drain and storage tanks are used to retain liquor between treatment cycles. Heavy contamination of the liquor with dyestuff removed from the yarn would lead to a change of shade in subsequent yarn lots and so a simple adsorptive filter system may be used to remove dyestuff before storage. This consists of a quantity of wool fibre packed into a filter housing and through which the liquor can be circulated. The liquor is preheated to a minimum of 70 ºC to assist effective dyestuff removal. Operating with this liquor renovation system permits reuse of the liquor without the need to discharge to drain.

In the absence of these abatement systems the spent treatment liquor can be pumped from the scouring machine and added to a dark shade dyeing, where uptake at the high dyeing temperatures minimises emissions of active substance. Both loose fibre and yarn dyeing can be done in this way.

A third abatement option uses chemical hydrolysis of the active ingredient to destroy residual insecticide. Spent liquor is pumped from the machine and treated in a separate tank at 98 ºC with sodium hydroxide (4g/l) for 60 minutes. The ester and cyano-ester linkages in permethrin and cyfluthrin undergo rapid hydrolysis under these conditions and more than 98 % abatement is achieved. The primary degradation products are at least one order of magnitude less toxic to aquatic invertebrates when compared to the parent molecule. Liquors treated in this way are normally discharged to drain, where the high alkali-content is neutralised by acids from dyeing processes.

Chemical twist setting

Five-bowl machines are normally employed if chemical twist setting is to be carried out at the same time as scouring. In this mode Bowls 1 and 2 contain sodium metabisulphite (10 to 20 g/l) in addition to detergent and alkali and Bowl 4 may be charged with hydrogen peroxide (5 to 10g/l) to neutralise any residual bisulphite. In all other respects the process is similar to that described above.

Hanks leave the final mangle of the scouring line with a moisture content of approximately 0.8 litres per kg (dry weight). If the material is to receive no further wet processing, this residual moisture is further reduced by centrifugal extraction before evaporative drying in a hot air dryer.

Scouring in hank form may also be carried out using batch *solvent processing equipment*, although this practice is now less common. Perchloroethylene is the solvent of choice, and these machines operate on the totally enclosed principle, washing, rinsing and drying being accomplished sequentially within a horizontal drum. All machines are fitted with solvent recovery systems to distil used solvent and recover solvent vapour during drying.

Hank and package dyeing processes

Traditionally, carpet yarn dyeing is carried out in hank form, where liquor circulation in the dyeing machine produces a yarn with a characteristic physical property, often described as loft or fullness. Hank dyeing machines are mostly of the Hussong type.

In other sectors of the textile industry it is common to dye yarn in package form – wound onto a perforated centre, through which dyeliquor can be circulated under pressure. This process has considerable cost advantage over hank dyeing in that it requires no reeling operation to form the hank and consequently no winding of the hank back onto cones in preparation for weaving or tufting. With wool and wool-blend yarns the extension applied during package winding results in the yarn being set in a "lean" condition and the resultant yarn does not have the required physical characteristics for carpet manufacture. There are, however, a number of ways of

overcoming these objections and package dyeing is slowly gaining credence in the carpet yarn dyeing industry. Three basic types of machines may be used for package dyeing wool yarns: horizontal or vertical spindle machines or tube type machines.

Although the machinery employed in hank and package-dyeing processes is different, the dyeing procedures and techniques are essentially the same and are described together.

Considerable care is required to obtain a level (even) dyeing on yarn as there are no opportunities to even up the colour by mechanical blending, as is the case with loose fibre dyeing. Faulty dyeings must be corrected by manipulation in the dyebath, by either removing or adding colour to achieve the final shade. This process can add significantly to the resources consumed in yarn dyeing.

In comparison to synthetic fibres, the rate of dyeing and the extent of dye uptake is less predictable when dyeing wool, as natural variations in the physical and chemical composition of the fibre have a marked effect on these important parameters.

The dyeing of carpet yarns predominantly composed of a blend of wool and polyamide fibre further compromises the dyer because the two fibres have markedly different dyeing properties and special dyeing auxiliaries must be used to achieve a commercially acceptable product. Problems associated with level dyeing are further compounded by the fact that very few shades can be achieved with one single dyestuff; most shades require the simultaneous application of a number of colours in various proportions and which may have different rates of uptake.

The usual approach is to carry out trial laboratory dyeing on a sample of the particular fibre blend and then to apply 5 – 10 % less dye in the full scale dyeing, the final shade being achieved by adding additional dye in small portions to achieve the final shade. Depending on the dyestuffs, it may be necessary to cool the dyebath for each of these additions in order to promote even migration of the added dye.

Dyeings which are "overshade" can be corrected by stripping dyestuff from the fibre using an excess of levelling agent or reducing conditions, and then adding further colour to achieve the correct shade. This is a practice of last resort in most dyehouses.

This shade matching procedure is an essential part of the dyeing processes as most dyeing is carried out to an agreed standard, either for internal use in the case of an integrated site or by agreement with the customer. Shade matching is predominantly carried out by eye, the dyer comparing the dyed material with a reference pattern under standard illumination.

In other sectors of the textile industry it is common to use colour matching spectrophotometers to determine the reflectance spectra of the dyed material for comparison with a numerical standard. In some instances these measurements may also be used to generate the dyeing recipe from the standard. These techniques are less successful with carpet yarn because a sample of yarn prepared to represent the cut pile of a carpet, viewed end on, must be used for the result to be meaningful. Despite these difficulties a number of manufacturers do use this technology, claiming significant improvements in batch-to-batch matching and subsequent reductions in material wastage.

Hank dyeing machines may be loaded with either dry or wet yarn. In the latter case the yarn may be carrying moisture from the scouring operation or may have been deliberately wetted out to facilitate even packing. This technique is often applied when loading large hanks of yarn with a high twist factor. Package dyeing machines are loaded dry.

Dyestuffs and chemicals typical of wool and polyamide fibres are employed. Preparation for dyeing normally consists of filling the machine with water at 15 – 30 ºC and adding acids, salts and dyeing auxiliaries as required by the recipe. With hank dyeing machines it is conventional to raise the lid and yarn from the dyebath before adding pre-dissolved dyestuffs. In closed package dyeing machines dyestuffs are added from linked transfer tanks.

The dye liquor is circulated for 10 - 15 minutes at 15 – 30 ºC before commencing the heating programme, raising the temperature of the dyebath, according to the dyeing programme in order to maximise exhaustion.

At this stage the dyer will obtain a sample of the dyed yarn for comparison with a standard, in the case of hank dyeing by raising the load from the dyebath, or with package dyeing equipment, through a sampling port in the machine case. A dyeing which is judged to be on shade at this stage is terminated and the dyebath drained. If further additions of dyestuff are required the dyebath may be cooled, in the case of hank dyeing machines by partial draining and refilling with cold water or in package dyeing machines by circulating cooling water through an internal heat exchange core.

Following addition of dyestuff, the dyebath will be returned to the boil and boiled for 30 - 60 minutes before a further yarn sample is taken for shade matching. This operation may be repeated several times before the dyer is satisfied that the bulk material matches the standard. The spent dyebath is then drained and the yarn rinsed in clean water at 15 – 30 ºC for 10 - 20 minutes before finally being allowed to drain, ready for unloading.

In some instances the spent rinse bath may contain little or no residual colour. As the temperature of this liquor is compatible with dyeing start temperatures, it may be retained in the dyeing machine and used for a subsequent dyeing. This practice reduces water usage by up to 50 %.

Application of functional finishes

A number of functional finishes may be applied, either with the dyestuffs or from additional baths of clean water following dyeing. These include insect-resist treatments, flame-retardant treatments and anti-static treatments.

Insect-Resist treatments

Traditionally formulated insecticides, based on synthetic pyrethroids or Sulcofuron, were added to the dyeing with the dyestuffs. To minimise residues and control fugitive emissions this basic procedure has been modified. The formulated product is now added to the dyeing at a later stage; to avoid the spillages that occur during yarn lowering and dyeing, auxiliaries are selected which do not interfere with exhaustion. Emissions from dyeings carried out under acidic conditions are normally within permitted limits, but experience has shown that these standards cannot be met when dyeing under more neutral conditions. In this case, the insect-resist agent is applied from a blank aftertreatment bath in the presence of formic acid at a temperature of 70 - 80 ºC.

Anti-static treatments

Anti-static finish applied to the pile yarn is mainly based on a cationic surfactant system, which is readily applied to the fibre under mildly alkali conditions. Cationic compounds are not compatible with anionic dyestuffs and these materials cannot, therefore, be incorporated in the dyebath, but must instead be applied as aftertreatments. The process consists of preparing a fresh bath of clean water, adjusting the pH and adding the required quantity of the proprietary product. The liquor is raised to 60 ºC and run at this temperature for 20 - 30 minutes, followed by rinsing in clean water.

Flame-retardant treatments

Potassium salts of fluoro complexes of zirconium (potassium hexafuorozirconate) are typically used for wool and wool-blend fibres. Typical application conditions for carpet wool yarn are as follows:

- rinsing is required to remove interfering sulphate and phosphate ions, if present
- bath set up at 20 – 30 ºC, pH 3 with hydrochloric acid (10 % o.w.f.) or formic acid (15 % o.w.f.) and citric acid (4 % o.w.f.)
- addition of potassium hexafuorozirconate (3 to 8 % o.w.f. depending on the final specification to be achieved and the substrate) dissolved in 10 times its weight of hot water
- temperature raised at 1 – 2 ºC per minute to 60 ºC and held at this temperature for 30 minutes
- rinsing in cold water for 10 - 20 minutes.

Other treatments

In addition to application of the above functional finishes, which are all invariably carried out in conjunction with colouration, yarn dyeing equipment may be used for other specific yarn preparation or treatment procedures, principally bleaching and twist setting. These are described separately below.

Bleaching

The industry favours the neutral white colour obtained by an oxidation bleach, followed by a reductive bleach. Typical processing conditions would be:
1. at 40 ºC run yarn in liquor containing 3 % o.w.f. proprietary stabiliser, 1.5 % o.w.f. sodium tri-polyphosphate, 20 % o.w.f. hydrogen peroxide (35 %). Raise liquor to 70 ºC, circulate 40 minutes. Drain
2. run in a fresh bath containing 0.2 % o.w.f. formic acid (85 %) and 0.75 % o.w.f. sodium hydrosulphite. Raise to 50 ºC, circulate 20 minutes, drain and rinse in cold water.

Yarn (dyebath) twist setting

This process is not always carried out as a separate treatment. In fact, during the hank dyeing of wool yarns the twist inserted during spinning is stabilised by chemical changes within the fibre at the temperatures reached by the boiling dyebath.

Yarn may, however, be twist set in hank form using conventional hank dyeing equipment. Typical processing conditions would be:
1. raise dyebath to 80 ºC, add 5 % on the weight of yarn sodium metabisulphite, immerse yarn, circulate liquor for 15 minutes, drain machine
2. rinse cold with liquor containing 0.8 % o.w.f. hydrogen peroxide (35 %) for 15 minutes.

2.13.6 Integrated Carpet Manufacturing Mills

Fully integrated carpet manufacturers carry out all the mechanical processes, wet processes (pretreatment, dyeing, printing and finishing operations) required to convert natural and synthetic fibres into finished carpet. Such companies may also produce their own synthetic fibres from raw polymer feedstock. Regarding the natural fibres processed they can in some cases select and purchase natural fibres and operate the whole chain of processes from wool scouring to dyeing, yarn spinning and carpet weaving/tufting. However, usually not all of these operations are carried out at the same site.

The conversion of the fibre into finished carpet can follow different routes depending on the style of the carpet to be produced.

Tufted carpet

Yarn can be manufactured from:
- staple fibres, from both synthetic (PA, PP, PES, PAC) and natural (wool and cotton) fibres
- continuous filaments, exclusively from synthetic fibres (mainly PA, PP and PES).

The carrier materials (primary backing) usually consist of:
- PP woven fabrics or webs
- PES woven fabrics or webs
- jute fabrics.

Finishing of tufted carpets involves:
- dyeing and/or printing
- coating
- mechanical finishing
- chemical finishing (in the dyeing step?).

Dyeing and chemical finishing can be applied on loose fibre, yarn or piece, while the other operations are carried out on the final carpet.

Needle felt carpet

Almost all fibres may be used for the production of needle felts; however, mostly man-made fibres are used (PP, PA, PES, PAC, wool, jute/sisal, viscose).

Needle felts finishing involves:
- dyeing (yarn or piece dyeing)
- coating
- mechanical finishing (rare)
- chemical finishing (in the dyeing step?).

Woven carpet

Both natural and synthetic fibres are used in woven carpet production.

Carpets are woven using dyed yarns (so piece dyeing is not applied in woven carpet production). The final carpet is then submitted to mechanical and chemical finishing treatments.

3   EMISSION AND CONSUMPTION LEVELS

3.1   Introduction

The textiles industry has been always regarded as a water-intensive sector. The main environmental concern is therefore about the amount of water discharged and the chemical load it carries. Other important issues are energy consumption and air emissions from stenter frames.

Air emissions are usually collected at their point of origin. Because they have been controlled for quite a long time 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:
- the types of fibres involved
- the types of make-ups processed
- the techniques applied
- the types of chemicals and auxiliaries used in the process.

Furthermore, since the production may vary widely not only during a year (because of seasonal changes and fashion), but also over a single day (according to the production programme), the resulting emissions are even more difficult to standardise and to compare.

The ideal approach would be a systematic analysis of the specific processes, but the data available are very poor for many reasons, including the fact that legal requirements have tended to focus on the final effluent rather than on the specific processes.

Mindful of these limitations on the characterisation of wastewater emissions, it has proved appropriate to identify narrow categories of finishing industries 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 consumption and emission factors of mills within the same category, it is possible to verify given data and identify key issues and macroscopic differences between the similar activities.

Input/output considerations will therefore be addressed step by step, starting from overviews of the overall mass streams and ending in a more detailed analysis of single processes and/or issues that are of some concern.

This is the approach that will be followed in this chapter for all categories of industries identified in Chapter 2 (Section 2.13).

3.2   Wool scouring mills

This section refers to a well defined category of companies whose general features are briefly described in Section 2.13.1, while the scouring process itself is described in Section 2.3.1.1. The information reported in this section reflects an industry survey of raw wool scouring and effluent treatment practices in the European Union, undertaken by ENCO in 1997/98 on behalf of [INTERLAINE].

The number of responses received from each of the Member States where there is wool scouring activity was as follows:

Belgium	0
France	2
Germany	1
Italy	1
Portugal	2
Spain	1
UK	5
Total	*12*

In addition, a completed questionnaire was received from an Australian subsidiary of a European company.

Production volumes varied greatly, from 3000 to 65000 tonnes of greasy fibre per year. Working patterns also varied, ranging from companies working 24h per day on 7 days per week, to companies working 15 - 16h per day on 5 days per week.

As already highlighted in Section 2.3.1.1, the arrangements for circulating the scour and rinse liquors may vary widely. There are also significant differences in processing conditions due to the nature of the wool processed (fine or coarse) and the contaminants present. All these factors, combined with the type of wastewater treatment adopted, influence the quality of the effluent from the scouring mill. Table 3.1and Table 3.2 summarise the data collected at eight different sites. Some companies have been grouped together in an attempt to find a relationship between the liquor handling system adopted and the resulting consumption and emission levels. The original identification letters for the different companies have been kept. Fine and coarse wool processors appear in separate groups to enable easier comparison.

FINE WOOL	Mill F	Mill E	Mill G	Mill J	Mill N
Loop	No	Yes		Yes	
Recycle	No	No		Yes (from ww treatment plant)	
Water consumption [l/kg of g.w.] Gross:	6.67	?	6.30	?	5.00
of which recycled:					
- from grease recovery loop:	0	?	3.33	?	1.31
- from the rinse effluent:	0	0	0	0	0
- from the ww plant:	0	0	0	2.37	2.38
Net:	6.67	10.00	2.97	0.36	1.31
Detergent [g/kg of g.w.]	7.78	15.83	5.96	4.50	6.15
Builder [g/kg of g.w.]	4.20	0.00	?	5.55	3.84
Grease recovered [g/kg of g.w.]	34.5	71 [a]	27	19.10	34.6
% of the total	25 - 30		20	20	25 - 30
COD before ww treatment [g/kg g.w.]		?			
- from rinse water flow		13.40	?	?	7.35
- from scour flow		?	?	?	143
Source [INTERLAINE] Notes: g.w. = greasy wool; Loop = use of dirt removal and/or grease recovery loop with recycle of the water to scour; Recycle = use of recycled water from the wastewater treatment plant and/or from the rinse bowl by means of UF system; Gross = total flow in scour, i.e. sum of fresh and recycled water feeds; Net = net consumption [a] Centrifugal grease + acid cracked grease					

Table 3.1: Wool scouring process mass streams overview (fine wool)

COARSE WOOL	Mill C	Mill H	Mill L
Loop	No	Yes	Yes
Recycle	No	No	Yes (from rinse bowl by UF)
Water consumption [l/kg of g.w.] Gross:	13.20	10.28	?
of which recycled:			
- from grease recovery loop:	0	5.71 [a]	?
- from the rinse effluent:	0	0	?
- from the ww plant:	0	0	?
Net:	13.20	4.57	1.80
Detergent [g/kg of g.w.]	9.09	8.00	7.00
Builder [g/kg of g.w.]	7.09	1.00	7.00
Grease recovered [g/kg of g.w.]	0	13	7.5
% of the total	0	25	15
COD before ww treatment [g/kg g.w.]			
- from rinse water flow	?	4.46	1.6
- from scour flow	?	218.5	105.2 [b]
Source [INTERLAINE] Notes: g.w. = greasy wool Loop = use of dirt removal and/or grease recovery loop with recycle of the water to scour Recycle =u se of recycled water from the wastewater treatment plant and/or from the rinse bowl by means of UF system Gross = total flow in scour, i.e. sum of fresh and recycled water feeds; Net = net consumption [a] the mill has two separate recovery loops (one for dirt removal and one for grease recovery) [b] concentrate from the UF system + waste flow from grease recovery loop			

Table 3.2: Wool scouring process mass streams overview (coarse wool)

Water Usage

The wool scouring industry has a reputation for high water consumption. [VITO] reports 20 – 30 l/kg as the range of water consumption for traditional installations, although lower values were observed in the surveyed companies.

Net specific consumption can be reduced by installing a grease and dirt recovery loop, through which water is recycled to the scouring bowls. It is also possible to apply similar recycling technology to waste rinse water. Mill L had such an arrangement, using ultrafiltration to treat the rinse water.

In addition to the above within-process recycling arrangements, it is also possible for mills with evaporative effluent treatment plants to re-use the evaporator condensate for feeding scour and/or rinse bowls. Five of the mills surveyed treat effluent by evaporation, but only three of these recycle the condensate. One of those that does not recycle the condensate, cites problems with build-up of ammonia and odours as the reason for not recycling.

In fine wool scouring, gross water flow in the scour varies greatly, from 5 l/kg in the case of Mill N to more than 10 l/kg for Mill E. The latter apparently operates in similar conditions to Mill G, but it has an old and complex system for collecting, settling and filtering effluent, which probably explains its lower performance. Mill G recycles scour liquors at three times the rate of Mill N.

Net water consumption varies even more widely than the gross liquor circulation (from 10 l/kg in the case of Mill E to 0.36 l/kg for Mill J). In the latter this very low net specific water

consumption is achieved through total recycling of condensate from the effluent treatment plant (anaerobic lagoon/evaporation), plus an unstated amount of within-process recycling via a grease/dirt removal loop.

Of the coarse wool scourers, two have dirt removal/grease recovery loops recycling to the first scour bowl; one of these latter also has a rinse water recycling loop (Mill L). All three scourers bleach in the last bowl of the scour train using hydrogen peroxide and the bleaching bowls are isolated from the counter-current.

It is possible to calculate gross circulation in the scour at two of the mills. In both cases, it is significantly higher than encountered in all but one of the fine wool scourers. This may be because the coarse wools contain more dirt than fine wools. [INTERLAINE]

Net water consumption varies considerably in the three mills. Mill C has the highest net water consumption of any of the mills that responded in detail to the questionnaire. This mill recycles no liquor at all. Mill H has a moderately low net water consumption, which is achieved by using the highest capacity dirt removal/grease recovery loop encountered in this survey. Mill L recycles rinse water and also presumably has other recycling arrangements to achieve its low net consumption.

Another factor playing a potential role in net water consumption is the production volume. Figure 3.1 shows, by plotting net consumption against production volume, a tendency for net specific water consumption to fall as production volume increases. There are clearly mills whose net water consumption is below the norm, represented by the drawn curve.
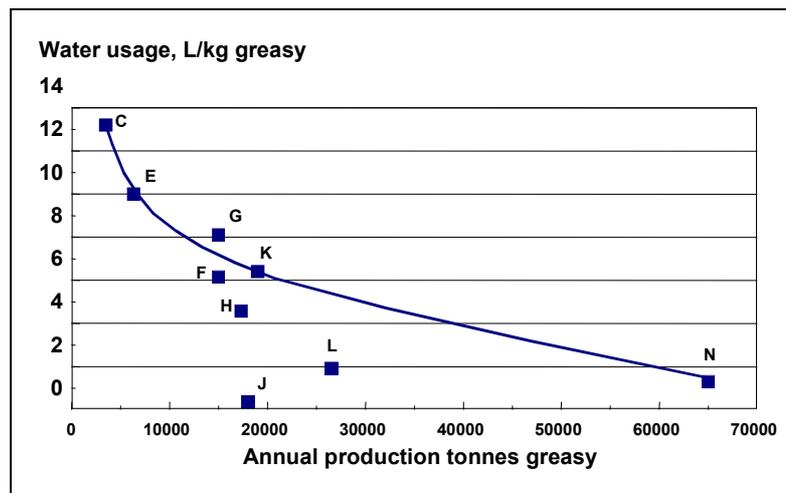
Figure 3.1: Net specific water consumption plotted against production volume [INTERLAINE]

There may be several reasons for this relationship between water consumption and production volume. Besides economies of scale in larger companies, possibly the most important reason is the mill's perception of the economics of reducing water consumption. Some of the medium-sized mills may feel unable to make the required investment or may not have the staff resources to devote to the task. [INTERLAINE]

Grease recovery

One scourer (Mill C) has no grease recovery plant, while the remaining mills recover between 8 and 71 kg grease per tonne of greasy wool processed. The scourers at the bottom end of this range (Mill H, 13 kg/tonne and Mill L, 8 kg/tonne) are wholly or predominantly scourers of coarse wools, which contain lower percentages of grease in a more oxidised (less hydrophobic) form, which is more difficult to separate centrifugally. At the top end of the range is Mill E,

which recovers 71 kg of grease per tonne of wool processed. This mill is a fine wool scourer with a centrifugal grease recovery plant and an acid cracking plant. The acid cracking plant produces a lower quality grease which must now be regarded as a waste rather than a by-product, since it cannot usually be sold and has to be landfilled. The remaining four mills, wholly or predominantly fine wool scourers, recover between 22 and 37 kg of grease per tonne of wool (average, 30 kg/tonne).

Chemical Usage

The most important chemicals used by scourers are detergents and builders. Seven of the scourers use alcohol ethoxylate detergents and five use alkylphenol ethoxylates (the data are reported only for two mills). Two UK scourers also report the use of "solvent assisted detergent" for the removal of marking fluids from fleeces. Eight scourers use sodium carbonate as builder, two use sodium hydroxide and two use no builder.

Scourers of coarse (carpet) wools are often asked by customers to bleach the fibre by adding hydrogen peroxide and acid to the last rinse bowl. Five of the scourers do this routinely or on occasion.

The seven users of alcohol ethoxylates consume an average of 9.1g detergent per kg greasy wool (range 3.5 – 16g/kg), whilst the five users of alkylphenol ethoxylates use an average of 8.0g detergent per kg greasy wool (range 5 – 16g/kg). There is therefore no evidence of economies of scale, nor of the often-claimed greater efficiency of alkylphenol ethoxylates over alcohol ethoxylates.

It is also frequently claimed that fine wools require more detergent for scouring than coarse wools. The survey shows that the fine wool scourers use an average of 7.5g detergent per kg greasy wool (range 5 – 10g/kg) while coarse wool scourers use an average of 8.5g detergent per kg greasy wool (range 3.5 – 16g/kg), so this claim also seems to be without foundation.

Figure 3.2 shows that there is a relationship between detergent feed rate and the rate at which effluent is discharged to the mills' effluent treatment plants. Detergent which is discharged in the effluent from the scour is lost, whilst recycling detergent via the grease recovery/dirt removal loop conserves much of it within the scour. Note that the values used in compiling this figure are calculated from annual usage divided by total wool processed and may differ from detergent feed rates to scour bowls used in the tables reported earlier (Table 3.1 and Table 3.2).
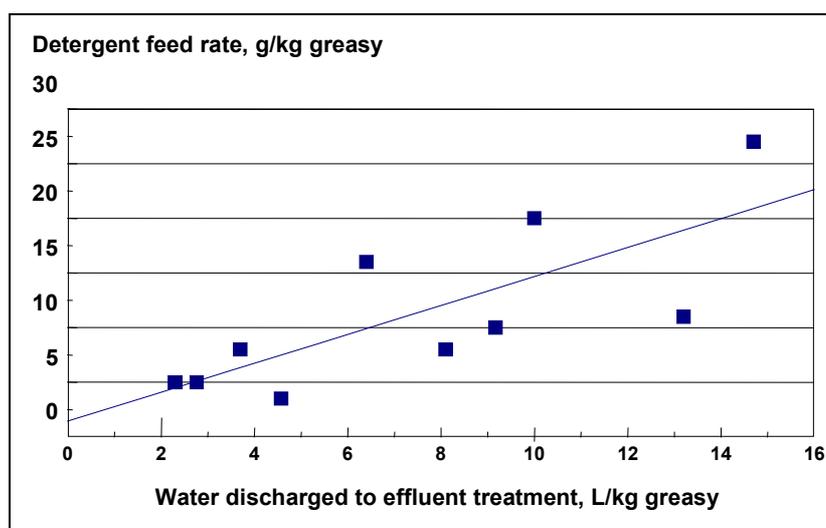
Figure 3.2: Relationship between the detergent feed rate and the rate of discharge of effluent to treatment
[INTERLAINE]

For builders, on the other hand, there is no obvious pattern related to wool type, detergent consumption or type or size of operation.

Several of the scourers also reported using varying quantities of acids and alkalis for cleaning purposes. These included hydrochloric, nitric, phosphoric and sulphuric acids, a mixture of organic and inorganic acids, and caustic soda. The use of sodium chloride for regeneration of the water treatment plant was also mentioned. Significant quantities of chemicals are used by some scourers in effluent treatment processes, but few data are available. [INTERLAINE]

Energy Consumption

The mills in this survey were not asked to give energy consumption figures. Data presented here come from a survey carried out in UK in 1998[3].

Figure 3.3 shows the specific energy consumption (MJ/kg greasy wool) and the specific net water consumption (l/kg greasy wool) of the 11 mills which supplied data (the reported data refer only to the scouring process and do not include energy consumption for the wastewater treatment plant).

The relationship between energy and water consumption is immediately obvious and is emphasised in Figure 3.4, where energy consumption is plotted against water consumption. As far as possible, the consumption figures used relate only to the scouring and related processes, such as effluent treatment.

Energy and water consumption both vary widely. Energy consumption ranges from 4.28 to 19.98 MJ/kg (average 9.29 MJ/kg) and water consumption varies from 1.69 to 18.0 l/kg (average 8.16 l/kg). R^2 for the correlation is 0.906.
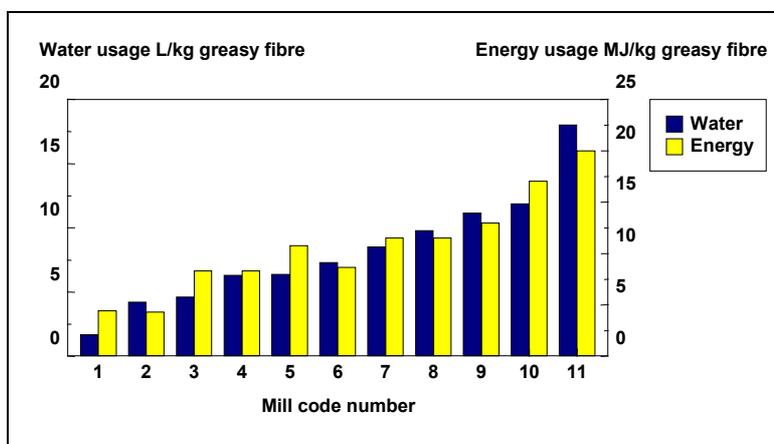
Figure 3.3: Energy and water consumption in 11 UK scouring mills [INTERLAINE]

---

[3]   M Madden, ENco, personal communication, 1999.
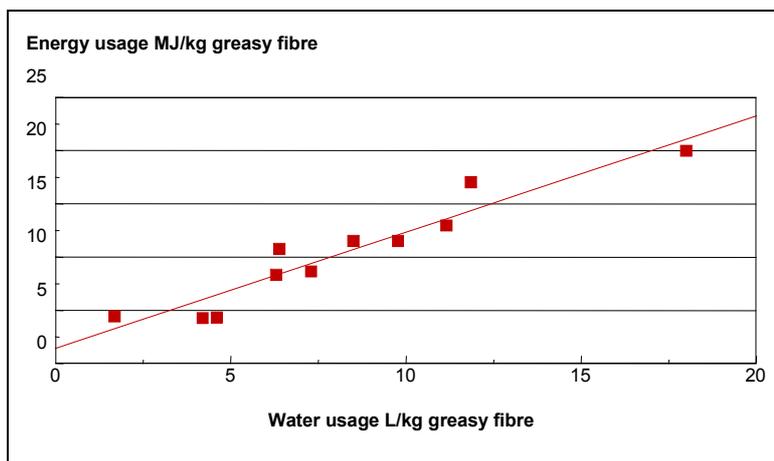
Figure 3.4: Energy consumption plotted against water consumption for 11 UK scouring mills [INTERLAINE]

The variation in water consumption in the UK study bore no relationship with throughput (as it did in the Europe-wide study). See Figure 3.5.
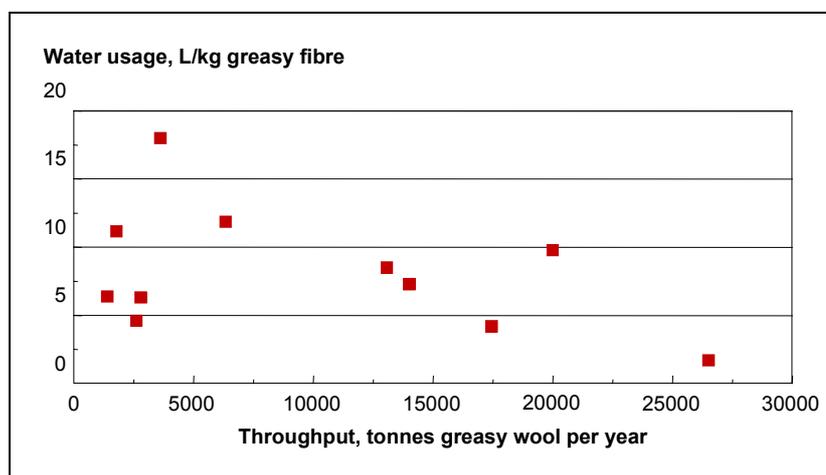
Figure 3.5: Water consumption against throughput for 11 UK scouring mills [INTERLAINE]

There are probably two reasons for the relationship between energy and water consumption. The more obvious is that much of the thermal energy consumed in wool scouring is used for heating water. Rather less obviously, it is likely that the mills which have expended time and effort (and perhaps capital) on reducing water consumption will also have given attention to reducing energy consumption. This assumption is supported by the fact that heating 1 litre of water to scouring bowl temperature consumes 0.21 MJ, whilst the slope of the regression line in Figure 3.9 is 1.09 MJ/l. [INTERLAINE]

Chemical Oxygen Demand

Specific COD loads before wastewater treatment are indicated in the [INTERLAINE] document for only a few mills (see Table 3.1 and Table 3.2). A global COD range of 150 – 500 g/kg of raw wool has, however, been estimated in the final summary (see Figure 3.6).

COD in the effluent immediately after the process is also influenced, apart from the quantity of contaminants present on the raw material, by the efficiency of the grease and dirt recovery

system. Wool grease, dirt and suint are in fact the main contributors to the COD load, while detergent can be regarded as the most minor contributor. In this respect the specific COD loads could be roughly estimated, using the data available, by considering:

- the amount of COD contained in the raw wool (556 kg COD/tonne fine raw wool and 315 kg COD/tonne coarse raw wool, see also Section 2.3.1.2)
- the amount of grease removed/recovered from the effluent (assuming the grease is the main contributor to the COD).

Concerning the COD levels after wastewater treatment, the available data from the surveyed mills are summarised in Table 3.3. The mills have been subdivided in direct dischargers (companies that discharge directly to surface water) and indirect dischargers (companies that discharge to sewer after an on-site pretreatment. One mill recycles the effluent completely by evaporative treatment and therefore does not have any wastewater discharge at all.

Some of the figures in Table 3.3 are estimated or calculated from other data supplied. To distinguish values supplied directly by the mills from estimated or calculated data, the former are printed in bold type.

In calculating the COD load entering the environment as a result of the activities of those wool scourers who discharge pre-treated effluent to sewer, it has been assumed that the rate of mass removal of COD in the sewage treatment works is 80 %. This is believed to be an appropriate removal rate, although there is no hard evidence to support the assumption.

The processes used by the mills which responded include all process types (coagulation/flocculation, evaporation, membrane filtration and aerobic/anaerobic biological treatment).

Unfortunately, not all effluent treatment sub-types are represented. For example, none of the responding mills uses dissolved air flotation (DAF) as a means of separation after addition of coagulants/flocculants to the effluent stream (all use either decanter centrifuges or hydrocyclones).

Only one mill uses membrane filtration (in this case ultrafiltration [UF] on rinse effluent only) – other types of membrane filtration are not represented. There is no mill which uses anaerobic digestion only to treat scouring effluent although the existence of such a mill in Italy is known.

There are also mills in Italy using conventional aerobic biological treatment (plants similar to those used for the treatment of municipal sewage) and combinations of anaerobic and aerobic biological treatment. [INTERLAINE]

Four of the mills discharge effluent directly to surface waters. Two of these (Mills C and N) treat to high standards before discharge. Surprisingly, the other two discharge untreated effluent. One of these mills is known to have installed a flocculation/coagulation effluent treatment plant since responding to the questionnaire.

Mill J recycles effluent completely after evaporative treatment. Mill N recycles scour effluent after treatment by evaporation and bio-filtration, but discharges rinse effluent to surface waters following treatment by prolonged aeration.

All the other mills (six in number) discharge to sewer and, in all cases, the discharged effluent receives aerobic biological treatment in a municipal sewage treatment works. The majority of these mills (four) use physico-chemical coagulation/flocculation processes to pre-treat their effluent on site, though only Mill K treats rinse effluent as well as scour effluent.

	On-site treatment		COD after on site treatment		Sludge	COD after off-site treatment	Mill
	Scour liquors	Rinse liquors	[mg O₂/l]	[g/kg]	[g/kg]	[mg O₂/l]	
No discharge	Scour liquors (after grease recovery) and rinse liquors are recycled after anaerobic lagoon and evaporative treatment		0	0	55?	0	J
Direct discharge	None		19950 c)	299 c)	?	19950 c)	B
	None		19950 c)	299 c)	?	19950 c)	D
	Evaporator (the company does not have a grease recovery plant)		**260**	**3.4**	315 b)	**3.4**	C
	Evaporator + bioreactor (the water is recycled to rinse bowl)	Extended aeration (4 - 5 days)	**120**	**0.2**	75 d)	**0.2**	N
Indirect discharge	Al/polymeric flocculation Hydrocyclone	None	9000 e)	73 e)	233 b)	14.6 f)	G
	Acid/polymeric flocculation Decanter centrifuge	None	**15000**	**60**	145 a)	12.0 f)	H
	Fe/lime/polymeric flocculation Decanter centrifuge		**3900**	**33**	135 a)	6.6 f)	K
	Acid cracking Filter press	None	**4000**	**42**	154 a)	8.4 f)	E
	Aeration (4 - 5 days)		**2800**	**25**	113 a)	5.0 f)	F
	Evaporator	Recycling by UF (the concentrate is passed to the evaporator)	**500**	**1.3**	185 a)	0.3 f)	L

Source [INTERLAINE]
Notes:
a) dry weight
b) may be dry or wet
c) calculated as follows: COD content of coarse wool: 315 kg/tonne of which 95 % occurs in untreated wastewater; water usage is assumed to 15 l/kg greasy wool
d) estimated dry weight
e) calculated as follows: COD content of fine wool 556 kg/tonne of which 95 % occurs in untreated wastewater; water usage is assumed to 15 l/kg greasy wool
f) calculated assuming that municipal aerobic treatment plant removes 80 % of COD

Table 3.3: Overview of effluent treatment processes and associated output of COD and sludge

Discharges from the mills vary widely, from zero to 73 kg COD/tonne of greasy wool processed, reflecting differences in the on-site treatments applied. However, all mills discharging more than 3.4 kg COD/tonne discharge to sewer and pay the sewerage operator for further treatment. This reduces the range of COD entering the environment to 0 – 15 kg/tonne. The best performance for a mill which does not completely recycle treated effluent (from evaporative treatment) is 0.2 kg COD/tonne for Mill N, but the estimated COD emissions to the environment from Mill L, which discharges via sewer, are similar at 0.3 kg/tonne.

Sludge

With regard to sludges arising from effluent treatment, many scourers did not state whether the weights given were wet or dry weight. These instances are noted in Table 3.3. Sludge

production (dry basis) ranged from about 100 to 300 kg/tonne greasy wool except for two cases. Mill J treats effluent by anaerobic lagooning followed by evaporation and yet states that sludge production is only 55 kg/tonne. This figure possibly refers to the sludge or concentrate arising from evaporation and does not include the sludge from the anaerobic lagoon. In any case, it is unlikely to represent total sludge production at Mill J. Mill N treats scour effluent by evaporation and incineration. This produces 20 kg/tonne of ash, but no sludge. Sludges arise at this mill from gravity settling, plus decanter centrifuging, in the grease recovery/dirt removal loop and from aerobic biological treatment of rinse effluent. The figures given, equivalent to 75 kg/tonne, are believed correct. [INTERLAINE]

The sludge is sent to landfill without pretreatment, or it finds other uses such as brickmaking or soil conditioner in agricultural land after composting. In one case it is incinerated.

Ectoparaciticides

Residues of veterinary medicines in wool scour effluent have potential to cause harm in the environment. The most commonly found ectoparasiticides and the environmental issues related to their release in the effluent have already been described in Section 2.1.1.9.

The questionnaire sent to scourers involved in the survey asked them to give quantitative information on the source countries of the wools they scour. Thanks to this information in combination with the ENCO Wool & Hair Pesticide database (see Section 2.1.1.9) it was possible to estimate the average biocide content of the incoming raw material. The results of this calculation are reported in Table 3.4, which shows concentrations of individual ectoparasiticides in the range of 2 – 15 mg/kg of raw wool.

Mill	Total organochlorines [a] g/tonne greasy wool	Total organophosphates [b] g/tonne greasy wool	Total synthetic pyrethroids [c] g/tonne greasy wool
B	2.73	1.13	0.29
C	5.05	4.14	0.31
D	2.31	1.09	0.05
E	0.12	4.61	1.41
F	0.10	3.93	1.18
G	0.60	4.86	6.25
H	0.22	18.7	4.55
J	3.03	4.02	4.30
K	0.32	16.3	4.36
L	0.53	19.0	3.79
M	0.57	4.65	5.73
N	0.30	4.98	2.76

Source [INTERLAINE]
Notes
[a] Sum of *alpha-, beta-, gamma* and *delta*-hexachlorocyclohexane, hexachlorobenzene, heptachlor, heptachlor-epoxide, aldrin, dieldrin, endrin, endosulphan, DDD and DDT.
[b] Sum of chlorfenvinphos, dichlofenthion, diazinon and propetamphos.
[c] Sum of cyhalothrin, cypermethrin, deltamethrin and fenvalerate.

Table 3.4: Average organochlorine, organophosphate and synthetic pyrethroid biocide content of the wools processed by 12 scourers

The emission loads of pesticides discharged in the effluent from the surveyed companies are not available. However, they could be estimated based on the water-grease partition factors of these compounds.

Biocides are in fact removed by the dirt removal/grease recovery loops which are integrated with the scour as well as by the end-of-pipe effluent treatment plant. For example, a mill which removes 25 % of the total grease on the incoming wool in its grease recovery loop, perhaps a further 5 % in its dirt removal loop, and 80 % of the remaining 70 % (i.e. 56 % of the total) in its effluent treatment plant, has an overall grease recovery rate of 86 %. Removal of lipophilic biocides would be expected to follow a similar pattern to that of grease removal. Rinse water recycling loops, if used, may also remove some biocide.

Many studies of the fate of ectoparasiticides in the wool scouring process have been carried out and these issues have already been dealt with in Section 2.3.1.2. Possible assumptions are listed as follows [NRA]:

- 96 % of the pesticides are removed from wool (4 % is retained on the fibre after scouring)
- of this 96 %, an additional percentage (which is usually 30 %, but in some examples it has shown to be lower) is retained on site in recovered grease
- in the case of water soluble pesticides (e.g. cyromazine and dicyclanil) it is assumed that 4 % of the initial amount remains on the fibre, but no further pesticide is removed by wool grease recovery or on-site treatment; therefore 96 % of the initial amount is found in the wastewater
- another exception is represented by triflumuron for which the retention rate is higher (it associates partly to grease and partly to dirt)
- the remaining fraction (which does not associate with wool, grease and dirt) is discharged in the effluent and submitted to wastewater treatment.

Concerning the effect of the wastewater treatment, Table 3.5 summarises the monitoring results for woolscour effluent treatment plants, carried out by ENCO in 1997/98[4]. The results in the table compare the effluent before and after treatment and were obtained by analysis of 24 h composite samples, taken on 10 separate days. The table also shows the reduced efficiency of evaporative systems in the removal of OPs due to their steam volatility (see also Section 2.3.1.2).

Mill	Plant type	Removal rate (%) in effluent treatment plant						
		Grease	COD	SS	OC	OP	SP	Total biocides
1	CF/Fe	86	84	89	83	88	94	88
2	CF/acid	89	73	89	69	78	40	77
3	HAC	82	70	75	72	75	75	75
4	BF/Fe	93	75	83	96	56	71	59
5	CF	73	70	75	76	91	94	91
6	CF/Fe	80	80	77	81	76	74	76
7	HBF/Fe	96	83	94	90	92	89	92
8	Evap	100	99	100	97	72	100	78

Source [INTERLAINE]
Notes:
COD = chemical oxygen demand   SS = suspended solids   OC = organochlorines
OP = organophosphates   SP = synthetic pyrethroids   CF = continuous flocculation
HAC = hot acid cracking   BF = batchwise flocculation   HBF = hot batchwise flocculation
Evap = evaporation

Table 3.5: Performance of effluent treatment plants in removing wool grease, COD, suspended solids and ectoparasiticides from woolscour effluent

---

[4]   ENco, unpublished results, 1997 and 1998.

Additional data come from another ENCO separate study[5], where the mass loads of the three most commonly used sheep treatment chemicals – diazinon (OP), propetamphos (OP) and cypermethrin (SP) – discharged to sewer from seven scouring mills, were calculated and compared with the loads present on the incoming greasy wool. The latter values were obtained by using the average residue concentrations taken from the ENCO database for the mix of wool sources scoured at each mill. The results are shown in Table 3.6.

Mill	Diazinon			Propetamphos			Cypermethrin		
	In wool g/tonne	In effluent g/tonne	Removal %	In wool g/tonne	In effluent g/tonne	Removal %	In wool g/tonne	In effluent g/tonne	Removal %
T	8.63	1.63	81	9.99	0.57	94	5.58	0.05	99
U	8.16	0.66	92	8.63	0.37	96	5.30	0.04	99
V	5.30	0.59	89	2.72	0.17	94	3.45	0.15	96
W	6.14	1.14	82	7.80	0.61	92	4.12	0.21	95
X	4.59	0.10	98	0.19	0.02	91	3.60	0.52	86
Y	8.16	1.48	82	10.60	0.78	93	5.41	0.20	96
Z	10.76	0.17	99	12.10	0.36	97	7.06	0.02	100
Source [INTERLAINE]									

Table 3.6: Sheep treatment chemical residues in incoming greasy wool and in scouring effluent discharged to sewer at six mills

By comparing the results in Table 3.5 and Table 3.6, it can be seen that the overall removal rates of sheep treatment chemicals from scouring effluent are significantly higher than the removal rates in the effluent treatment plants. As indicated earlier, the balance is presumably removed in the dirt removal/grease recovery loops.

The above discusses the removal of sheep treatment chemicals in physical and physico-chemical effluent treatment plants. It is possible that prolonged biological treatments will destroy at least some of the chemicals. One of the scourers in the European survey described here treats rinse effluent by prolonged (4 – 5 day) aeration and this is known to remove all SPs and all OPs except dichlofenthion[6,7]. OCs are only partly removed. Biological treatments of short duration are not expected to break down the chemicals but may remove them by absorption into the lipid components of the biomass.

Figure 3.6 attempts to define for 1 tonne of raw wool the ranges of consumption and emission for the scouring process and the wastewater treatment. The ranges are defined based on the results of the survey integrated with some results obtained from previous surveys of scouring mills carried out by ENCO in 1996 and 1998. It has to be noted that some of the given ranges are not a generally applicable. For example, the range of values for flocculants used in on-site treatment is valid only for those companies with coagulation/ flocculation effluent treatment plant.

---

[5]   ENco, unpublished results, 1998.

[6]   Dichlofenthion is an OP which was formerly registered for sheep treatment in New Zealand. It is particularly resistant to biodegradation and its registration has been withdrawn.

[7]   G Timmer, Bremer Wollkämmerei, private communication, 1998.
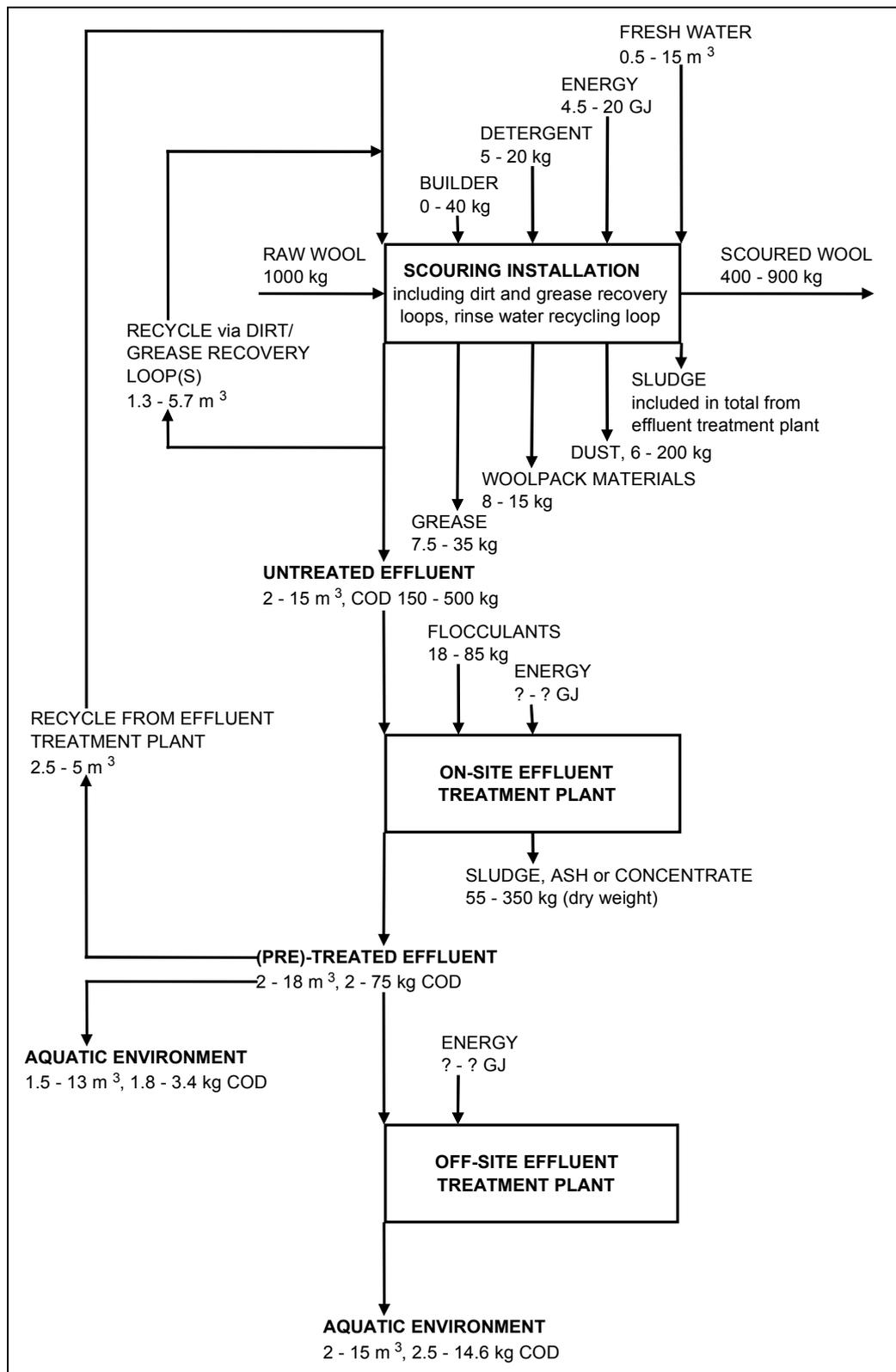
Figure 3.6: Diagram showing the ranges of inputs to and outputs from the scouring processes and effluent treatment plants (on- and off-site) at the mills surveyed [INTERLAINE]

3.3   Mills finishing yarn and/or floc

In the following sections, emissions and consumption levels are illustrated for a group of different sites belonging to the categories identified in Chapter 2 (Section 2.13.2).

Information comes from [UBA, 2001] and is the result of surveys carried out in 14 textile finishing industries (TFI) in Germany in a five years timeframe (1995 to 2001).

With respect to the consumption of chemicals, where not otherwise specified, calculations have been carried out on the so-called "telquel"-basis. This means that the quantities of ready-for-use products have been considered, including water in case of liquid formulations. This must be kept in mind when comparing the consumption levels of different companies. For instance, companies using mainly liquid dyestuff formulations (often the case for big TFI) show specific dyestuff consumption higher than companies using powder or granulates.

A common feature of floc and yarn finishing (mainly in hank form or package) is that all process steps (pre-treatment, dyeing and finishing) are normally carried out in the same apparatus. In many cases (when impurities on the fibre are not present in significant amount and are easy to remove) pre-treatment is not performed as a separate operation, but rather it is carried out together with dyeing by adding additional specific auxiliaries in the dyeing bath.

The main environmental concerns for yarn finishing mills arise from emissions to water, while air emissions are not significant. Therefore the emission factors presented below refer only to water emissions.

3.3.1 Mills finishing floc: mainly CV, PES, PAC and/or CO

For this category the only information available regards emissions to water. The values are compiled in Table 3.7. Because of low liquor ratios and the small number of process baths, the specific wastewater flow is low. The values in Table 3.7 are confirmed by [FhG-ISI, 1997] reporting specific flows for three further TFI between 14 and 18 l/kg.

		TFI 1	TFI 2
Specific. Q_{WW} [l/kg]		34	10
COD	Conc. [mg O_2/l]	1945	1300
	E-Fac [g/kg]	67	13
BOD_5	Conc. [mg O_2/l]	850	370
	E-Fac [g/kg]	29	4
AOX	Conc. [mg Cl/l]		
	E-Fac [g/kg]		
HC	Conc. [mg/l]	12.4	
	E-Fac [g/kg]	0.4	
PH			
L[mS/cm]		14.9	
T[°C]		40	
NH_4	Conc. [mg/l]		
	E-Fac [g/kg]		
org.N	Conc. [mg/l]		
	E-Fac[g/kg]		
Cu	Conc. [mg/l]	1.2	0.05
	E-Fac [mg/kg]	41	0.5
Cr	Conc. [mg/l]	0.13	0.2
	E-Fac [mg/kg]	5	2
Ni	Conc. [mg/l]		<0.02
	E-Fac [mg/kg]		
Zn	Conc. [mg/l]	0.71	0.3
	E-Fac [mg/kg]	25	3
Zn	Conc. [mg/l]	0.71	0.3
	E-Fac [mg/kg]	25	3
Source [UBA, 2001] Notes: Blank cells mean that relevant information is not available			

Table 3.7: Concentration values and textile substrate specific emission factors for wastewater from TFI mainly finishing floc material consisting of CV, PES, PAC or CO

3.3.2 Mills finishing floc mainly consisting of WO

?

3.3.3 Mills finishing yarn mainly consisting of WO

?

3.3.4 Mills finishing yarn: mainly CO

Table 3.8 contains the concentration values and emission factors of three TFI finishing yarn mainly consisting of cotton. Specific water flows are between 100 and 120 l/kg. These values are roughly confirmed by [FhG-ISI, 1997] reporting lower and higher values (68, 73, 78, 83, 120, 128, 149, 181, 271 l/kg). In this respect, the high value of 271 l/kg (from a small TFI processing less than 0.5 t/d) has to be questioned critically.

	TFI 1	TFI 2	TFI 3
specific Q_{WW} [l/kg]	105	108	120
COD Conc. [mg O_2/l] E-Fac [g/kg]	690 73	632 69	805 97
BOD_5 Conc. [mg O_2/l] E-Fac [g/kg]	260 27	160 17	200 24
AOX Conc. [mg Cl/l] E-Fac [g/kg]			0.36 0.04
HC Conc. [mg/l] E-Fac [g/kg]	<0.5 <0.05	1.2 0.1	
pH			9.8
L[mS/cm]	7	6.2	
T[°C]	27.3	33.5	
NH_4 Conc. [mg/l] E-Fac [g/kg]			0.6 0.07
org.N Conc. [mg/l] E-Fac[g/kg]			11.1 1.3
Cu Conc. [mg/l] E-Fac [mg/kg]	0.19 20	0.12 13	0.13 16
Cr Conc. [mg/l] E-Fac [mg/kg]		<0.05 <6	
Ni Conc. [mg/l] E-Fac [mg/kg]	0.32 34	<0.1 <11	
Zn Conc. [mg/l] E-Fac [mg/kg]			
Zn Conc. [mg/l] E-Fac [mg/kg]			
Source [UBA, 2001] Notes: Blank cells mean that relevant information is not available			

Table 3.8: Concentration values and textile substrate specific emission factors for waste water from TFI mainly finishing yarns consisting of CO

The most important factors influencing water consumption and consequently wastewater flow are:
- the liquor ratio of the equipment
- the make-up of the yarn (hanks involve considerably higher consumption of water than cones)
- the machine load (quite often the batches are too small for the apparatus because market demands tend more and more to smaller batches)
- the pattern of usage of chemicals (e.g. the predominant class of dyestuffs, the bleaching treatment required or not, etc.). For instance, dyeing cotton yarn with azoic (or developing) dyestuffs requires considerably more water than common dyeing with reactive dyestuffs (a higher number of steps is required, which results in a higher number of baths to be discharged).

It is also interesting to note the differences in COD emission factors associated with the patterns of dyestuffs usage. Mills like TF1 and TF2, dyeing mainly with reactive dyes, show a significantly lower COD (about 70 g/kg, see TFI 1 and TFI 2 in Table 3.8) compared to TF3 which uses predominantly vat dyes (nearly 100 g/kg, see TFI 3 in Table 3.8). Dyeing with vat colorants involves the use of additional textile auxiliaries (e.g. dispersing agents).

The applied chemicals are grouped as dyestuffs, textile auxiliaries and basic chemicals. Typical values are:

- dyestuffs: 25 [g/kg textile substrate]
- textile auxiliaries: 70 [g/kg textile substrate]
- basic chemicals: 430 [g/kg textile substrate]

Note that for companies dyeing mainly with reactive colorants the consumption of basic chemicals can be higher because of the high neutral salt input.

The total specific energy consumption is about 11 kWh/kg, where the consumption of electricity is about 2 kWh/kg.

Available information on solid waste is limited. Relevant solid waste is packaging material, barrels and tanks for dyestuffs, textile auxiliaries and basic chemicals which require adequate removal; tanks are often recycled. With wastewater equalisation, sludge can be formed which has to be removed and disposed of. The same occurs with wastewater treatment by flocculation/precipitation.

3.3.5 Mills finishing yarn: mainly PES

Table 3.9 contains the concentration values and emission factors for wastewater for four TFI mainly finishing polyester yarn.

		TFI 1	TFI 2	TFI 3	TFI 4
specific Q_{WW} [l/kg]		125	65	66	148
COD	Conc. [mg O_2/l]	870	1917	1520	655
	E-Fac [g/kg]	109	124	101	97
BOD_5	Conc. [mg O_2/l]	139		380	169
	E-Fac [g/kg]	17		25	25
AOX	Conc. [mg Cl/l]	0.7	1.26	0.45	0.65
	E-Fac [g/kg]	0.09	0.08	0.03	0.1
HC	Conc. [mg/l]		19		
	E-Fac [g/kg]		1.2		
pH		8.2		7.7	8.6
L[mS/cm]		1.9		5.0	3.0
T[°C]		23.9	26.3	44.2	34.6
NH_4	Conc. [mg/l]	31.2		8.2	7.6
	E-Fac [g/kg]	3.9		0.5	1.1
org.N	Conc. [mg/l]	13		17.3	9.5
	E-Fac[g/kg]	1.6		1.2	1.4
Cu	Conc. [mg/l]				0.05
	E-Fac [mg/kg]				7
Cr	Conc. [mg/l]				
	E-Fac [mg/kg]				
Ni	Conc. [mg/l]				
	E-Fac [mg/kg]				
Zn	Conc. [mg/l]				
	E-Fac [mg/kg]				
Source [UBA, 2001] Notes: Blank cells mean that relevant information is not available					

Table 3.9: Concentration values and textile substrate specific emission factors for waste water from TFI mainly finishing yarns consisting of PES

The reported specific water flows vary between 65 and 148 l/kg. They are confirmed by [FhG-ISI, 1997] reporting for three similar mills 63, 86 and 122 l/kg. The figures are in the same range as mills finishing cotton yarn.

The upper value in the range (148 l/kg) is for a mill also processing yarn in hank form (this is normally associated with higher consumption of water due to higher liquor ratios). The higher water consumption is also justified by the fact that this company also treats some cotton yarn which is mercerised and dyed with azoic (development) dyestuffs, both operations requiring relatively high amounts of water.

The finishers of PES yarn generally have higher COD emission factors (97 - 124 g/kg) than the corresponding finishers processing cotton. This is mainly attributable to two different factors:
- the use of disperse dyes
- the removal of preparation agents present on the incoming fibre.

Concerning the first factor, the use of disperse dyes involves relevant emissions of dispersing agents (see Sections 2.7.6.2 and 8.6.3). These auxiliaries (usually naphthalene sulphonates-formaldehyde condensates and lignine sulphonates) besides contributing to the increase of the COD load of the final effluent, are water-soluble and hardly biodegradable.

Regarding the preparation agents, it has already been mentioned in Section 2.6.4 that they are applied during fibre and yarn manufacturing, but they need to be removed before dyeing. Since the formulations applied may have a significant content of refined mineral oils (see Section 8.2), this leads to higher COD emission factors. The amount of mineral oils, which is defined with the parameter "hydrocarbons" (HC), was measured in only one company. The contribution of mineral oils to the overall COD load, however, does not seem to be relevant (1.2g/kg measured as hydrocarbons, corresponding to a COD of 3g/kg, where the overall COD is 124 g/kg).

The applied chemicals are grouped as dyestuffs, textile auxiliaries and basic chemicals. Typical ranges are:

- dyestuffs: 18 - 36   [g/kg textile substrate]
- textile auxiliaries: 80 - 130   [g/kg textile substrate]
- basic chemicals: 95 - 125   [g/kg textile substrate]

When high amounts of softening agents are applied, the consumption of textile auxiliaries can be up to 175 g/kg.

The total specific energy consumption is in the range of 11 - 18 kWh/kg. The higher value applies to companies which also have spinning, twisting and coning sections. The consumption of electricity is about 1 - 2 kWh/kg.

Information on solid waste is very poor. The considerations outlined for cotton yarn finishing mills also apply to this category.

3.3.6 Mills finishing yarn: WO, PAC and/or CV

Table 3.10 contains data for emissions to water for five mills finishing yarn consisting mainly of wool and polyacrylonitrile blends along with some viscose in blend with wool and polyacrylonitrile.

	TFI 1	**TFI 2**	**TFI 3**	**TFI 4**	**TFI 5**
specific Q_{WW} [l/kg]	120	212	167	66	74
COD Conc. [mg O_2/l]	590	480	584	782	1023
E-Fac [g/kg]	71	102	97	52	78
BOD_5 Conc. [mg O_2/l]	190	170	265	355	220
E-Fac [g/kg]	23	36	44	23	16
AOX Conc. [mg Cl/l]		0.4	0.76		0.17
E-Fac [g/kg]		0.08	0.1		0.01
HC Conc. [mg/l]					
E-Fac [g/kg]					
pH		7.7	6.9	7.3	6.8
L[mS/cm]			4.4		1.4
T[°C]			41		
NH_4 Conc. [mg/l]		4.6			
E-Fac [g/kg]		1			
org.N Conc. [mg/l]		11.2	16.6		22.8
E-Fac[g/kg]		2	2.8		1.7
Cu Conc. [mg/l]		0.02	<0.01		
E-Fac [mg/kg]		4	<2		
Cr Conc. [mg/l]		0.03	<0.1	0.38	1.2
E-Fac [mg/kg]		6	<17	25	89
Ni Conc. [mg/l]			<0.1		<0.01
E-Fac [mg/kg]			<17		<0.7
Zn Conc. [mg/l]			0.63		0.47
E-Fac [mg/kg]			105		35

Source [UBA, 2001]
Notes:
Blank cells mean that relevant information is not available

Table 3.10: Concentration values and textile substrate specific emission factors for wastewater from TFI mainly finishing yarns consisting of WO/PAC/CV

Specific water flow may vary widely (ranges between 74 and 212 l/kg have been observed).

COD emission factors are similar to mills finishing cotton yarn. All parameters are quite similar to the other categories except for chromium, which is encountered in the effluent in significantly higher amount. This is due to the use of metal-complex and chrome dyes, the latter involving the use of potassium or sodium dichromate. Chromium emissions may vary widely depending on the amount of wool processed and the dyeing method applied. In the case of companies with high percentage of wool among the other fibres, emissions factors up to 100 mg/kg (TFI 5) are observed.

The applied chemicals are grouped as: dyestuffs, textile auxiliaries and basic chemicals. Typical ranges are:

- dyestuffs: 13 – 18 [g/kg textile substrate]
- textile auxiliaries: 60 – 90 [g/kg textile substrate]
- basic chemicals: 180 - 325 [g/kg textile substrate]

The total specific energy consumption is in the range of 4 - 17 kWh/kg. The higher value is for finishing mills that also have spinning, twisting and coning sections. Of the overall energy

consumption the actual consumption of electricity is about 0.9 - 6.5 kWh/kg, the higher value relating to mills with the above-mentioned additional processes.

Available information on solid waste is limited. The considerations outlined for cotton yarn finishing mills also apply to this category.

3.3.7 Analysis of some relevant specific processes for mills finishing yarn and/ or floc

In yarn finishing it is interesting to show the wide variability of the characteristics (particularly in concentration) of the different baths involved in a typical dyeing process. This is put in evidence by showing the behaviour of four different parameter, namely COD, pH, conductivity, temperature and colour (determination of adsorption coefficients at wavelengths 435, 500 and 620 nm) in three different typical dyeing processes:

- exhaust dyeing of CV yarn on cones (L.R. 1:8 - 1:12) with reactive dyestuffs (Table 3.11)
- exhaust dyeing of PES yarn on cones (L.R. 1:8 - 1:12) with disperse dyestuffs (Table 3.12)
- exhaust dyeing of CO yarn on cones (L.R. 1:8 - 1:12) with vat dyestuffs (Table 3.13).

No. of bath	Name of bath	COD [mg O_2/l]	pH	Conduc-tivity [mS/cm]	Tempe-rature [°C]	AC 435 nm [1/m]	AC 500 nm [1/m]	AC 620 nm [1/m]
1	Exhausted dye bath	3170	10.2	35.1	48	27	13	2
2	Rinsing bath	550	10.1	11.7	42	14	10	3
3	Neutralisation bath	1220	4.4	3.8	44	4	4	1
4	Soaping bath	4410	6.2	2.4	57	16	11	4
5	Rinsing bath	1040	7.1	0.9	59	7	5	3
6	Rinsing bath	320	7.3	0.5	60	10	8	5
7	Rinsing bath	190	7.4	0.3	49	7	6	4
8	Conditioning bath (softening)	790	4.4	0.6	35	0	0	0
Source [UBA, 2001]								

Table 3.11: Sequence of discharged baths from exhaust dyeing of CV yarn with reactive dyestuffs along with values for COD, pH, conductivity, temperature and colour (absorption coefficients, AC)

No. of bath	Name of bath	COD [mg O_2/l]	pH	Conduc-tivity [mS/cm]	Tempe-rature [°C]	AC 435 nm [1/m]	AC 500 nm [1/m]	AC 620 nm [1/m]
1	Pretreatment bath	610	7.4	20	134	3.9	2.7	1.4
2	Exhausted dye bath	10320	5.0	3.4	130	290	375	125
3	Rinsing bath	1310	7.2	0.6	85	51	78	8.6
4	Reductive after-treatment	3610	9.5	6.1	89	18	11	6.3
5	Rinsing bath	615	9.2	1.4	84	6.3	4.2	2.7
6	Rinsing bath	140	8.6	0.5	66	0.9	0.7	0.3
7	Conditioning bath (softening)	2100	7.2	0.5	55	23.6	17.9	11.8
Source [UBA, 2001]								

Table 3.12: Sequence of emitted baths from exhaust dyeing of PES yarn with disperse dyestuffs along with values for COD, pH, conductivity, temperature and colour (absorption coefficients, AC)

No. of bath	Name of bath	COD [mg O₂/l]	pH	Conduc-tivity [mS/cm]	Tempe-rature [°C]	AC 435 nm [1/m]	AC 500 nm [1/m]	AC 620 nm [1/m]
1	Exhausted dye bath	14340	12.9	46	70	254	191	190
2	Overflow rinsing	6120	12.6	24	46	95	59	59
3	Interim purification	1900	12.2	12.7	34	9	8	7
4	Oxidation bath	4780	11.7	5.6	51	4	3	2
5	Rinsing bath	580	10.6	2	32	1	1	1
6	Soaping bath I	1510	10	2.3	55	4	4	5
7	Rinsing bath	230	9.3	1.5	36	2	2	2
8	Soaping bath II	860	10.1	3.4	74	4	3	2
9	Rinsing bath	47	8.9	1.2	37	1	1	1
10	Rinsing bath	27	8.5	1	31	0.5	0.5	0.4
11	Conditioning bath (softening)	1740	4.7	1.2	45	17	11	6
Source [UBA, 2001]								

Table 3.13: Sequence of emitted baths from exhaust dyeing of CO yarn with vat dyestuffs along with values for COD, pH, conductivity, temperature and colour (absorption coefficients, AC)

The examples reflect the typical sequences applied in exhaust dyeing of yarn with reactive, disperse and vat dyes. However, they should not be taken as fixed sequences, in the sense that they do not apply as such to any finishers of yarn. A finisher may need to apply, for example, additional rinsing baths, the yarn could be mercerised, the application of softening agents in the last bath could be avoided etc.

However, the examples show some key issues:

1. First, it is significant (although maybe also obvious) to show how much the concentration values of the mixed final effluent (Table 3.7 - Table 3.10) can differ from the corresponding values reported in the tables above for the single baths. Thanks to a dilution effect, the global COD concentration levels are much lower than the values for spent dyeing baths.

2. The spent dyeing baths are those that show the highest concentration levels in all three examples. However, the COD of the exhausted dye bath is significantly lower for reactive dyeing than for dyeing processes using disperse and vat dyes. As mentioned earlier in this chapter, the main reason is the application of dispersing agents which are needed to apply the water-insoluble disperse and vat dyestuffs.

3. Operations like soaping, intermediate purification (?) and reductive after-treatment, which are carried out in order to remove the unfixed dyestuff, are also associated with high values of COD as well as colour. In particular, for softening treatment, the high COD concentration is indicative of the poor exhaustion level typical of softening agents.

4. Rinsing baths can have a very low-concentration, 10 - 100 times lower than the exhausted dyeing bath. This shows the importance of optimising the rinsing process, for example by recycling low-concentration rinsing water.

Table 3.14 and Table 3.15 illustrate water & energy consumption figures observed in loose fibre and yarn (package) dyeing processes.

LOOSE FIBRE DYEING	Electricity	Thermal energy	Water for dyeing	Water for rinsing
Unit	kWh/kg	MJ/kg	l/kg	l/kg
WO (acid, chrome or metal-complex dyes)	0.1 - 0.4	4 - 14	8	8 - 16
PAC (cationic dyes)	0.1 - 0.4	4 - 14	4	4 - 16
PES (disperse dyes)	0.1 - 0.4	4 - 14	6	12
CO (direct, reactive dyes)	0.1 - 0.4	4 - 14	8	8 - 32
PA (direct, acid dyes)	0.1 - 0.4	4 - 14	6	6 - 12
Source: [EURATEX] (Audits in Prato textile district)				

Table 3.14: Water & energy consumption levels in loose fibre dyeing processes

YARN DYEING (on package)	Electricity	Thermal energy	Water for dyeing	Water for rinsing
Unit	kWh/kg	MJ/kg	l/kg	l/kg
WO/ PA (not specified dye)	0.8 - 1.1	13 - 16	15	30
PAC (not specified dye)	0.8 - 1.1	13 - 16	15	30
CO (direct dyes)	0.8 - 1.1	13 - 16	15	45
CO (reactive dyes)	0.8 - 1.1	13 - 16	15	60 [1]
CO (sulphur dyes)	0.8 - 1.1	13 - 16	100 [2]	
Source: [EURATEX] Notes: [1] Water consumption for washing + rinsing (?) [2] Total water consumption (?)				

Table 3.15: Water & energy consumption levels in yarn dyeing processes

3.4   Mills finishing knitted fabric

?

3.5   Mills finishing woven fabric

?

3.6   Carpet industry

3.6.1 Wool and wool-blend carpet yarn dyehouses

The processes dealt with in this section are described in detail in 2.13.5.1. Literature data on consumption and emission levels for the wool carpet yarn sector is very poor. Information presented below comes from the report that [ENCO] has submitted to the EIPPC Bureau. Quantitative data have been gathered from a group of UK companies representative of this sector. The survey covered a range of enterprises, varying in size from a yarn dyehouse

processing approximately 1000 tonnes/annum of fibre to an integrated loose fibre and yarn dyeing/finishing plant, processing over 7000 tonnes of fibre per annum.

Three categories of companies were involved:
- loose fibre dyehouses which dye and dry only loose fibre
- yarn dyehouses which scour, dye and dry only yarn. In one or two cases the scouring of previously dyed yarn is also included
- integrated loose and yarn dyehouses.

In this document, data on consumption and emission levels are presented for the first two categories of mills in Table 3.16 and Table 3.19. Integrated dyehouses can be seen as mixtures of these processes. Figure 3.8 attempts to give ranges of inputs to and output from the wool carpet yarn activities (outputs after wastewater treatment are not included). The reported figures should be used with caution, as the diversity of the sector makes these generalisations subject to considerable error.

Consumption and emission figures are based on information for a twelve month period within a 1999 - 2000 time-frame.

Emission data are given only in respect of water pollution, from which the main environmental issues associated with the activities carried out in this sector arise.

Emissions factors have been calculated from wastewater volume, measured wastewater concentration at the outfall to public sewer (after flow balancing only) and textile product throughput over a corresponding time-frame. There are typically wide variations in the composition of wastewater due to the predominantly batch nature of the dyeing process used and natural variation in the fibre. Data available from longer term measurements have been preferred, as individual measurements made on a few batches of material are unlikely to reflect long term trends.

The emissions have been quantified in terms of the following environmentally significant parameters:
- Chemical Oxygen Demand (COD)
- Suspended solids (SS)
- Metals (copper, chromium, cobalt, nickel)
- Organochlorine pesticides (HCH, dieldrin, DDT)
- Organophosphorus pesticides (diazinon, propetamphos, chlorfenvinphos)
- Synthetic pyrethroid insecticides (permethrin and cyfluthrin from mothproofing agents) and cypermethrin (from sheep-dip ectoparasiticides).-

3.6.1.1 Loose fibre dyehouses

LOOSE FIBRE DYEHOUSE		Units/tonne (textile product)	Site A	Site B	Site C
PROCESS INPUTS					
Water		m³	34.9	28.7	53.5
Energy, total		GJ	11.18	15.52	15.64
Dyeing & finishing chemicals	Basic chemicals	kg	36.39	28.81	72.11
	Dyes total, of which *chrome+metal complex*	kg	7.65 *2.90*	3.60 *2.10*	4.39 *2.81*
	Dyeing aux. of which *Levelling agents*	kg	10.27 *5.67*	15.84 *5.85*	4.30 *2.53*
	Finishing aux. total, of which *mothproofer active*	kg	0.40 *0.18*	5.89 *0.78*	0.08 *0*
PROCESS OUTPUTS					
Emissions to water: COD		kg	20	28	20
SS		kg	0.05	0.30	1.03
Metal total, of which:		g	67.33	54.85	2.97
- Chromium		g	66.08	52.78	1.67
- Copper		g	0.47	1.19	0.15
- Cobalt		g	0.78	0.88	1.15
SPs total, of which:		g	0.462	0.172	0.015
- Permethrin (from mothproofer)		g	0.458	0.165	0.010
- Cyfluthrin (from mothproofer)		g	n.d.	n.d.	n.d
- Cypermethrin (from raw fibre)		g	0.004	0.007	0.005
OCs total (from raw fibre) [a]		g	0.003	0.007	0
OPs total (from raw fibre) [b]		g	0.811	0.664	0.722
Waste water		m³	27.7	24.46	45.44
Source [ENCO] Notes: n.d. = not detectable in the effluent [a] Sum of: HCH total; Dieldrin; DDT total [b] Sum of Diazinon, Propetamphos, Chlorfenvinphos					

Table 3.16: Overview of emission and consumption levels for three typical loose fibre dyehouses

Water & energy consumption

As a general consideration, it has to be noted that the water consumption figures reported in the table above are inevitably higher than the theorethical values obtained considering the liquor ratio of the machines (which is typically 10:1 for loose fibre dyeing) and the subsequent water additions for rinsing or other after-treatments. These values include water used to raise the steam for heating the liquor, spillage on loading and re-loading, cooling additions made for shade matching, etc.

The three loose fibre dyehouses referenced in Table 3.16 indicate a wide range of specific water consumption figures, attributable to different working practices and water recycling measures. Plant A operates a standard dyeing regime consisting of the dyeing cycle followed by rinsing in a separate bath, with all waste liquors discharged directly to drain. Site C operates similar machinery, but rinses and cools dyeings using the overflow methods in which clean water is allowed to overflow from the dyeing machine to drain. Site B recycles a proportion of both the dyeliquor and rinse liquor and has the lowest overall water consumption factor.

Reported data on energy consumption account for the operations of raising the temperature of the dyeliquor from ambient to boiling point and evaporating water from the textile during drying.

Heating 1 kg of water to $100^{O}C$ requires: 0.00042GJ
Evaporating 1kg of water requires: 0.00260GJ

Therefore, the theoretical requirements for loose fibre dyeing and drying would be:
- for dyeing (heating 10kg of water per kg of textile): 4.2GJ/tonne
- for drying (water content when the fibre enters the dryer: 0.5kg/kg textile): 1.3GJ/tonne.

The total theoretical energy requirement is, therefore, 5.5 GJ/tonne of textile. In practice the energy requirements of individual plants are significantly higher than the above figures would suggest, due to losses in steam generation and transmission and the use of process water at modest temperatures in rinsing and the application of finishes.

Data presented in Table 3.16 fall within a narrow range despite their widely differing water consumption figures. This is understandable on the basis that all three enterprises consume energy in essentially the same way (to raise the temperature of the dyebath and to dry the wet fibre) and that the additional water usage arises from cooler rinsing operations.

Chemical Oxygen Demand

The organic substances discharged in the wastewater and the corresponding COD emission factors reflect the pattern of usage of dyestuff and dyeing auxiliaries. In loose fibre dyehouses the use of metal-complex dyes is predominant. Most of the dyehouses employ levelling agents, but in contrast to yarn dyeing there is no requirement for polyamide reserving agents.

COD emission factors for the three selected mills range from 20 to 30 kg/tonne of processed fibres. A portion of this COD load, however, is attributable to contaminants already present on the incoming raw material. Scoured wool may contain variable amounts of residual wool grease and detergent, depending on the efficiency of the wool scouring process. Synthetic fibres on the other hand contain residual spin finish whose content in oxygen-demanding material varies depending on the lubricant employed.

The figures in the table below come from laboratory analyses performed by submitting samples of raw material to aqueous extraction procedure to simulate the removal of the contaminants in the first wet process.

Material	First wet process	COD equivalent of removable contaminants (Kg /tonne)
Scoured wool fibre	Loose fibre dyeing	5 – 15
Nylon fibre (as received)	Loose fibre dyeing	30 – 50
Source: [ENCO]		

Table 3.17: Concentrations of compounds present on raw loose fibres, which contribute to the wastewater COD load

Synthetic Pyrethroids from Mothproofer

The indicated emission factors of mothproofer active agent permethrin show a wide range of values, which reflects very different procedures on each site.

Site A operates a conventional mothproofing process in which each of the dyeings that will ultimately make up a bulk blend is treated at a level consistent with the desired overall application rate (typically 100 mg permethrin/kg fibre). Wastewater from each dyeing is discharged.

Site B operates with an over-treatment and dyeliquor re-circulation system designed to minimise mothproofer emissions. In this process only some of the fibre (perhaps as little as 10 % of the total blend weight) will be mothproofed, this portion receiving a correspondingly high application rate. Spent dyebaths from this process contain correspondingly high levels of permethrin, but they are retained in a holding tank and reused for the next sequence of dyeings or are used to dye fibre which requires no treatment. Overall the wastewater residues from this sequence of operations are significantly lower than from the conventional process. The remainder of the blend receives no treatment and spent process liquor from these dyeings contains no residual mothproofer. Finally the over-treated and un-treated fibre is intimately mixed during mechanical processing and yarn formation, resulting in an insect-resistant yarn with the correct average treatment level.

Site C does not carry out mothproofing. The low levels of permethrin detectable in the effluent arise from the dyeing of fibre which is inadvertently contaminated with low levels of permethrin. The source of this contamination is difficult to identify but may arise through the reprocessing of previously treated waste fibre, contamination during the raw wool scouring process when this process is used to mothproof scoured wool, etc.

Data presented in Figure 3.8 also illustrate typical permethrin emissions from a site operating with the conventional means of mothproofing, in which mothproofing is carried out in loose fibre dyeing. The resultant yarn is subsequently scoured to remove lubricant, contaminating the scour liquors with mothproofer. This process is no longer commonplace in the UK, where the majority of manufacturers using this production route are obliged to apply mothproofing agent from a special low-volume application bowl at the end of the scouring line, in order to meet local wastewater emission limits.

Metals

Reference Sites A and B use the highest proportions of afterchrome dyes, which is reflected by mill effluent loads in the range of 53 – 66g/tonne of dyed fibre. Note that loads are derived from effluent parameters and total dyed fibre and therefore do not represent loads from individual dyeings carried out with these materials, which are obviously higher (approximately 90g/tonne fibre for chrome dyes and 10g/tonne fibre for complex dyes).

Organochlorine pesticides and organophosphorous & synthetic pyrethroid ectoparasiticides

Meaningful quantitative data on the concentrations of the organochlorine (OC) pesticides present in mill effluent are difficult to obtain, not least because the levels present are often below the lower limit of detection of the analytical procedure, but also because the occurrence of these compounds on wool is intermittent and they therefore occur in effluents in an unpredictable pattern.

The reported data have been calculated from raw fibre consumption and data relating to the partition of the different pesticides between wastewater and the fibre for different wet processing sequences. Fibre consumption is identified by country of origin and the initial pesticide content calculated using data from the ENco wool & hair pesticide database. As an example, annual average pesticide content of scoured wool processed at six reference sites is reported in Table 3.18.

Average OC pesticides [a] (gm/tonne fibre)	Average OP Pesticides [b] (gm/tonne fibre)	Average SP pesticides [c] (gm/tonne fibre)
0.07	2.71	0.79
0.05	3.00	0.81
0.13	2.30	0.50
0.24	2.50	0.69
0.01	1.63	0.35
0.05	3.32	0.17

Source [ENCO]
Notes:
[a]   Sum of HCH isomers, HCB, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, DDD, DDT
[b]   Sum of propetamphos, diazinon, dichlofenthion, chlorfenvinphos
[c]   Sum of cypermethrin, cyhalothrin, deltamethrin

Table 3.18: Annual average pesticide content of scoured wool processed at six reference sites

The annual pesticide mass released in effluent is then calculated by applying a wastewater-fibre partition coefficient for each of the wet processes used. These coefficients were determined from trials with fibre selected to have a high initial pesticide loading, thus ensuring analytical detection at each processing stage. The same approach is also applied for OP and SP pesticides. Partition values for the most relevant OC, OP and SP pesticides are reported in Figure 3.7.

Recent studies indicate that individual OPs, (propetamphos, diazinon and chlorfenvinphos) and the SP cypermethrin behave differently when subjected to the wet treatments common in carpet fibre processing. [ENCO]

In high-temperature dyeing processes these compounds partition between the dyeliquor and the fibre in ratios which approximate to their relative water solubility, thus cypermethrin (solubility 0.009mg/l) is generally present at lower concentrations than propetamphos (solubility 110mg/l). Diazinon behaves somewhat differently and is degraded at the pH values used in wool dyeing, being present neither on the fibre nor in the effluent on completion of dyeing. This observation has been made only recently (ENCO, 2000, unpublished results) but explains why many dyehouse effluents appear to contain appreciably less diazinon than propetamphos when the average content of scoured wool is the reverse.

Dyeing also causes hydrophobic pesticides to migrate from the surface into the micro-structure of the wool fibre. Scouring ecru (undyed) yarn thus releases more of these compounds into the effluent than does the scouring of yarn spun from previously dyed fibre.

Where they can be measured, emissions of OC pesticides fall in the range 0.001 - 0.025gm/tonne of processed wool, reflecting the background environmental contamination responsible for their presence on the fibre. The OP and SP ectoparasiticides are present at higher levels as a result of their registered use as sheep medicines.

3.6.1.2 Yarn dyehouses

YARN DYEHOUSE		Units/tonne (textile product)	Site H	Site J	Site K	Site L
PROCESS INPUTS						
Water		m^3	22			17.9
Energy, total		GJ	23.27			11.9
Yarn scouring chemicals	Basic chemicals	kg	16.2		8	
	Detergents	kg	4.6	0.45	6	
	Mothproofer active	kg	0	0	1	
Dyeing & finishing chemicals	Basic chemicals	kg	144	103	56.6	38
	Dyes total, of which *chrome+metal-complex*	kg	5.6 *0.3*	12.3 *3.7*	7.1 *0.25*	11.4 *7*
	Dyeing aux. of which *PA reserving agents*	kg	33.6 *16.4*	58.2 *37.4*	25.0 *18.7*	47.9 *34.3*
	Finishing aux. total, of which *mothproofer active*	kg	1.0 *0.5*	0.4 *0.1*	1.6 *0.6*	2.2 *0*
PROCESS OUTPUTS						
Emissions to water: COD		kg	16.3	25.2	?	59
SS		kg	0.26	2.04	?	1.85
Metal total, of which:		g	0.8	3.54	?	22
- Chromium		g	0.1	2.19	?	21.2
- Copper		g	0.41	0.26	?	0.10
- Cobalt		g	0.07	0.82	?	0.09
- Nickel		g	0.28	0.27	?	0.36
SPs total, of which:		g	0.212	0.039	?	0.277
- Permethrin (from mothproofer)		g	0.24	0.035	?	0.023
- Cyfluthrin (from mothproofer)		g	0	0.002	?	0.24
- Cypermethrin (from raw fibre)		g	0.012	0.002	?	0.014
OCs total (from raw fibre) [a]		g	0.029	0.005	?	0
OPs total (from raw fibre) [b]		g	0.142	0.426	?	0.41
Waste water		m^3	16.6	23	?	17.9
Source [ENCO] Notes: [a] Sum of: HCH total; Dieldrin; DDT total [b] Sum of Diazinon, Propetamphos, Chlorfenvinphos						

Table 3.19: Overview of emission and consumption levels for four typical carpet yarn dyehouses

Water & energy consumption

Among the four sites analysed, data on water & energy consumption are available only for Sites H, K and L. Nevertheless they are useful to represent a range of yarn dyeing processes, resulting in quite different water requirements. Both sites H and K pre-scour yarn in hank form and hank dye in Hussong type machines (L.R. 15:1). On Site H, the bulk of production is not rinsed following dyeing, while on Site K the reverse is true. In the former case water consumption amounts to 22m^3/tonne of product while on the latter site 53m^3/tonne is required. Site L dyes yarn on packages (L.R. 12:1), without pre-scouring; in this case the water and energy requirements are significantly lower than for hank dyeing.

The considerations outlined for loose fibre dyeing regarding the meaning of the total water and energy consumption values reported in this report with respect to the corresponding theoretical requirements are also valid for yarn dyeing.

The theoretical energy requirements for yarn dyeing can therefore be defined as follows:
- yarn package dyeing (heating 10kg of water per Kg of textile): 4.2GJ/tonne
- hank dyeing (heating 15kg of water per kg of textile): 6.3GJ
- yarn drying (water content when entering the dryer: 0.5kg/kg textile): 1.3GJ/tonne.

The total theoretical energy requirement is, therefore, 5.5 and 7.6 GJ/tonne of textile for package and hank dyeing respectively.

The energy requirements of individual plant are two to three times higher than the above figures for the same reasons as those mentioned earlier for loose fibre dyeing. The wide range of values also reflects the types of processes employed on each site. Sites H an K operate hank dyeing equipment and pre-scour the yarn before dyeing, whilst Site L operates with package dyeing equipment at a liquor ratio closer to that employed in loose fibre dyeing.

Data from the survey record only total energy consumption in wet processing and it was not possible to estimate reliably the proportions attributable to dyeing and drying. However, values are available from other studies (Table 3.20) for hank scouring, dyeing and drying processes and package dyeing of textiles. These sources typically indicate an overall energy requirement of between 17 and 28 GJ/tonne of textile for the hank dyeing route and 5 to 18 GJ/tonne when package dyeing. The values recorded in the industry survey fall within this range, so can be taken as representative of current industry practice. In the majority of cases, approximately 75 % of the energy use arises from scouring and dyeing and 25 % from the drying operations.

		Process	Energy requirement (GJ/tonne textile product)	Percentage of total energy requirement %
Hank dyeing route		Continuous hank scouring	3.0 - 5.0	18
		Hank dyeing	10.0 - 16.0	57
		Hank drying	4.5 - 6.5	25
		Total	*17.5 - 27.5*	*100*
Package dyeing		Package dyeing	5 - 18	
Source: UK, Department of the Environment, Energy Efficiency Best Practice Programme Good practice guide No. 168				

Table 3.20: Literature values for practical energy requirements in yarn dyeing

Chemical Oxygen Demanding Load

The reported figures record the COD load of the final effluent. It is possible, however, to estimate that the proportion of COD arising from the scouring process accounts for up to 80 % of the total. The total load from scouring is not distributed evenly between scour bowls and, in most installations, bowls 1 and 2 contain up to 95 % of the residues. Note that this operation is not carried out at Site L. (How can be explained that Site L is the one with the highest COD load, when it uses the package dyeing process, which is not reported to use either spinning oils or scouring?)

In the yarn dyeing sector, acid dyes predominate due to the requirement for level dyeing and may account for up to 90 % of total usage on any given site. Individual manufacturers may dye yarn from specific market segments which require a higher degree of fastness and the use of metal-complex and reactive dyes. The use of chrome dyes is normally restricted to the production of black and navy shades and the proportion of these dyes is typically no more than

5 % of total usage. Among the dyeing auxiliaries consumed, a significant percentage is represented by polyamide reserving agents.

In assessing the COD load in yarn dyeing effluents, it has to be pointed out that, besides the chemicals and auxiliaries used by the finisher, fibrous raw materials carry an additional amount of organic contaminants into the process stream. Synthetic fibres, in particular, invariably contain spinning lubricants which are often based on mineral oils. These substances are largely removed during the first wet process to which the fibre is subjected, thus contributing to a proportion of the chemical oxygen demand present in wastewater.

Table 3.21 indicates the approximate loading of COD-contributing compounds present on raw materials entering the production chain. The figures were generated by subjecting samples of the raw material to a simple aqueous extraction procedure to simulate the first wet process. Oxygen-demanding chemicals present on spun yarn prior to scouring are related to the quality of the raw materials, as described above, and to the quantity and nature of the spinning lubricant applied by the spinner. Residual COD carried forward from yarn scouring into dyeing reflects the efficiency of the scouring process. Inevitably the COD attributable to this source varies widely.

Material	First wet process	COD equivalent of removable contaminants (kg /tonne)
80/20 wool nylon yarn "in oil"	Yarn scouring	40 – 80
80/20 wool nylon yarn Scoured for dyeing	Yarn dyeing	10 – 20
Source: [ENCO]		

Table 3.21: Concentration of compounds present on raw fibre, which contribute to the wastewater load

Synthetic Pyrethroids from Mothproofer

Emission levels associated with yarn dyeing are generally a function of dyebath pH and auxiliary usage. Dyeing under the strongly acidic conditions associated with the use of level dyeing acid dyes produces the lowest feasible residues, while dyeing under the more neutral conditions necessary when using metal-complex dyes will produce significantly higher residues. Emission factors can vary from 0.7 g/tonne of yarn, under acid levelling conditions, to 9.2 g/tonne when dyeing at pH>4.5 with metal-complex dyes. Moreover, some dyeing auxiliaries, particularly levelling agents, can exert a significant retarding action with respect to mothproofer uptake.

Of the companies involved in the survey, Site H shows a higher permethrin emission factor (0.24 g/tonne) than Site J (0.035 g/tonne). The difference cannot be attributed to the classes of dyestuffs used, however, because the two companies operate in similar conditions, both using predominantly acid dyes. The difference must therefore be attributed to the fact that the consumption of mothproofing agents at Site J (kg/kg of textile) is less than 20 % compared of that at Site H.(?)

Site L does not use permethrin-based mothprofer and residues in its effluent must, therefore, arise from the processing of previously contaminated fibre (how (?).

Metals

Residual metals in the wastewater invariably mirror dyestuff usage patterns. In particular, the levels of chromium reflect the usage of chrome dyes. In yarn dyeing the use of acid and metal complex dyes is predominant. The emission levels of chromium are therefore not as high as for loose fibre dyeing. The highest emission factor corresponds to Site L, where metal-complex and chrome dyes (in lower percentage) account for 60 % of the total amount of dyestuffs consumed.

Organochlorine pesticides and organophosphorus & synthetic pyrethroid ectoparasiticides

The considerations outlined for loose fibres are also valid for yarn dyehouses. The partition factors for yarn dyeing processes are reported in Figure 3.7

Figure 3.7: Wastewater: fibre partition coefficients for OC, OP and SP pesticides in wet processing
Source: [ENCO]

OC pesticides	gm/tonne	0.01 - 0.25
OP pesticides	- ., -	1.6 – 3.5
SP pesticides	- ., -	0.17 – 0.8
Chemical oxygen demand	kgO$_2$/tonne	5 - 50

Clean Raw Fibre

Wastewater (m^3/tonne product):	34
Chemical Oxygen Demand (kg/tonne product):	18
Suspended Solids (kg/tonne product):	0.2

Permethrin (gm/tonne treated fibre):	0.10
Chromium from Afterchrome dyes (gm/tonne dyed fibre):	90
Chromium from premetalised dyes (gm/tonne dyed fibre):	10

Energy	GJ/tonne	11 – 16
Water	m^3/tonne	28 – 54
Inorganic salts	kg/tonne	6 – 20
Acids and bases		6 – 25
Dyeing auxiliaries		4 – 27
Dyes: Total		3 – 13
of which afterchrome		0.4 – 1.8
Finishes: Total		0.4 – 1.8
of which mothproofer active		0.02 - 0.8

Loose fibre dyeing and Drying

Spinning lubricant	kg/tonne	21 – 53

Conversion to yarn

Approx. COD & S. Solids Distribution in scouring:	Wastewater (m^3/tonne product):	5
bowl 1: 66 %	Chemical Oxygen Demand (kg/tonne product):	104
bowl 2: 27 %		
bowl 3: 4 %		
bowl 4: 3 %	Suspended Solids (kg/tonne product):	3.0

Permethrin from stock dyed & mothproofed yarn (gm/tonne yarn):	14
Permethrin from contaminated Ecru yarn (gm/tonne yarn):	0.4

Dry spun product

Energy	GJ/tonne	3 – 5
Water	m^3/tonne	4 – 8
Alkali salts	kg/tonne	6 – 16
Detergent		1 – 13
Reducing agents (setting only)		3 – 6
Finishes: (mothproofer active)		0.03 - 0.2

Yarn scouring of ecru yarn and dyed yarn

Loose fibre dyed & scoured product

Wastewater (m^3/tonne product):	22
Chemical Oxygen Demand (kg/tonne product):	20
Suspended Solids (kg/tonne product):	1.5

Permethrin from dyeing under acid levelling conditions (pH 3.5 – 4) (gm/tonne product):	0.7
Permethrin from dyeing under premetalised dyeing conditions (pH > 4.5) (gm/tonne yarn):	9.2

Energy	GJ/tonne	11 – 23
Water	m^3/tonne	17 – 53
Inorganic salts	Kg/tonne	24 – 116
Acids and bases		10 – 35
Dyeing auxiliaries		25 – 70
Dyes: Total		5 – 15
of which afterchrome		0.1 – 1.4
Finishes: Total		0.4 – 2.4
of which mothproofer active		0.02 - 0.8

Yarn dyeing and drying

Yarn dyed product

Figure 3.8: Diagram showing the ranges of inputs to and output from wool and wool-blend carpet yarn mills

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

4.1 General best management practices

4.1.1 Training

4.1.2 Equipment maintenance and auditing

4.1.3 Machinery checking and leaks control

4.1.4 Storage and handling of chemicals

4.1.5 Automated preparation and dispensing of chemicals

4.2 Quality management of incoming substrate

4.3 Selection/ substitution of chemicals used

4.3.1 Substitution of alkyl phenol ethoxylate detergents

Description

Many surfactants give rise to environmental concerns due to their poor biodegradability, toxicity (including that of their metabolites) and potential to act as endocrine disrupters.

Concerns currently focus on alkyl phenol ethoxylates (APEO) and in particular on nonyl phenol ethoxylates (NPE), which are often contained in the formulations of detergents and many other auxiliaries.

Alkylphenol ethoxylates are themselves believed to be endocrine disruptors and to cause feminisation of male fish. More importantly, however, they produce metabolites which are believed to be many times more potent as endocrine disruptors than the parent compounds. The most potent of these are octyl- and nonylphenol.

Even with highly effective effluent treatment systems, which allow only trivial amounts of APE or their metabolites to enter the aquatic environment, concerns arise from the resultant sludge. Unless these sludges are subject to treatments such as incineration or pyrolysis, capable of destroying the organic material, the APE or their metabolites may enter surface water or ground waters in run-off from composting, spreading of treated or untreated sludges on agricultural land, or in leachate from landfill.

Several countries have already placed restrictions on the use of NPE. Moreover, these surfactants are on the draft list of the 32 "Priority Hazardous Substances" targeted for priority regulatory action under the new Water Framework Directive.

The main alternatives in the textile industry are alcohol ethoxylates (AE).

Main achieved environmental benefits

Reduced amount of potentially toxic endocrine disrupters in the receiving water.

Operational data

AE are already employed in textile industry as detergents in substitution of APEO.

AEs are claimed, however, to be slightly less effective detergents than APEO, which means that higher concentrations and feed rates may be required for equivalent effects. Investigations carried out in the wool scouring sector showed that mills using alkyl phenol ethoxylates used an average of 7.6 g detergent per kg greasy wool (range 4.5 - 15.8 g/kg), while the users of alcohol ethoxylates consumed an average of 10.9 g detergent per kg greasy wool (range 3.5 – 20).

Cross-media effects

AEs are easily biodegradable surfactants and there are no known adverse environmental effects arising from their use. The possibility of foaming in rivers exists in cases where sufficient amounts pass through sewage treatment works unchanged or as partial metabolites with residual surfactant properties. The formation of foam is, however, typical of many other surfactants, including APEO.

Applicability

General applicability throughout the textile industry.

Economics

AEs are 20 – 25 % more expensive than APEO. The fact that they appear to be less effective can further increase the operational costs over those of APEO. However, mills making the change from APEO to AE are more likely to take care to optimise their use.

An example is given for a UK scouring mill which made the substitution in 1996. Annual costs for detergent use were estimated to have increased from EUR 84700 to EUR 103600: an increase equivalent to about EUR 1.09 per tonne of wool processed. In the past few years the cost of APEO has been reduced significantly from EUR 1000/tonne (1997/98) to EUR 700 (1999). As a result the increase in cost involved with the use of AEs could be even higher. [INTERLAINE]

Driving force for implementation

Enforcement of regulations at national and European level.

Reference plants

Many plants throughout the world.

4.4 Low-waste techniques

4.4.1 Use of integrated dirt removal/grease recovery loops in wool scouring plants

Description

As already described in Section 2.3.1.1(see Figure 2.3), a wool scouring plant operating in counter-current mode normally produces three liquid waste streams:
- a dirt-rich flow, from the bottoms of the scouring bowls
- a less concentrated dirty flow, from the bottoms of the rinse bowls
- a grease-rich flow, from the top of the first scour bowl, or from the side tank of the first scour bowl, which receives the liquor removed from the wool as it exits the bowl through the squeeze press.

All of these flows can be partially decontaminated and recycled to the scour, by means of grease recovery and dirt removal loops.

There is no consensus on the best way to operate the loop(s). Some mills prefer to treat the dirt-rich flow and the grease-rich flow separately, whilst others combine the two streams and carry out sequential treatment, first for dirt removal, then for grease recovery.

For grease recovery, plate-type centrifuges are employed. There are usually protected from the abrasive effects of dirt by hydrocyclones in cases where separate rather than sequential grease recovery and dirt removal is practised. The centrifuge produces a top phase, known as "cream", which is grease containing a small amount of water. This "cream" is usually passed to a secondary centrifuge, which produces an upper, a lower and a middle phase. The upper phase consists of anhydrous grease, which can be sold as a by-product. The bottom phase is enriched with dirt and may be passed to the input side of the dirt recovery loop, or to the effluent treatment plant. The middle phase is impoverished in both grease and dirt and may be completely or partially recycled to the scour, by addition to the first scouring bowl. A portion of the middle phase may flow to effluent treatment.

Dirt removal may employ gravity settling tanks, hydrocyclones or decanter centrifuges – or combinations of these methods.

In mills with more than one scouring line, the lines normally share dirt removal/grease recovery facilities.

Main achieved environmental benefits

The implementation of dirt removal/grease recovery loops allows:
- a reduction in water consumption ranging from a minimum of 25 % to a maximum of more than 50 %, taking as reference point the consumption of water of a conventional plant operating in counter-current (between 5 and 10 l/kg of greasy wool)
- a reduction in energy consumption equivalent to the amount of thermal energy carried by the recycled liquor (the liquor temperature is generally about 60 ºC)
- the production of a valuable by-product, that is wool grease
- a reduction in detergent and builder consumption proportional to the water savings achieved
- the conversion of suspended dirt into spadeable sludge
- a reduction of the load (oxygen-demanding substances and suspended solids) sent to the effluent treatment plant, which means a reduction in the consumption of energy and chemicals for the treatment of the waste water. This reduction is proportional to the dirt removal and grease recovery rate achieved.

Operational data

Medium-to-large scouring mills (say 15000 – 25000 tonnes greasy wool per year) employing dirt removal/grease recovery loops should be able to achieve net specific water consumption figures of 2 - 4 l/kg of greasy wool for most types of wool. Both coarse and fine wool scourers in the survey are already achieving these figures. With continuous (24 h) operation, bowl drops should not have to be made more often than once or twice per week.

The amount of grease recovered as sellable by-product in the surveyed companies ranges between 10 and 35g/kg of greasy wool. The best performance for a fine wool scourer is almost 35 g/kg greasy wool and for a coarse wool scourer about 13 g/kg. These recovery rates represent about 25 % of the grease estimated to be present in the wool scoured.

There is probably a maximum amount of grease that can be recovered centrifugally, which is governed by the ratio between hydrophobic and less-hydrophobic grease (top grease and oxidised grease) present on the scoured wool. [INTERLAINE]

Cross media effects

The dirt and part of the grease which is not recovered as by-product may be transferred as pollutants, from water to land.

Applicability

This measure is applicable in all new and most existing wool scouring plants.

For plants scouring hair, or wools giving low yields of poor quality grease, the measure might not be an economically attractive proposition.

The COD concentration of the effluent resulting from the dirt removal and grease recovery loop may be too high for on-site aerobic treatment plants. The installation of a coagulation/flocculation or anaerobic biological treatment before the aerobic biological plant would overcome this problem.

Economics

A calculation of net economic benefit per tonne greasy wool can be done, based on the assumptions reported in Table 4.1. The unit costs refer to the UK situation at the time of the research, therefore they can only be indicative for considerations at European situation.

Benefits per tonne of greasy wool processed	Unit cost
Water saved: 4 m^3	EUR 0.68 /m^3 mains water
Energy saved: 836.8 MJ [a]	EUR 0.00245 /MJ
Detergent saved: 1 kg	EUR 1.40 /tonne
Builder saved: 1 kg	EUR 0.27 /tonne (Na_2CO_3)
Avoided treatment of waste water: 4 m^3	EUR 0.53 /m^3 water discharged [b]
Avoided disposal of sludge: about 150 kg (wet weight)	EUR 0.041 /kg of sludge (wet weight)
Grease produced for sale: - 32.5 kg (fine wool scourers) - 13 kg (coarse wool scourers)	EUR 2 /kg of wool grease [c] (but very variable)
Source [INTERLAINE] except (c), I.M. Russell personal communication Notes: [a] The energy saved to heat water to operating temperature of 60 ºC can be estimated at 209.2 MJ per m^3 of saved water (using direct gas at 90 % efficiency). [b] UK cost (1999) considering only the volume charge. In a real case energy, chemicals, manpower, etc. should be taken into account	

Table 4.1: Estimate of the economic benefits achievable with the installation of integrated dirt removal/ grease recovery loops

It is estimated that the installation of dirt removal/grease recovery loops at a mill processing 15000 to 25000 tonnes/year of greasy wool would cost between EUR 400000 and EUR 800000, depending on the nature, the quality and the capacity of the particular system chosen. The payback time on the installation, ignoring the benefits of reduced effluent disposal costs, would be between 2.04 and 4.08 years. [INTERLAINE]

Driving force for implementation

The driving forces are economic benefit for medium and large mills, especially those processing fine (high grease content) wools. Economic benefit derives from savings in water, energy, sewage treatment and chemical costs and the proceeds from sales of wool grease. Disincentives are the high capital cost, high maintenance costs and complexity.

Reference plants

Many plants throughout Europe (see also survey referred to in Section 3.2).

4.5   Emission abatement techniques

5   BEST AVAILABLE TECHNIQUES

6 EMERGING TECHNIQUES

6 EMERGING TECHNIQUES

7 CONCLUDING REMARKS

8   ANNEX I TEXTILE AUXILIARIES

8.1   Surfactants

The description of surfactants in this section is somehow anomalous because they do not represent a category of auxiliaries, but rather a category of organic compounds. The reason for dedicating a section to these compounds is that they are present in the formulation of most textile auxiliaries (e.g. lubricants, antistatics, wetting agents, etc.). Dealing with them in a common section such as this avoids repetitions in other parts of this annex.

Surfactants are classified as non-ionic, anionic, cationic and amphoteric.

Non-ionic surfactants

Non-ionic surfactants are widely used in the textile industry for various purposes (e.g. as washing/ dispersing agents, as levelling agents, etc.). Some examples of commonly used non-ionic surfactants are:
- fatty alcohol ethoxylates
- fatty amines ethoxylates
- fatty acids ethoxylates
- triglyceride ethoxylates
- alkylphenol ethoxylates.

Ethoxylated fatty alcohols, acids and triglycerides are generally easy to biodegrade. On the other hand, fatty amines and alkylphenol ethoxylates (APEO) are examples of surfactants that are difficult to biodegrade and, due to their solubility in water, they are also difficult to eliminate.

The APEO in particular and the well-known nonyl phenol ethoxylates (NPE), which are the most commonly used surfactants in the group of alkyl phenol ethoxylates, pose serious environmental concerns. APEO degrade by stepwise removal of the ethoxy groups. In this way they form the corresponding alkyl phenols, which are bioaccumulative due to their lipophilic character and poor degradability. Alkyl phenols (particularly octyl- and nonyl phenols) are highly toxic to aquatic life and are reported to influence the reproduction of aquatic species by disrupting the endocrine system. NPE are on the draft list of the 32 "Priority Hazardous Substances" targeted for priority regulatory action under the new Water Framework Directive.

Anionic surfactants

Anionic surfactants commonly used in textile processing are:
- sulphates (e.g. alcohol ethoxysulphates, alkanolamides sulphates, sulphated vegetable oils)
- sulphonates (e.g. alkylbenzen sulphonates, sulphonated vegetable oils, naphthalene sulphonates, ligninsulphonates)
- alkyl ether phosphate.

The linear, more biodegradable compounds are the most commonly used (e.g. alkylbenzene sulphonates, fatty alkyl sulphates, etc.). Examples of recalcitrant anionic surfactants are the lignin sulphonates and the condensation products of naphthalene sulphonic acid with formaldehyde that are widely used as dispersants for vat and disperse dyes.

Anionic surfactants have several advantages: they are good oil emulsifiers and dye dispersants, they are excellent wetting agents and they are not expensive. In turn, they generate high levels of foam and sulphate surfactants are sensitive to calcium and magnesium. [EPA]

Cationic surfactants

Cationic surfactants are relatively uncommon in textile processing. One example is quaternary ammonium compounds used as retarders for cationic dyes, which are water-soluble recalcitrant substances. Cationic surfactants are in general characterised by a very high aquatic toxicity. [EPA]

Amphoteric surfactants

Amphoteric surfactants are not widely used in the textile industry. Their main advantage is the fact that they can be used in alkaline and acid media and in combination with either cationic or anionic surfactants. Nonetheless, they are expensive and their use is required only in specialised situations where wide ranges of compatibility are needed.

8.2   Auxiliaries and finishing agents for fibres and yarns

The names used for these auxiliaries in this section are taken from the TEGEWA nomenclature [TEGEWA nomenclature, 1987].

Within this class are included those organic compounds that are applied to the fibre during its manufacturing and yarn formation processes. They are classified as follows:
- spinning solution additives and spinning additives, spinning bath additives
- preparation agents for primary spinning
- preparation agents for secondary spinning (conditioning agents and lubricants)
- coning oils, warping oils and twisting oils.

Special attention is given to them because they are removed during textile pretreatment, in some cases contributing to a significant proportion of the emissions to water and to air at the finishing mills.

The general chemical composition of preparation agents is based on four main classes of components, whose relative amount changes depending on the function of the specific preparation agent:
- lubricants (slippery agents)
- emulsifiers
- wetting agents
- antistatic agents
- additives (e.g. biocides, antioxidants, agents for the compactness of the thread).

Lubricants (slippery agents)

Typical applied lubricants are:
- highly refined mineral oils, so-called white oils (mixture of hydrocarbons with $C_{12} - C_{50}$ chain length, having a range of boiling points between 220 ºC and 450 ºC); their use is strongly declining
- fatty acid triglycerides (refined natural oils)
- ester oils (e.g. butyl stearate, tridecyl stearate)
- EO/PO-adducts
- silicones.

Mineral oils are hardly biodegradable, but easily removed by absorption. Since their boiling temperatures range between 220 and 550 ºC, they smoke and give rise to air emissions during high-temperature treatments. Nevertheless, due to their low cost, they are still widely used as lubricants.

Esters oils are usually esters of fatty acids (lauryl, stearyl acid) with fatty alcohols, fatty alcohols or polyhydroxylic alcohols. Ester oils are used as lubricants as an alternative to mineral oils. Compared to mineral oils, ester oils are more thermally stable, biodegradable and easy to emulsify. They are increasingly substituting mineral oils in primary spinning while, in secondary spinning, mineral oils still have the highest market share.

EO/OP copolymers are used as lubricants for texturised chemical fibres because they do not interfere with the process as mineral oils do.

Their chemical structure can be schematised as follows:

$S-(EO)_x-(PO)_y-B$
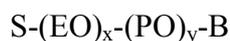
S = starting component which can be short-chain alcohols (e.g. C_4-), polyoles, organic acids or primary amines;
B = block component which can be ethers (OR), esters (OCOR), acetales (CHR'OR) or OH

The high molecular EO/PO-adducts (sum of EO and PO units is more than 15 mols) are non- or hardly biodegradable.

Silicones are used as lubricants for elastomeric fibre (elastan). They show the highest level of COD of all lubricants and they are hardly biodegradable. An additional disadvantage is that they are difficult to emulsify and to remove from the fibre. APEO are usually used to remove them and still a quite high percentage (approximately 40 %) remains on the fibre after washing, giving rise to air emissions in the subsequent high-temperature treatments.

Emulsifiers

Anionic and non-ionic surfactants are used as emulsifiers. The main surfactants employed are:

Anionic surfactants: -   sulphonated and sulphated vegetable oils

Non-ionic surfactants: -   ethoxylated fatty alcohols
                                  -    ethoxylated fatty acids
                                  -    ethoxylated sorbitan esters
                                  -    partial glycerides and triglycerides ethoxylated

Wetting agents

These are usually short-chain alkyl phosphates.

Antistatic agents

The anionic surfactants also have anti-electrostatic properties. Mono and diesters of phosphorus pentoxides (mainly their potassium salts) are in use as special anti-electrostatic agents as well as amphoteric surfactants such as sarcosides, amine oxides and sulpho succinates.

Additives

Biocides such as formaldehyde-containing compounds are applied as preservatives with a load of about 50 mg/kg fibres. Heterocyclic compounds (imidazolinone and isothiazolinone derivatives) with a load of about 2 mg/kg fibres are also encountered.

The amounts of active substances added to the fibres and the composition of the applied formulations may vary widely with fibre type and with end-use. A rough overview is given in Table 8.1, but a more detailed description of typical formulations used and loads applied on the substrate is given in the following sections.

		Fibre manufacturing		Yarn manufacturing		Total	
		g/kg substrate	COD mgO$_2$/g	g/kg substrate	COD mgO$_2$/g	g/kg substrate	COD mgO$_2$/g
Flat filament	Non-elastomeric						
	Elastomeric						
	Filament for knitted fabric						
Texturised filament	Non-elastomeric						
	Elastomeric						
	Filament for knitted fabric						
Staple fibres	Non-elastomeric						
	Elastomeric						
	Filament for knitted fabric						
TABLE TO BE COMPLETED							

Table 8.1: Overview of the loads of auxiliary agents applied on the fibre and yarn during its production process

The information given below is based on an updated version of [UBA, 1994].

8.2.1 Spinning solution additives, spinning additives and spinning

Within this group of auxiliaries only those that are washed off during pretreatment operations are mentioned. In this respect, the so-called "modifiers" are most relevant. They are only applied for special viscose qualities (not for viscose common qualities, nor viscose staple fibres). The applied load is around 5 mg/kg fibres. They mainly consist of ethoxylated fatty amines or polyethylene glycol ethers with molecular weights of about 1500. During pre-treatment, more than 90 % of these substances are washed off.

8.2.2 Preparation agents for primary spinning

These preparation agents are applied (mainly as aqueous solutions) during the manufacture of chemical fibres, directly after the spinning process (primary spinning process). They enable subsequent processes such as drawing, twisting, warping, texturising and further spinning (secondary spinning).

The preparation agents give the chemical fibres the necessary slippery properties (optimal friction properties, avoidance of electrostatic charging and cohesion in case of multifilament yarns) not only between the fibres, but also between the fibres and the guide elements of the machines.

The application loads and the characteristics of the formulations applied are given for:
- non-texturised filament fibres (Table 8.2)
- texturised filament fibres (Table 8.3)
- staple fibres (Table 8.4).

Textile substrate	Load [g/kg textile substrate]	Explanations
PES	5 – 10	The content of lubricants is 40 - 70 %, the remaining fraction consists of emulsifiers (mixtures of non-ionic and anionic surfactants such as fatty alcohols and fatty acids ethoxylates, sulphonated and sulphated vegetable oils), wetting agents (short chain alkyl phosphates), anti-static agents (e.g. mono and diesters of phosphorous pentoxides, sarcosides, amine oxides and sulphosuccinates)
PA	8 – 12	Same composition as above
CA	20	The content of lubricants in the formulations is about 60 - 85 %. Less refined mineral oils can be used than for PES and PA fibres
CV	10	
PP	5 – 15	Preparation agents consist of 100 %surfactants (typically 90 % fatty acid and fatty alcohol ethoxylates and 10 % phosphoric esters as anti-electrostatic agents)
EL	30 - 70	Preparation agents mainly consist of dimethyl siloxanes
Source: [UBA, 2001] Notes: The reported loads relate to the quantity of active substance, not to the quantity of applied aqueous emulsion		

Table 8.2: Load of preparation agents on non-texturised filament yarns (flat yarns)

Textile substrate	Load [g /kg textile substrate]	Explanations
PES	3 - 5	Spinning preparation agents consist of 90 % EO/PO-adducts. As with flat filaments, they contain non-ionic and anionic components (see Table 8.2)
PA	3.5 – 5.5	Preparation agents are based on EO/PO-adducts as well as on ester oils (mineral oils are not used).
	7 - 12	In the case of yarns for carpets. In the past preparation agents consisted of emulsified mineral oils, but today these formulations are very rarely used. They have been substituted by ester oils (trimethyl propane ester and pentaerythril ester) applied together with non-ionic surfactants
PP	8 – 12	The preparation agents consist of 100 % surfactants (the same used for flat filaments - see Table 8.2)
	8 - 15	Load used for carpet yarns
Source: [UBA, 2001] Notes: The reported loads relate to the quantity of active substance, not to the quantity of applied aqueous emulsion		

Table 8.3: Load of preparation agents applied on texturised filament yarns (texturised yarns)

Textile substrate	Load [g /kg textile substrate]	Explanations
PES - CO-type - WO-type	 1 – 1.8 2 – 2.5	They consist of 50 – 80 % phosphoric esters and their salts and of 20 – 50 % non-ionic surfactants such as fatty acid ethoxylates and fatty alcohol ethoxylates
PA	4 – 6	PA stable fibres are normally used for carpet yarns. Their preparation agents have compositions similar to those used for PES. Mineral oils and ester oils can also be part of the recipes
CV	3 – 6	Non-ionic surfactants (fatty acid ethoxylates) are used; fatty acid soaps and phosphoric ester salts are additional typical ingredients
PP	5 – 10	The formulations have the same composition as those used for filament yarns (see Table 8.2)
PAN	3 - 8	Different types of formulations are used (e.g. polyamine fatty condensates, short-chain quaternary ammonia compounds). These compounds are difficult to remove in the subsequent processes. Anionic systems as well as non-ionic systems are applied (the same used for PES).
Source: [UBA, 2001] Notes: The reported loads relate to the quantity of active substance, not to the quantity of applied aqueous emulsion		

Table 8.4: Load of preparation agents applied on chemical staple fibres

8.2.3 Preparation agents for secondary spinning (conditioning agents and spinning lubricants)

For these agents there is no clear definition. In the following, preparation agents for secondary spinning of synthetic stable fibres and cotton are referred to as "conditioning agents", while preparation agents for wool will be referred to as "spinning lubricants".

Lubricants are applied to natural fibres to assist efficient mechanical processing during yarn manufacturing (spinning).

Conditioning agents are required also during secondary spinning of synthetic fibres, when the fibres have been previously submitted to bleaching or dyeing processes. The initial applied amount is lost, in fact, during these processes. (?)

The chemical composition of conditioning agents for synthetic fibres is similar to that of the preparation agents used for primary spinning of staple fibres (see Table 8.2). The load ranges between 1 and 5 g/kg fibres.

The loads for cotton, viscose staple fibres and wool are reported in Table 8.5.

Textile substrate	Load [g /kg textile substrate]	Explanations
WO and CO-wool-type; (staple fibre length is > 60 mm) (?)	30	Load applied during "oil spinning" of carded yarns. The used lubricants consist of technical white oils (ca. 80 %) and compounds such as EO/PO-adducts, fatty alcohols, fatty acids, polyoles (?)
	8 – 10	Load applied during "dry spinning" of carded yarns without subsequent dyeing
CO or CV	4	For spinning many recipes are in use, mostly containing white oils and ester oils (30 – 40 %) and non-ionic surfactants. Oil-free systems are also available.
Source: [UBA, 2001] Notes: The reported loads relate to the quantity of active substance, not to the quantity of applied aqueous emulsion		

Table 8.5: Load of conditioning agents and lubricants applied on cotton, viscose (stable fibres) and wool

If further processing of dyed yarns or flocs is foreseen (?), an additional amount of conditioning agents (3 - 5 g/kg) is applied normally in discontinuous by bath exhaustion at the textile finishing mill. Thereby the exhaustion rates for PES and PA can be very low (10 – 30 %). On the contrary, they are relatively high for CO and PAN (>80 %).

8.2.4 Coning oils, warping and twisting oils

For processes such as coning, twisting and warping of flat and texturised filament yarns as well as of staple fibre yarns, chemicals have to be applied in order to enhance smoothness, slippery and anti-static properties. Only in exceptional cases, solid paraffin are used (normally liquid formulations are applied).

Oils for coning, texturising, warping or twisting consist of 70 – 95 % white oils and of 5 – 30 % non-ionic surfactants, especially fatty alcohols and fatty acids ethoxylates. Twisting oils often consist of ester oils which can be more difficult emulsify than white oils but their biodegradability is higher. Ester oils are used especially if evaporation has to be avoided or minimised especially during heat setting.

The load of coning oils depends on the further processing and the volume of the yarn. It varies for PES from 5 to 30 g/kg (15 g/kg average). For common PA the load is 5 g/kg and in the case of highly elastic PA it is up to 15 - 20 g/kg. It is reported that imported fabric can have loads of coning oils above 50 g/kg.

The load for warping oils and twisting oils is about 5 g/kg.

8.2.5 Knitting oils

The needles of knitting machines have to be lubricated with so-called knitting machine oils (loss lubrication). They consist of highly refined mineral oils with additives (?). Due to machine losses, up to 5 g/kg of these oils remain on the knit fabric.

8.3 Sizing agents

In this section the following information is presented:
- characteristics of the most common sizing agents
- typical amounts of sizing agents applied on the different substrates (Table 8.6)
- specific COD and BOD_5 values for the most common sizing agents (Table 8.7).

Starch

Starch is the most common natural size and can be derived from various substances, especially corn and potatoes. For high performance weaving mills it is not always suitable. When stored at lower temperatures, it tends to solidify to pulpy mass and lose the hydratation water (retrogradation). This retrogradation leads to poor storage properties, skin formation, formation of deposits on the rollers and reduced adhesive strength. As a result natural starch is commonly used in formulation with other sizes. [ULLMANN'S]

Starch is completely biologically removed, but it is only sparingly soluble in water, the action of animal or vegetable enzymes is needed. These enzymes decompose starch into water-soluble sugars, which are then removed by washing before scouring. As a result starch cannot be recycled and is responsible for most of the COD load in finishing effluents. Moreover, in comparison with other sizing agents, starch must be applied at about twice the rate of carboxymethyl cellulose, because of the poorer sizing effect, thereby leading to a higher COD in the wastewater.

Starch derivatives

Starch derivatives include dextrins, starch esters and starch ethers. They are increasingly replacing natural starches, as their tendency to retrogradation is considerably reduced.

The starch esters most commonly used are the esters with phosphoric acid (phosphate starches) and acetic acid (acetyl starches).

The three most important starch ethers are the hydroxyethyl, hydroxypropyl and carboxymethyl starches.

Starch derivatives based on esters can to a great extent, be biologically reduced, while starches based on ethers are more difficult to biodegrade. However, the great variety of possible chemical modifications makes it possible to produce good slashing agents, which can be virtually completely biodegraded.

Like natural starch, starch derivatives must be also applied at about twice the rate of CMC or synthetic agents, thereby leading to higher COD in the effluents.

Cellulose derivatives (Carboxymethyl cellulose)

Sodium carboxymethyl cellulose (CMC) is the only water-soluble cellulose derivative used as a sizing agent. It is produced by reacting cellulose with sodium hydroxide and sodium chloroacetate, whereby the cellulose polymer is also depolymerised.

CMC is the preferred additive for increasing the adhesion of starch sizes for cotton.

Its chain length and degree of substitution influence the level of biological reduction. However carboxymethylcellulose (CMC) must be classified as being very difficult to reduce. According to [UBA, 1994] only 20 % of the initial amount is eliminated after 7 days. However, it is also reported that CMC can be reduced after long periods of adaptation (>4 weeks) and favourable

conditions (especially higher temperatures). Other sources mentioned by [UBA] state that a biological reduction rate of 60 % is attained after 7 days.

Galactomannan derivatives

Hydroxypropyl and carboxymethyl galactomannan derivatives are water-soluble and easy to remove by washing. In general they can reach high levels of biological reduction (greater than 90 %). However, biodegradability as well as other properties can vary significantly with molecular weight and the mannose/ galactose ratio.

Polyvinyl alcohol (PVA)

Since the monomeric vinyl alcohol does not exist, poly(vinyl alcohol) is produced by the hydrolysis of the poly(vinyl acetate).

The parameters that determine sizing properties are the degree of polymerisation and the degree of hydrolysis. There are two grades: the partly hydrolised grade with a degree of hydrolysis of ca. 88 % and the fully hydrolysed grade with a degree of hydrolysis of ca. 98 %.

Partially hydrolysed PVA grades are preferred for use as sizing agents because they show maximum water solubility and they adhere strongly to non-polar fibres such as PES. In addition to these conventional poly(vinyl alcohol) grades, copolymers with methyl methacrylate or with co-monomers having carboxyl groups are also used as sizing agents.

The degree of polymerisation and the degree of hydrolysis lead to significant differences in terms of biodegradability between the individual types of polyvinyl alcohols. PVA is not acutely toxic to micro-organisms and does not inhibit nitrification. It can be quantitatively eliminated by biological reduction after adaptation of the sludge. The conditions for a 90 % reduction are: relatively high concentrations (20 mg/l), temperature above 18 ºC and a regular load over a long period of time (in wintertime and in the holiday period problems can occur) [UBA]. Given such adaptation, PVA can be classified as having good bioeliminability.

Poly(meth)acrylates

Poly(meth)acrylates show considerable variation in chemical structure (the building blocks can be: acrylic acid, acrylic esters, acrylamide, acrylonitrile, methacrylic acid) and therefore have a very wide range of applications. Hydrophilic monomers like methacrylic acid and its salts and acrylamide give good adhesion to polar fibres and ease of removal by washing. Hydrophobic monomers such as the acrylic esters increase the elasticity of the sizing film and improve the ease of removal from wastewater.

Poly(methacrylates) cannot be reduced biologically, not even after a period of adaptation. Hydrophilic products cannot even be eliminated from the aqueous phase, because they behave as hydrophilic polyelectrolytes.

An improvement is represented by poly(methacrylates) based on esters. In this case, thanks to the presence of hydrophobic groups, the poly(methacrylates) can be 90 % bio-eliminated by adsorption onto sludge after a residence time of 6 – 9 hours (which in practice is secured many times over). [VITO] However, it is important to point out that the bio-elimination curve gives rise to a number of questions about the elimination mechanisms (the elimination mechanisms are not clear).

Polyesters

Polyesters are in general condensates of aromatic dicarboxylic acids with diols (e.g. ethylene glycol, diethylene glycol) and sulphonated aromatic dicarboxylic acids (the latter provides solubility or dispersability in water).

Their biodegradability is bad, but they show a certain degree of bio-elimination [EURATEX]. They are mainly used for sizing flat filament yarns. They are also found as co-components in sizing agents for staple fibres made of polyester blends.

Textile substrate	Load [g /kg warp yarn]	Explanations
Staple fibres - CO and CO/PES	80 – 200	As sizing agents starch and starch derivates, very often in combination with PVA, CMC or polyacrylates are applied. Thereby the ratio of starch/starch derivates to synthetic sizing agents is generally 3:1, for air jet weaving machines 1 : 1. The loads depend especially on the density of warp yarns and on the kind of sizing agent (for starch/starch derivates is significantly higher (150 – 200 g/kg)).
- CV	40 – 120	The load is 60 g/kg average. Normally combinations of all available sizing agents are applied, e.g. polyacrylates in combination with CMC and/or starch derivates
- WO	0 – 20	Woven fabric consisting of wool is usually produced with twisted yarn, so the warp yarns for the weaving process do not need to be sized. In the case of simple yarns (in practice not very relevant) up to 200 g/kg starch/starch derivate in combination with synthetic sizing agents are applied.
Filament yarns - PES	40 – 60	For 90 % of PES flat yarns polyester sizing agents (which can be dispersed) are applied; the rest is sized with modified PVA and polyacrylate.
	80 – 120	This is the load for texturised yarns; about 80 g/kg for polyester sizing agents, about 120 g/kg for PVA and about 100 g/kg for polyacrylates
- PA	20 – 50	Polyacrylic acid is used as sizing agent; 50 g/kg is applied for very thin fabric only
- CV	15 – 30	Mostly in case of linings for which polyacrylates as sizing agents are used
- CA	15 - 60	Polyacrylates and polyvinyl acetate are applied

Table 8.6: Amounts of sizing agents applied on different types of substrates (the figures refer to woven fabrics with 60 % of warp yarn)
[UBA, 2001]

Knowing the loads of sizing agents on the different substrates the calculation/estimation of organic loads as BOD_5 and COD is possible, provided that specific BOD_5 and COD values are available. These values are given in Table 8.7.

Kind of sizing agent	Specific COD-value [mg O_2/g]	Specific BOD_5-value [mg O_2/g]
Starch	900 – 1000 [1]	500 – 600
CMC	800 – 1000 [1]	50 – 90
PVA	c. 1700 [1]	30 – 80 [2]
Polyacrylates	900 – 1650	< 50
Galactomannans	1000 – 1150 [1]	400
PES-dispersions	1450 – 1700	< 50
Protein sizing agents	1200	700 – 800
Protein sizing agents	1200	700 – 800
Source - [UBA, 2001] Notes: [1] Considering the usual moisture content of commodity [2] For non-adapted "inocula"		

Table 8.7: Specific COD and BOD_5 values for the most common sizing agents

8.4   Detergents/ wetting agents

These auxiliaries are mainly used in pre-treatment operations (scouring, mercerising, bleaching) in order to allow:

- thorough wetting of the textile material
- emulsification of lipophilic impurities
- dispersion of insoluble matter and degradation products.

Non-ionic and anionic surfactants are the compounds more frequently used for this purpose (see also Section 8.1). Some examples of products available on the market are listed in Table 8.8. [EURATEX]

Class	Examples of products available on the market	Bio-degradability	Bio-eliminability
Non-ionic	Alcohol and fatty alcohols ethoxylates		
	Fatty acids ethoxylates		
	Alkylphenol ethoxylates (APEOs)	Poor	Toxic metabolites
	Fatty amines ethoxylates		Poor
Anionic	Alkyl sulphonates		
	Alkyl aryl sulphonates		
	Dialkylsulphosuccinates		
	Alkyl carboxylates (e.g. sodium palmitate, -stearate)		
	Sulphated alkanolamides		
Cationic (used?)	Alkylaminammonium derivates		
	Benzyldimethylalkylammonium chloride		
Amphoteric	Amino compounds with carboxylic, sulphate or sulphonic groups		
Source [EURATEX]			

Table 8.8: Typical compounds used as detergents/ wetting agents

8.5   Products containing sequestering agents

The presence of ions of alkaline earth metals (calcium and magnesium) and/or other metals (especially iron) may have important negative effects on various wet processes not only in pre-treatment, but also in dyeing. Purified and softened water is used in textile finishing mills, but often this is not enough and specific auxiliary formulations containing complexing agents need to be added to the baths.

Auxiliaries with this effect can fall under different names (extractants, sequestering agents/ dispersants, etc.) according to the specific process in which they are applied. Commonly used complexing agents are EDTA, NTA, DTPA, phosphonic acid and gluconic acid derivatives.

The hydrogen peroxide stabilisers represent another important category of auxiliaries containing complexing agents.

When bleaching under alkaline conditions with hydrogen peroxide, two secondary reactions are in competition with the desired bleaching reaction:
- the decomposition of the hydrogen peroxide into water and oxygen with no bleaching action ($2H_2O_2 \rightarrow 2H_2O + O_2$)
- the cleavage of the hydrogen peroxide to form radicals OH* according to the reaction: $H_2O_2 \rightarrow 2OH*$. These radicals attack the cellulose fibre starting with oxidation of the hydroxyl groups and eventually ending with the cleavage of the cellulose molecules, decreasing the degree of polymerisation. This reaction is catalysed by heavy metals such as iron, manganese, copper and cobalt.

In order to inhibit these reactions, bleach stabilisers, containing sequestering agents, must be used. EDTA, DTPA, NTA, gluconates, phosphonates and polyacrylates are commonly used as stabilisers.

Environmental problems associated with sequestering agents arise from the same properties for which they are used, which is their ability to form stable complexes with heavy metals. EDTA and DTPA in particular form very stable metal complexes. EDTA and DTPA are also poorly eliminable compounds. There is therefore the risk they pass undegraded through the common wastewater treatment system and then eventually release the metals into the receiving effluent.

Concerning the other organic substances used as complexing agents, NTA and gluconates are biodegradable, while phosphonates are substances with very low bio-eliminability that can pass undegraded through wastewater systems (photocatalytic degradation is observed [EURATEX]).

8.6   Dyeing auxiliaries

8.6.1 General characteristics and environmental aspects

Auxiliaries are essential components in dyeing processes. This section describes the ones most commonly used to assist the dyeing process are described. They are presented based on their function in the process as follows:
- wetting, penetrating agents
- dispersing agents
- levelling agents
- acid donors
- antifoaming
- carriers.

Other auxiliaries such as, for example, the complexing agents that are also commonly used in dyeing processes but that can also be encountered in other operations, are described in other parts of this annex.

Commercial products are in general preparations containing several components. These are mainly surfactants, but non-surface-active substances such as water-soluble polymers and oligomers and polymer dispersions are also frequently employed.

With a few exceptions dyeing auxiliaries are released to wastewater. Some of them are biodegradable (e.g. fatty alcohol ethoxylates, linear alkylbenzene sulphonates), while others have poor biodegradability, but they are sparingly soluble in water and are therefore largely eliminated by absorption on the activated sludge in wastewater treatment plants. There is, however, a list of substances that are soluble in water and poorly eliminable in common wastewater systems. Compounds that belong to this category and that are frequently encountered in dyeing auxiliaries are listed as follows:

	Remarks
- Condensation products of beta-naphthalene sulphonic acids and formaldehyde - lignin sulphonates - acrylic acid-maleic acid co-polymers	
- o-phenylphenol derivatives - N-alkylphthalimide derivatives - methylnaphthalene derivatives	Also toxic for aquatic species
- cyanamide-ammonia salt condensation products	
- Polyvinylpyrrolidones	
- Quaternary ammonium compounds	Also toxic for aquatic species
- Ethoxylated fatty amines	
- Alkylphenol ethoxylates	Metabolites of alkylphenol ethoxylates are reported to influence the reproduction of aquatic species by disrupting the endocrine system (see also Section 8.1)

Substances characterised by high acute toxicity that can be encountered in some dyeing auxiliaries (and that have not been mentioned above) are:
- chlorinated aromatic compounds such as trichlorobenzenes or dichlorotoluene (carriers)
- biphenyl derivatives (carriers).

8.6.2 Wetting, penetrating and de-aerating agents

This group of products is perhaps the most difficult to define in terms of technical function. Wetting and de-aerating agents often perform the same function: that of expelling air from the textile assembly contained in the dyebath. The use of penetrating agents is invariably associated with the dyeing of yarns with a high twist factor, where they enhance transport of the dye into the yarn assembly. In this respect it could be argued that they are in fact a levelling agent. All the products in this class are invariably powerful surfactants.

Commonly used commercial products are mainly readily bio-eliminable compounds such as alcohol polyglycol ethers and esters (also in blends with alkane sulphone), but poorly degradable products such as ethoxylated amines can also be encountered.

8.6.3 Dispersing agents

Vat and disperse dye formulations already have a high content of dispersing agents which allow the application of these water-insoluble colourants in the form of aqueous dispersions.

Additional amounts of dispersants are usually added in the subsequent steps of the dyeing process.

Substances commonly used as dispersing agents are condensation products of naphthalene sulphonic acid with formaldehyde, ligninsulphonates and non-ionic surfactants.

Considerations about the environmental properties of these substances are reported in Section 8.6.1 (more general consideration about surfactants can also be found in Section 8.1.

8.6.4 Levelling agents

Levelling agents are used in batch dyeing processes to improve the uniform distribution of the dye in the fibre. They are probably the most important class of dyeing auxiliaries, as a grossly unlevel dyeing is of no commercial value and is difficult to correct. They are employed for different types of fibres, therefore the substances employed can be different. Nevertheless two main groups of levelling agents can be identified: products which have an affinity for the fibre and products which have an affinity for the dye. Products which have an affinity for the fibre compete with the dye for dye-sites on the fibre. In this way they reduce the rate of absorption of the dye and improve their migration. To the second group belong substances that form loosely bound complexes with the dye, reducing its mobility and in some cases neutralising the electrostatic attraction between the dye and the fibre.

The most common substances used as levelling agents are reported below, divided on the basis of the fibre to which they are applied and dyestuff.

Fibre	Dye	Possible components
Cellulose fibres	Vat dyes	Fatty alcohol ethoxylates Fatty amines ethoxylates Polyamide amines Polyvinylpyrrolidone
	Direct dyes	Non-ionic surfactants such as ethoxylated fatty alcohols, fatty amines, fatty acids, alkylphenols or propylene oxide polymers Anionic surfactants such as fatty alcohol sulphates and alkyl aryl sulphates Polyvinylpyrrolidone
Wool	Acid, metal complex and reactive dyes	Ethoxylated fatty amines Quaternary ammonium compounds Other non-ionic surfactants such as ethoxylated fatty alcohols, fatty acids, alkylphenol and fatty mercaptans may also be found in specific products
Polyamide	Acid and metal complex	Anionic, cationic and non-ionic surfactants used for wool Condensation products of aromatic sulphonic acids, alkyl sulphates (also called "PA reserving/ blocking agents")
	Disperse dyes	Non-ionic surfactants
Polyester	Disperse dyes (at HT conditions)	Ethoxylated castor oil, searic acid, alkylphenols Mixtures of alcohols, esters or ketones of medium chain length with emulsifying systems Hazardous carriers were used in the past as levelling agents, today they are no longer used in high-temperature dyeing processes
Polyacrylonitrile	Basic dyes	Quaternary ammonium salts with C_{12}-C_{14} fatty alkyl side chains (also known as retarders) Quaternary ammonium salts with aromatic ring systems

Table 8.9: Typical compounds encountered in levelling agents

Consideration of the environmental aspects associated with the use of these compounds is reported in Section 8.6.1 and more general information about surfactants can be found in Section 8.1.

8.6.5 Acid donors

The so-called acid donors represent a more sophisticated range of formulated products designed to create shifts in dyebath pH. They are hydrolisable acid esters which break down during dyeing, progressively lowering the pH. They are widely used for wool and/or polyamide fibres to control the absorption of anionic dye onto the fibre. They are also employed for cotton and polyester blends when dyeing with disperse and reactive dyes in the one-bath one-step procedure.

Organic acid esters, fatty alcohol ethoxylates and aromatic sulphonates are commonly found in commercial products. They usually have good bio-eliminability.

8.6.6 Antifoaming agents

Formulated products designed to suppress foam formation are used, which do not adversely influence the quality of the resultant dyeing. The majority are based on silicone derivatives.

8.6.7 Carriers

Dyeing accelerants (so-called carriers) are used in batch dyeing of synthetic fibres (particularly polyester fibres) to promote the absorption and diffusion of disperse dyes into the fibre under low-temperature conditions. They are still important for dyeing blended fibres of wool and polyester, as wool cannot withstand dyeing under high temeprature conditions (above 100 ºC). Typical carrier formulations contain 60 – 80 % of active substance and 10 – 30 % of emulsifier and sometimes a small percentage of solvent.

Typical active substances for dyeing accelerants include:
- halogenated benzenes (1,2 dichlorobenzene; 1,2,4-trichlorobenzene; dichlorotoluene)
- aromatic hydrocarbons such as alpha- and beta-methylnaphthalene, diphenyl, etc.
- phenols such as o-phenylphenol, benzylphenol, etc.
- carboxylic acid and their esters such as methyl, butyl and benzyl benzoate, methylsalicylate, phthalic acid and dimethylphthalte
- alkyl phthalimides such as N-butylphthalimide.

Most of the above-mentioned substances are toxic to humans, aquatic organisms and sewage sludge. Hydrophobic carriers exhaust at about 75 – 90 % onto the substrate, while hydrophlic types like phenols derivatives (e.g. o-phenylphenol), benzoate, N-alkylphthalimides and methylnaphthalene are mainly found in wastewater. They are all poorly bio-degradable and they may pass through the wastewater treatment system. On the other hand the carriers that remain on the textile material are partially volatilised during the subsequent heat treatments (drying or fixing processes), thus producing air emissions.

8.7   Printing auxiliaries

8.7.1 Auxiliaries for dye printing

Thickening agents

Thickening agents are essential components of printing pastes. They are responsible for preventing capillary flow between the threads of the fabric, thus inhibiting dye diffusion. Oil/water emulsions, used in the past as thickeners, have been now largely replaced by

formulations similar to those used for warp sizes. Standard components of modern thickeners include natural polysaccharides, both unmodified and chemically modified (e.g. seed derivatives, starch degradation products, alginates) and fully synthetic polymers (mainly based on polyacrylic acid). Thanks to the improvements made in the characteristics of the starting materials, thickening agents are now supplied almost exclusively in cold-soluble form.

8.7.2 Auxiliaries for pigment printing

Thickening agents

Water-in-oil emulsions were widely used in the past as thickeners. They contained up to 70 % of white spirit (mixture of aliphatic hydrocarbons with C_{12}-C_{50} chain length), which resulted in emissions of volatile organic carbon in the exhaust air from drying and curing ovens. Half-emulsion printing pastes (oil in water) are only occasionally employed today. Nevertheless, modern thickeners can still contain approximately 10 % of mineral oils, which are ultimately found in exhaust air. New generation thickeners have been developed which do not contain any volatile solvents. They are supplied in the form of non-dusting granules [BASF].

Current standard thickeners are liquid preparations of synthetic polymers which can be available either as aqueous formulation, completely neutralised with ammonia (with a solid content of 25 %) or as anhydrous, partially neutralised preparations (with a solid content of 60 %). In the latter case it is necessary to add the ammonia to the print paste before use.

Binders

The pigment has no affinity for the fibre. Therefore, in order to coat the pigment and protect it from mechanical abrasion, a binder is added to the printing paste. Binders are in general self-cross-linking polymers which reticulate during the fixation step. They are supplied as aqueous polymer dispersions, based mainly on acrylates and less commonly on butadiene and vinyl acetate.

Fixing agents

Additional fixing agents are sometimes necessary to enhance the level of wet-fastness, especially with smooth fibres such as PES. Melamine-formaldehyde condensates are used for this purpose. In order to reduce the consequent formaldehyde emissions, modified compounds of the same chemical type, but with a low formaldehyde content, are now common.

Plasticizers

Plasticizers are mainly silicones or fatty acid esters, which are used to improve the dry rubbing fastness and give a smooth dry handle to the fabric.

Emulsifiers

In high- and low solvent pigment printing pastes, the emulsifiers serve to stabilise the solvent (white spirit). In solvent-free pigment printing they are used to prevent agglomeration of the pigment, screen blocking and separation of components of the print paste. [ULLMANN'S] Non ionic surfactants such as aryl- and alkyl polyglycol ethers are the most commonly used for this purpose.

8.8   Finishing auxiliaries

8.8.1 Easy-care finishing agents

Easy-care finishing agents are chemical finishes which are applied to woven and knitted fabrics composed of cotton, other cellulosic fibres and their blends with synthetic fibres. Their function is to reduce the propensity of cellulose-containing fabrics for wrinkling when treated under wet and dry conditions and to stabilise them against progressive shrinkage during laundering. Their action is based on the introduction of cross-links between the cellulose molecule of cotton and viscose, thus reducing swellability and extensibility of the fibre (the fabric tends to return to the state in which it was when the cross-links were introduced).

Other names also commonly used for to name these finishing agents are: resin-finishing, wash-and-wear finishing, no-iron, wrinkle resistant, etc.

Recipes for resin-finishing liquors are in general aqueous solutions or dispersions which consist of a cross-linking agent, a catalyst, a wetting agent/emulsifier (mainly a non-ionic surfactant) and a number of additives.

Among the additives a distinction is drawn between those that are used to improve the handle and to compensate the adverse effects of the cross-linking agent and some others that serve to impart additional functional properties to the final textile good (e.g. water-repellents, hydrophilising agents, etc.). Only the first group of additives is discussed in this section while the others, being less specific to this finishing treatment, are described in other parts of this Annex.

Cross-linking agents

The cross-linking agents play an essential role in this finishing treatment: they are also the major components in the formulation (they represent approximately 60 to 70 % of the total preparation).

From a chemical point of view there are three distinct groups:
* cross-linking agents based on melamine and formaldehyde
* cross-linking agents based on urea and formaldehyde
* heterocyclic linking agents based on urea, formaldehyde and various other substances such as diamines and, in particular, glyoxal.

All these products may potentially produce emissions of free formaldehyde and methanol. In particular, formaldehyde is suspected of carcinogenity and its presence in these finishing agents represents a potential risk not only for wastewater and exhausted air, but also for the workplace and the final user of the textile good.

Manufacturers have put much effort into producing cross-linking agents with a low to very low content of free formaldehyde and one compound is also available on the market, which is formaldehyde-free.

Existing cross-linking agents are therefore better classified as:
* formaldehyde-rich
* formaldehyde-poor or very poor
* formaldehyde-free.

The first group includes compounds (so-called "self-crosslinking" agents) like (HOCH$_2$-NH-CO-NH-CH$_2$OH) hydroxymethyl urea and (CH$_3$OCH$_2$-NH-CO-NH-CH$_2$OCH$_3$) (bis(methoxymethyl) urea or the correspondent melamine derivatives (hydroxymethyl melamine and bis(methoxymethyl) melamine).
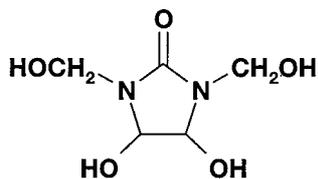
Low to very low levels of free formaldehyde are hetorocyclic compounds (so-called "reactant cross-linking" agents) which are mainly based on the derivatives of the molecule better known as bis(hydroxymethyl)-dihydroxyethylene urea.

Modified derivatives of this compound with methanol and diethyleneglycol are among those reported to have a very low free-formaldehyde content in the product (<0.5 %, but also <0.1 % for some products are now achievable).

Among the formaldehyde-free cross-linking agents, only the compounds based on dimethyl urea and glyoxal have gained a small share of the market [BASF]. In the absence of other sources of formaldehyde such as fixing agents and preservatives, the finishes obtained using these cross-linking agents are formaldehyde-free.
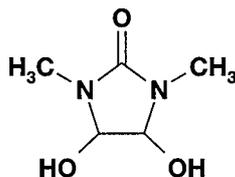
The emissions of formaldehyde, methanol and other volatile organic substances in the exhaust air (from curing and drying operations) and in the workplace (especially with melamine resins) represent the main environmental issue in the application of these agents.

Water pollution is also an issue since these active substances (ethylene urea and melamine derivatives), when in their not-cross-linked form, are water-soluble and in general hardly biodegradable. This problem is, however, restricted to residual liquors, which as a fundamental rule should not be discharged together with the other effluents in order to avoid contamination with these concentrated liquors.

Catalyst

The function of the catalyst in the resin-finishing recipe is to allow the curing reaction to be carried out at the usually employed curing temperatures (130 – 180 ºC) and times.

The most commonly used catalyst is magnesium chloride. In many cases liquid mixtures are used, based on magnesium chloride and organic acids (e.g. alpha-hydroxycarboxylic acids) or inorganic Lewis acids.

Ammonium salts (e.g. chloride, sulphate and nitrate) commonly used in the past, particularly with cross-linkers based on urea and formaldehyde or melamine, are in decline today, following the corresponding decline in importance of these cross-linking agents.

Additives (softeners, stiffening agents, etc.)

As mentioned above, easy-care recipes contain various different additives. Attention is given here only to those whose function is to improve the handle and to offset the reduction in softness, tear strength and abrasion resistance that is produced on the fibre as secondary effect of the cross-linking reaction.

In particular the following groups of additives are worth mentioning:
- products that are added to easy-care recipes to offset the reduction in softness, tear strength and abrasion resistance that is produced on the fibre as a secondary effect of the cross-linking reaction (their content in easy-care recipes is in general in the range of 10 – 40 %): these can be dispersions of polyacrylates, polysiloxanes, polyethylene waxes (partially oxidised polyethylenes), polyurethanes
- product that are added as softeners to improve the handle of the fabric: fatty acid condensation products (cationic softeners) represent the most important group. They can also be supplied as emulsified mixtures with other products (e.g. polyethylene wax)
- products that are used as stiffeners, hand builders: these can be dispersions of polyvinyl acetate, polyacrylate derivatives.

These substances are responsible for emissions of VOCs in the exhaust air from curing and drying operations.

The poor biodegradability of the above mentioned polymer dispersions has also to be taken into account when considering water pollution.

8.8.2 Biocides

Some commonly used biocides are those that are applied in the carpet sector to impart wool fibre lifetime protection against a range of textile pests. These auxiliaries are usually known as mothproofing agents.

Currently used mothproofing agents are formulated from the following active ingredients:
- permethrin (synthetic pyrethroid)
- cyfluthrin (synthetic pyrethroid)
- sulcofuron (halogenated diphenylurea derivatives).

Permethrin-based formulations account for approximately 90 % of the market. Cyfluthrin based products are only available in the UK, while sulcofuron-based products are currently not used to any significant degree.

Permethrin and synthetic pyrethroids in general are reported to have low toxicity to humans but high aquatic toxicity. Dyphenylurea derivatives may exhibit less aquatic toxicity but, in some cases, are less biodegradable [EPA].

Other types of biocides are used in the textile industry as antimicrobial finishes, (e.g. hospital textile material), or as odour suppressants for socks and hosiery. The active substances used for this purpose are most commonly [EURATEX]:
- zinc organic compounds
- tin organic compounds
- dichlorophenyl(ester) compounds
- benzimidazole derivatives
- triclosane
- isothiazolinones.

All biocides give rise to environmental concern when they are discharged in wastewater, because of their toxicity to aquatic life.

8.8.3 Antistatic agents

In this section we refer to the antistatic agents that are applied as functional finishes to selected textile materials for use in static-sensitive environments. They are commonly used in the carpet sector.

From a chemical point of view, formulated products are mostly based on:
* quaternary ammonium compounds
* phosphoric acid ester derivatives.

Quaternary ammonium compounds are highly toxic to aquatic life. Furthermore, the discharge of these substances in wastewater can give rise to high levels of AOX due to incomplete quaternarisation (epichloridrine and chloromethane are often used as initial reagents).

Alkylphosphates and alkyetherphosphates used as antistatic agents are water-soluble hard-to-treat substances which may pass undegraded through common wastewater systems. Nevertheless the use of phosphoric acid esters in antistatic finishing treatment leads to emissions loads that are negligible if compared with other potential sources of this pollutant. According to [EURATEX], in fact, the pollution load released during pretreatment and attributable to antistatics from preparation agents is more than 100 times higher compared to the amount of antistatics discharged in wastewater from antistatic finishing treatments.

On the other hand, for air emissions, the use of phosphoric esters-based antistatics may lead to emissions of non-reacted alcohols (mostly n-butanol, which is very odour intensive) and phosphoric acid in the exhausted air from drying processes.

8.8.4 Flame retardants

The most commonly used flame retardant (FR) agents can be classified as follows:
* inorganic
* antimony trioxide-based FR
* phosphor-organic, reactive
* phosphor-organic, non-reactive.

Inorganic FR agents

Inorganic FR agents, used for cellulosic fibres, are water-soluble salts such as diammonium phosphate, aluminum sulphate, ammonium sulphate, etc. They are applied by padding or spraying followed by drying. They are non-durable retardants, which means that they are removed by laundering. They are therefore suitable only for fabrics which are seldom or never laundered or can be re-treated whenever laundering is carried out.

Other types of inorganic FR agents are used in the wool carpet sector. Although wool may be generally regarded as resistant to burning, the introduction of stringent flammability standards for floorcoverings fitted in aircraft and public service buildings necessitates the use of FR agents in some specific cases. Zirconium and titanium salts have been developed to meet the needs of this specialised market. The first ones, commonly referred to as "Zirpro treatments", are the most widely used (potassium hexafluorozirconate). The do not give rise to significant water pollution.

FR agents based on antimony trioxide (Sb_2O_3)

These types of flame retardant always contain halogenated organic compounds as synergistic agents. These include decabromo- or pentabromophenylether, hexabromocyclodecane, chloroparaffins. These substances may give rise to dioxins during heat treatments. In water they

behave as recalcitrant pollutants, which means that they may pass undegraded through the waste water treatment system. Most of them are persistent and biomagnifying compounds that may undergo metabolic transformations, forming metabolites that may be either water soluble, and therefore excreted, or lipophilic enough to be retained in the organism. Due to their structural similarity to hormones or to other endocrine disrupting compounds they are thought to have potential hormone modulating capacity. Chlorinated paraffins are acutely toxic for aquatic life and contribute to AOX load in the final effluent.

Short-chain chlorinated paraffins and pentabromophenylether are on the draft list of "Priority Hazardous Substances" to be targeted for priority regulatory action under the new Water Framework Directive.

With these particular FR agents, dust emissions of Sb_2O_3 (carcinogenic) from dried pastes and mechanical treatment (cutting, etc.) on finished fabrics have also to be taken into account.

Phosphor-organic, reactive FR agents

Reactive, phosphor-organic FR agents are formulations based on halogen-free phosphonates derivatives. Since melamine resins are often present in the finishing liquor as cross-linking agents, formaldehyde and methanol can be found in the emissions. After padding, the fabric is submitted to a treatment with ammonia, to produce an insoluble polymer within the fibres, and finally it is cured. An after-washing treatment is always necessary with these particular FR agents to remove un-reacted agents and by-products. Organo-phosphorous compounds (which are substances with very low eliminability) are therefore discharged in the wastewater, but also in exhaust air from drying and curing operations.

Phosphor-organic, non-reactive FR agents

Phosphor-organic non-reactive FR agents release organic volatile compounds like glycols, alcohols, glycolether or parts of the active substances [EURATEX].

Organo-phosphorous substances are water-soluble and difficult to remove from the wastewater.

8.8.5 Hydrophobic/ Oleophobic agents

The most commonly applied commercial formulations fall under the following categories:
* fluorochemical repellents
* wax-based repellents (paraffin -metal salt formulations)
* resin-based repellents (fatty modified melamine resins)
* silicone repellents.

Wax-based repellents

These formulations consist of ca. 25 % of a paraffin and 5 – 10 % of zirconium-, aluminium-based salts. They are usually applied to natural and synthetic fibres by padding and drying without curing. The discharge of residual liquors leads to emissions of metals. Concentration can be high in some cases. However, from a global point of view the amounts discharged can be considered negligible compared to emissions of metals from dyeing and printing.

Concerning exhaust air emissions, the presence of paraffin waxes may produce fumes and high levels of volatile organic carbon during heat treatments.

Resin-based repellents

Resin-based repellents are produced by condensing fatty compounds (acids, alcohols or amines) with methylolated melamines. Formulations often also contain paraffin wax. They are applied by the pad-dry-cure process, often together with cross-linking agents in the presence of a catalyst.

Depending on the degree of completeness of the cross-linking reaction and on the temperature employed in heat treatments, different levels of formaldehyde and aliphatic alcohols are found in the exhaust air. The presence of paraffin wax contributes to increased levels of volatile organic carbon in the emissions.

Silicone repellents

These products are generally supplied as aqueous emulsions consisting of polysiloxane-active substances (dimethylpolysiloxane and modified derivatives), emulsifiers, hydrotropic agents (glycols) and water.

In the case of modified polysiloxanes with reactive functional groups, and depending on the drying and curing conditions, cyclic dimethylsiloxanes can be released in the exhaust air.

Fluorochemical repellents

The success of these agents, despite their high cost compared to other types of water repellents, is especially due to the fact that they provide both oil and water repellency.

Commercial fluorochemical repellents are mostly copolymers of fluoroalkyl acrylates and methacrylates. Marketed formulations contain the active agent together with emulsifiers (ethxylated fatty alcohols and acids, but also fatty amines and alkylphenols) and other by-products which are often solvents such as:
- acetic acid esters (e.g. butyl/ethyl acetate)
- ketones (e.g. methylethyl keton and methylisobutyl ketone)
- diols (e.g. ethandiol, propandiol)
- glycolethers (e.g. dipropylenglycol).

Fluorochemical repellents are usually applied in combination with other finishing auxiliaries by a pad-dry-cure process. In many cases they are applied with "extenders" which can be other repellents themselves (e.g. melamine resins repellents or polyisocyanates). The use of these "extenders" allows a reduction in the required amount of fluorochemical, with a corresponding reduction in costs for this treatment.

Finishing treatments with fluorochemical repellents produce emissions of volatile organic compounds in exhaust air. These emissions are attributable to:
- the solvents contained in the formulations (as regards ketons, esters, alcohols, diols)
- the "extenders", which under high-temperature conditions give rise to cracked by-products such as alcohols and ketones, but also oximes and in particular butanoxime (which is carcinogenic)
- the organo-fluoro components which also release cracked fluor-organic by-products.

As regards water pollution, it has to be taken into account that polysiloxanes, melamine and fluorocarbon resins are all characterised by poor biodegradability and bio-eliminability.

8.8.6 Softeners

There are anionic, non-ionic and the most important, cationic softeners.

Cationic softeners are mainly condensates of fatty acid esters /amides but quaternary ammonium compounds are also used.

Other softeners can be:
- paraffin waxes
- polyethylene waxes
- modified silicones
- sulphonated oils or sulphonated fatty esters
- phthlates (butyl, octyl).

Apart from the highly biodegradable sulphonated fatty esters/oils, the other compounds are difficult to biodegrade. In this respect, it has to be considered that the level of exhaustion of these substances is approximately 30 % or even lower in some cases (20 % for polyamide and polyester yarn), which means that high emission loads are produced, especially when these substances are applied in long liquor (batch processes).

Air emissions originate from an average 2 % of volatile organic compounds present in the formulations. Carboxylic acids, alcohols, aliphatic hydrocarbons and silicone can be found in exhaust air from high-temperature treatments.

9 ANNEX II DYES AND PIGMENTS

Textile dyes can be classified according to their chemical composition (azo, antrachinone, sulphur, triphenilmethane, indigoid, phtalocyanine, etc.) or according to their application class. At the industrial level the second method is preferred.

9.1 Acid dyes

Applicability

Acid dyes are mainly applied to polyamide (80 – 85 %) and wool (10 – 15 %). They are also used for silk and some modified acrylic fibres. Acid dyes exhibit little affinity for cellulose and polyester fibre.

Properties

Colours are generally bright and fastness to light and washing range from poor to excellent depending on the chemical structure of the dyestuff.

Chemical characteristics and general application conditions

Acid dyes are azo (the largest group), anthraquinone, triphenilmethane chromophoric systems which are made water-soluble by the introduction in the molecule of up to three sulphonate groups.
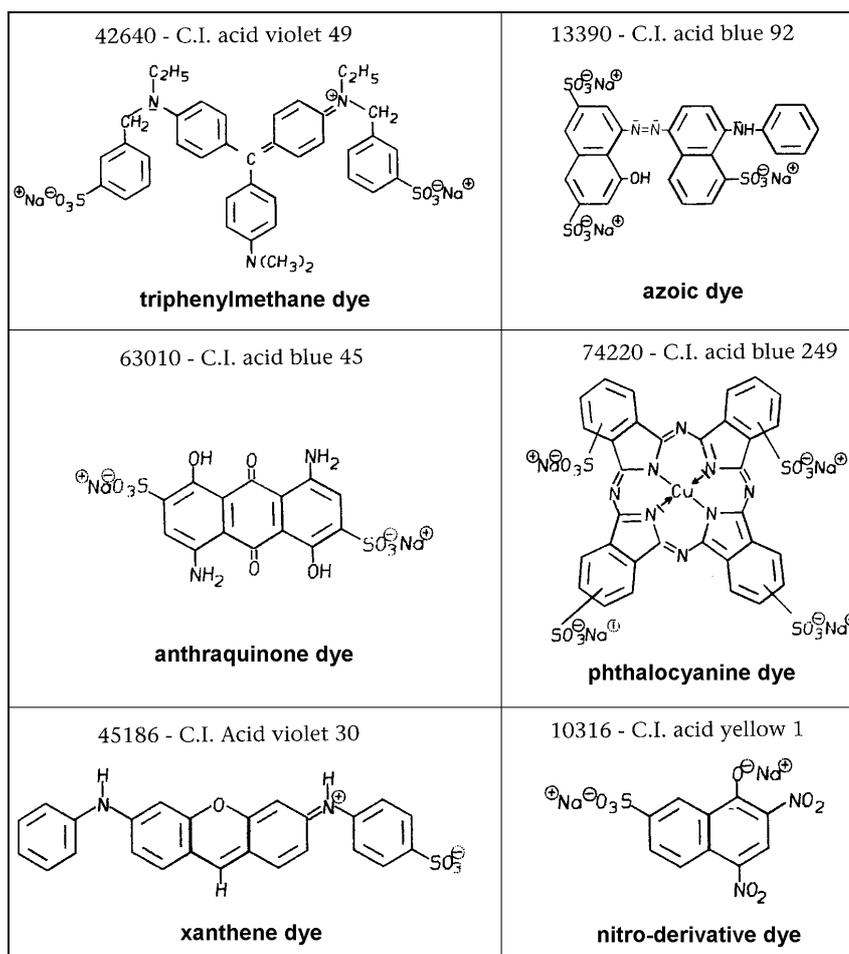

Figure 9.1: Examples of acid dyes

Their interaction with the fibre is based partly on ionic bonds between sulphonate anions and the ammonium groups of the fibre, as shown below for wool

$$\overset{\oplus}{N}H_3 \quad \overset{\ominus}{O}_3S-Col$$
$$W$$
$$COOH$$
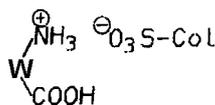
and for polyamyde, at different pH conditions.

pH $\approx$ 5 $Col-\overset{\ominus}{S}O_3 \ \overset{\oplus}{H}_3N-R-.....-\bar{N}H-CO-.....-R-COOH$

pH < 3 $Col-\overset{\ominus}{S}O_3 \ \overset{\oplus}{H}_3N-R-.....-\overset{\oplus}{N}H-CO-.....-R-COOH$
$$\overset{\ominus}{O}_3S-Col$$
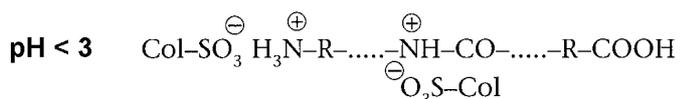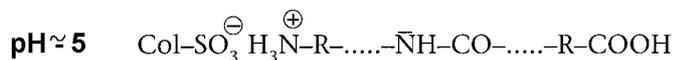
Moreover, the fibre/dye interaction is based on secondary bonds such as Van der Waals forces. Secondary bonds are established in particular in the case of higher molecular weight dyes, which form aggregates with high affinity for the fibre.

In use, acid dyes are classified by their dyeing behaviour and wet fastness properties, rather than chemical composition, hence the generic term acid dyes includes several individual dye classes. The arbitrary classification normally adopted, in order of increasing fastness is:
- level-dyeing or equalising acid dyes
- fast acid, half-milling or perspiration-fast dyes
- acid milling dyes
- supermilling dyes.

Level-dyeing or equalising dyes are subdivided into two classes, monosulphonated and disulphonated. Due to their poor affinity for the fibre, they all have very good levelling properties. Their wet fastness is, however, sometimes poor, limiting their use to pale/medium shades.

Fast acid dyes (also known as half-milling dyes or perspiration-fast dyes) are generally monosulphonated and exhibit superior fastness properties to level-dyeing acid dyes, while retaining some of the migration properties. The shade range available in this class is not as wide as that of the levelling or milling dyes and they therefore tend only to be used when alternatives would have poorer fastness properties.

Acid milling dyes are so named because they have a degree of fastness to the wet treatments employed when milling (mild felting) woollen fabrics. The class is further sub-divided to include supermilling dyes, which have good wet fastness properties, arising from long alkyl side-chains attached to the chromophore. Due to their high molecular weight, milling dyes have good affinity for the fibre and do not migrate well at the boil. Milling dyes may be used for those applications where good wet fastness is required, for example in the dyeing of loose fibre which will receive a further wet treatment during hank scouring.

Depending on the class they belong to, acid dyes are applied under pH conditions that vary from strongly acidic to more neutral ones (5 – 7.5). For low-affinity dyes it is necessary to increase the level of cationisation of the fibre (by acidification) in order to improve dye uptake. Conversely, dyes with higher molecular weight and high affinity would adsorb too rapidly on the fibre if applied under such strongly acidic conditions.

The most common *chemicals and auxiliaries* applied *when dyeing* with acid dyes are:
- sodium sulphate (for level-dyeing and fast acid dyes), sodium acetate and ammonium sulphate (for acid milling dyes)
- pH regulators: acetic, formic and sulphuric acid
- levelling agents, mainly cationic compounds such as ethoxylated fatty amines.

The most common *chemicals and auxiliaries* applied *when printing* with acid dyes are:
- thickening agents
- solubilising agents such as urea, thiourea, thiodiglycol, glycerine
- acid donors: ammonium sulphate, tartrate or oxalate
- defoamers (e.g. silicone oils, organic and inorganic esters) and "printing oils" (mainly mineral oils)
- after-treatment agents such as formaldehyde condensates with aromatic sulphonic acids.

Environmental issues

The ecological properties of acid dyes are assessed under the following parameters. The following table does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process.

Parameters of concern	Comments
Bio-eliminability	
Organic halogens (AOX)	
Eco-toxicity	Acid dyes are in general not toxic. However, two dyes (Acid orange 156 and Acid orange 165) have been classified as *toxic* by ETAD. Acid Violet 17(triphenylmethane dye) is reported to have an *allergenic effect*
Heavy metals	
Aromatic amines	
Unfixed colorant	Degrees of fixation in batch dyeing are found to be in the range of 85 - 93 % for monosulphonated dyes and in the range of 85 - 98 % for di- and tri-sulphonated dyes
Effluent contamination by additives in the dye formulation	

Table 9.1: Overview of the ecological properties of acid dyes

9.2   Basic (cationic) dyes

Applicability

Basic dyes were initially used to dye silk and wool (using a mordant), but they exhibited poor fastness properties. Nowadays these dyestuffs are almost exclusively used on polyacrylic fibres.

Properties

On polyacrylonitrile fibres fastness performances are excellent. In addition, they have unlimited colour range.

Chemical characteristics and general application conditions

Cationic dyes contain a quaternary amino group which can be an integral part (more common) or not of the conjugated system. Sometimes a positively-charged atom of oxygen or sulphur can be found instead of nitrogen.

Ionic bonds are formed between the cation in the dye and the anionic site on the fibre.
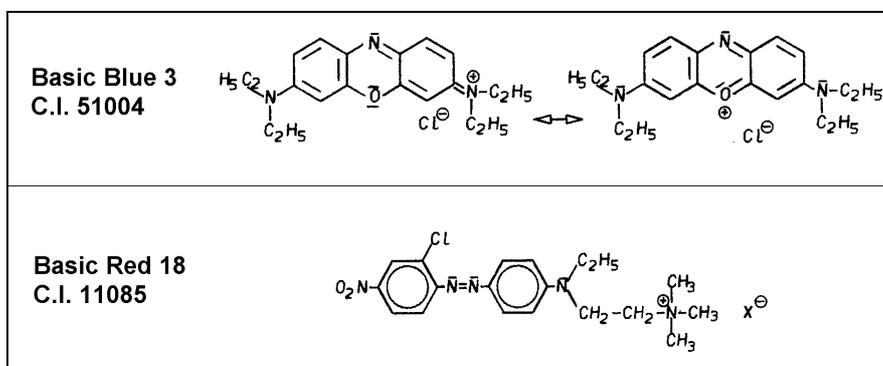
Figure 9.2: Examples of typical basic dyes

Cationic dyes are slightly soluble in water, while they show higher solubility in acetic acid, ethanol, ether and other organic solvents. In dyeing processes, they are applied in weak acid conditions. Basic dyes are strongly bound to the fibre and do not migrate easily. In order to achieve level dyeing, specific levelling auxiliaries, (also called retarders) are normally employed. The most important group is represented by quaternary ammonium compounds with long alkyl side-chains (cationic retarders). Electrolytes and anionic condensation products between formaldehyde and naphthalenesulphonic acid may also be found.

Environmental issues

Many basic dyes exhibit high aquatic toxicity but, when applied properly, they show fixation degrees close to 100 %. Problems are more often attributable to improper handling procedures, spill clean-up and other upsets. [EPA]

The following dyestuffs have been classified as toxic by ETAD:
- Basic Blue 3, 7, 81
- Basic Red 12
- Basic Violet 16
- Basic Yellow 21.

9.3   Direct (substantive) dyes

Applicability

Direct dyes are used for dyeing cotton, rayon, linen, jute, silk and polyamide fibres.

Properties

Colours are bright and deep, but light-fastness can vary greatly depending on the dyestuff. Wash-fastness properties are also limited unless the textile is after-treated. Only occasionally are direct dyes used in direct printing processes.

Chemical characteristics and general application conditions

Direct dyes (also called substantive dyes) can be azo compounds, stilbenes, oxazines, phtalocyanines. They always contain solubilising groups (mainly sulphonic acid groups, but carboxylic and hydroxyl groups can also be found) that ionise in aqueous solution.

Direct dyes are characterised by long planar molecular structures that allow these molecules to align with the flat cellulose macromolecules, the dye molecules being held in place mainly through Van der Waals forces and hydrogen bonds.

Direct dyes may require the use of the following *chemicals and auxiliaries* for satisfactory *dyeing*:

- electrolytes, usually sodium chloride or sodium sulphate. Their function is to favour the aggregation of dye ions on the fibre
- wetting and dispersing agents: mixtures of non-ionic and anionic surfactants are used for this aim
- after-treatment agents: they are used to improve wet-fastness properties. So-called fixative cationic agents are the most commonly used. They are usually quaternary ammonium compounds with long hydrocarbon chains. Formaldehyde condensation products with amines, polynuclear aromatic phenols, cyanamide or dicyandiamide may also be used for this purpose.
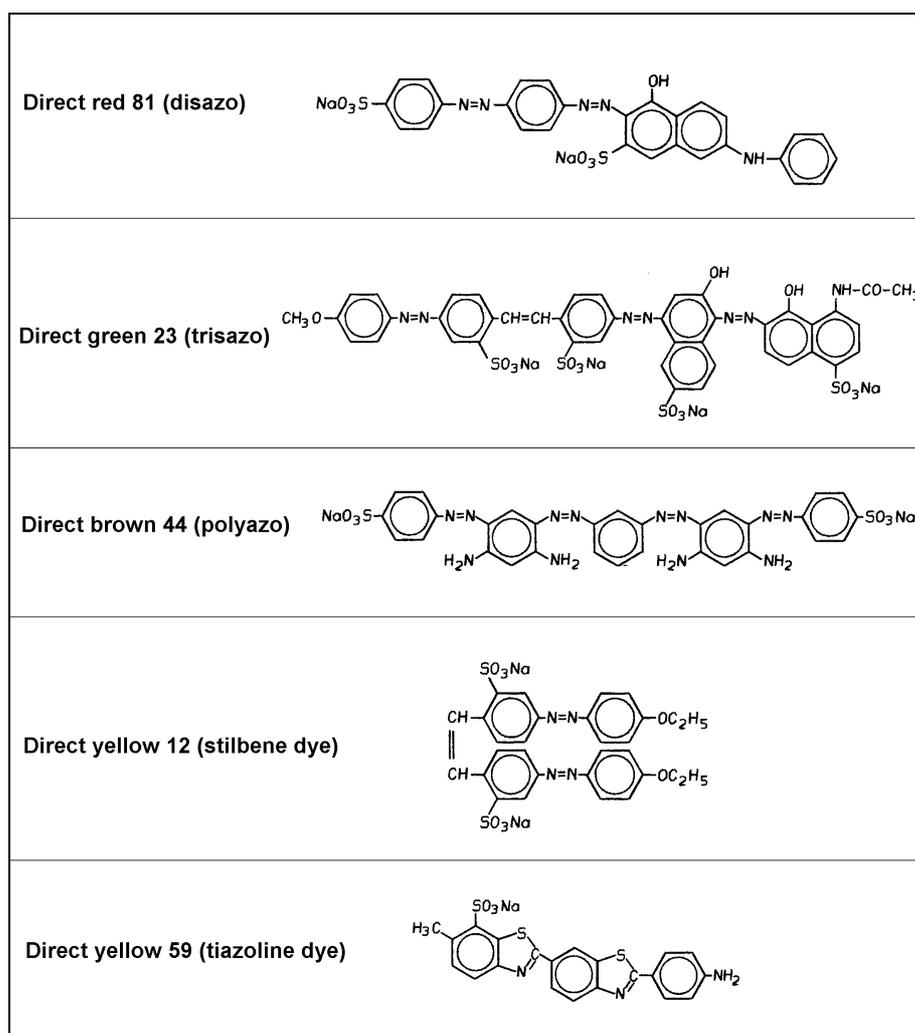

Figure 9.3: Examples of typical direct dyes

Environmental issues

The ecological properties of direct dyes are assessed under the following parameters. Table 9.2 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	
Organic halogens (AOX)	
Eco-toxicity	Direct Orange 62 has been classified as toxic by ETAD
Heavy metals	
Aromatic amines	The main emphasis of research for direct dyes was actually on the replacement of possibly carcinogenic benzidine dyes [ULLMANN'S] (Are these dyes still available on the market?)
Unfixed colorant	Degree of fixation in batch dyeing processes ranges from 64 - 96 % [EURATEX] (70 - 95 % according to [EPA])
Effluent contamination by additives in the dye formulation	

Table 9.2: Overview of the ecological properties of direct dyes

9.4   Disperse dyes

Applicability

Disperse dyes are used mainly for polyester, but also for cellulose (acetate and triacetate), polyamide and acrylic fibres.

Properties

Fastness to light is generally quite good, while fastness to washing is highly dependent on the fibre. In particular, in polyamides and acrylics they are used mostly for pastel shades because in dark shades they have limited build-up properties and poor wash fastness.

Chemical characteristics and general application conditions

Disperse dyes are characterised by the absence of solubilising groups and low molecular weight. From a chemical point of view more than 50 % of disperse dyes are simple azo compounds, about 25 % are anthraquinones and the rest are methine, nitro and naphthoquinone dyes.

The dye-fibre affinity is the result of different types of interactions:
- hydrogen bonds
- dipole-dipole interactions
- van der Waals forces.

Disperse dyes present in their molecule hydrogen atoms capable of forming hydrogen bonds with oxygen and nitrogen atoms on the fibre.

Dipole-dipole interactions result from the asymmetrical structure of the dye molecules, which makes possible electrostatic interactions between dipoles on the dye molecules and polarised bonds on the fibre.

Van der Waals forces take effect when the molecules of the fibre and colorant are aligned and close to each other. These forces are very important in polyester fibres because they can take effect between the aromatic groups of the fibre and those of the colorant.

Disperse dyes are supplied as powder and liquid products. Powder dyes contain 40 – 60 % of dispersing agents, while in liquid formulations the content of these substances is in the range of 10 – 20 %. Formaldehyde condensation products and ligninsulphonates are widely used for this purpose.

Dyeing with disperse dyes may require the use of the following *chemicals and auxiliaries*:

- dispersants: although all disperse dyes already have a high content of dispersants, they are further added to the dyeing liquor and in the final washing step
- carriers: for some fibres, dyeing with disperse dyes at temperatures below 100 ºC requires the use of carriers. This is the case with polyester, which needs the assistance of carriers to enable an even penetration of disperse dyes below boiling temperature. Because of environmental problems associated with the use of these substances, polyester is preferably dyed under pressure at temperature >100 ºC without carriers. However, carrier dyeing is still important for polyester-wool blends, as wool must not be submitted to wet treatment at temperatures significantly above 100 ºC
- thickeners: polyacrylates or alginates are usually added to the dyeliquor in padding processes. Their function is to prevent migration of the dyeliquor on the surface during drying
- reducing agents (mainly sodium hydrosulphite): they are added in solution with alkali in the final washing step.

Disperse dyes are widely used not only for dyeing, but also for printing synthetic fibres.

TYPICAL PRINTING CONDITIONS?

Environmental issues

The ecological properties of disperse dyes are assessed under the following parameters. Table 9.3 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	Owing to their low water-solubility, they are largely eliminated by absorption on activated sludge in the wastewater treatment plant
Organic halogens (AOX)	Some disperse dyes can contain organic halogens, but they are not expected to be found in the effluent after wastewater treatment (because they easily eliminated by absorption on the activated sludge)
Toxicology	The following disperse dyes potentially have an allergenic effect: Disperse Red 1, 11, 17, 15; Disperse Blue 1, 3, 7, 26, 35, 102, 124; Disperse Orange 1, 3, 76; Disperse Yellow 1, 9, 39, 49, 54, 64.
Heavy metals	
Aromatic amines	
Unfixed colorant	Level of fixation is in the range of 88 - 99 % for continuous dyeing (?) and 91 - 99 % for printing
Effluent contamination by additives in the dye formulation	Conventional dispersants (formaldehyde condensation compounds, ligninsulphonates, etc.) are poorly biodegradable (<30 % according to [ULLMANN'S], ca. 15 % according to [VITO]). More readily eliminable dispersants are already available for some dyes [BASF]

Table 9.3: Overview of the ecological properties of disperse dyes

9.5 Metal-complex dyes

Applicability

Metal-complex dyes (also called pre-metallised dyes) have great affinity for protein fibres. Among metal-complex dyes, 1:2 metal-complex dyes are also suitable for polyamide fibres.

More than 65 % of wool is today dyed with chrome dyes (see next section) or metal-complex dyes.

Properties

Light-fastness is excellent, while washing fastness is not as good as with chrome dyes (particularly in darker shades).

Chemical characteristics and general application conditions

Metal-complex dyes may be broadly divided into two classes, 1:1 metal-complexes, in which one dye molecule is co-ordinated with one metal atom and 1:2 metal complexes, in which one metal atom is co-ordinated with two dye molecules. The dye molecule will be typically a monoazo structure containing additional groups such as hydroxyl, carboxyl or amino groups, which are capable of forming strong co-ordination complexes with trivalent transition metal ions, typically chromium and cobalt. Typical examples of pre-metallised dyes are shown in Figure 9.4and Figure 9.5.
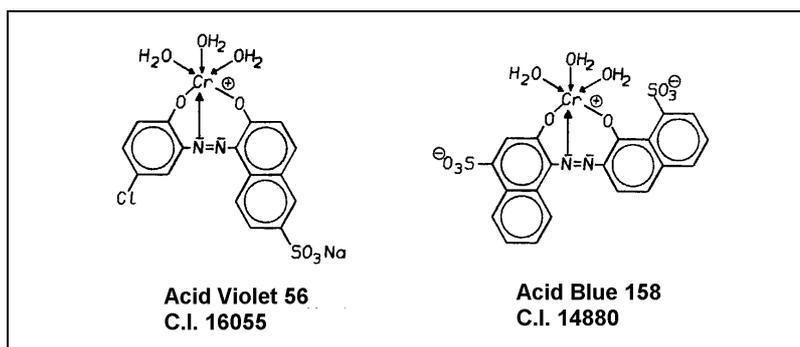
**Figure 9.4: Examples of molecular structures typical of 1.1 metal-complex dyes**
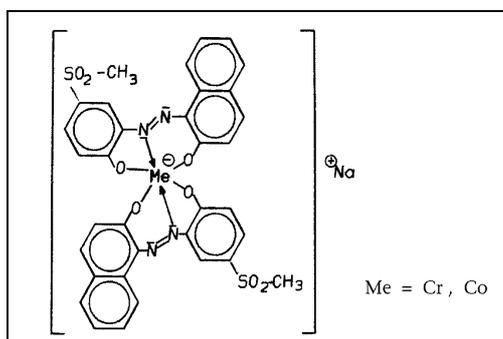

Figure 9.5: Molecular structure typical of 1.2 metal-complex dyes

When used in dyeing processes, metal-complex dyes are applied in acidic conditions. The pH levels range from strongly acidic (3 - 4.5 for 1:1 metal complex dyes) to moderately acidic-neutral (4 – 7 for 1: metal complex dyes).

1:1 metal-complex dyes exhibit the excellent level dyeing and penetration characteristics required for yarn dyeing and have the ability to cover irregularities in the substrate. Their light and wet fastness properties are good even in deep shades. They are also particularly suitable for piece dyeing of carbonised wool.

1:2 metal-complex dyes are used for both wool and polyamide. They form the most important group in this class and may be divided into two sub-groups:

- weakly polar 1:2 complexes – solubilised by the inherent anionicity of the complex or containing non-ionic, hydrophilic substituents such as methylsulphone ($-SO_2CH_3$). These dyes exhibit excellent fastness to light and wet treatments and excellent penetration properties.
- strongly polar 1:2 complexes – solubilised by one or more sulphonic or carboxylic acid residues, these dyes possess lower levelling power than the weakly polar dyes mentioned above but superior light and wet fastness properties and are generally suitable for use in those applications where mordant dyes are used. This second group is also more suitable for dyeing polyamide fibres.

Dyeing with metal-complex dyes may require the use of the following *chemicals and auxiliaries*:

- pH regulators: sulphuric, formic, acetic acid
- electrolytes: sodium sulphate, ammonium acetate and sulphate
- levelling agents: mixtures of anionic and non-ionic surfactants.

PRINTING?

Environmental issues

The ecological properties of metal-complex dyes are assessed under the following parameters. Table 9.4 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	Great differences from dye to dye (bio-eliminability can be <50 %)
Organic halogens (AOX)	Some products contain organic halogens: AOX in wastewater, therefore depends on the eliminability of the dyes concerned)
Eco-toxicity	
Heavy metals	Cr III is an integral part of the chromophore. Metals can therefore be found in the effluent due to unfixed dye
Aromatic amines	
Unfixed colorant	Degree of fixation ranges from moderate to excellent (from 85 to 98 % and greater in some cases)
Effluent contamination by additives in the dye formulation	Inorganic salts are present in the preparation of powder dyes. These salts, however, do not present any ecological or toxicological problems [BASF]

Table 9.4: Overview of the ecological properties of metal complex dyes

9.6   Mordant dyes (chrome dyes)

Applicability

Mordant dyestuffs are generally used for protein (wool and silk) and polyamide fibres. Occasionally they are used to print wool and silk.

Properties

Thanks to their good levelling properties and very good wet fastness after chroming, chrome dyes are used principally to obtain dark shades (greens, blues and blacks) at moderate cost. There are disadvantages, however, in their use: long dyeing times, difficulties with shading, the risk of chemical damage to the fibre during chroming and the potential release of chromium in wastewater.

Chemical characteristics and general application conditions

The *Colour Index* classifies these colorants as mordant dyes, but chromium has become the almost universally used mordant and the class is commonly referred to as chrome dyes.

From a chemical point of view they can be regarded as acid dyestuffs that contain suitable functional groups capable of forming metal complexes with chrome. They do not contain chrome in their molecule, which instead is added as dichromate, or chromate salt to allow dye fixation.

Interaction with the fibre is established through ionic bonds formed between the anionic groups of the colorant and ammonium cations available on the fibre. In addition chromium acts as a link between dye and fibre. This gives rise to a very strong bond, which is reflected in the excellent fastness obtained. Figure 9.6 shows the ionic and coordination bonds in the case of wool.
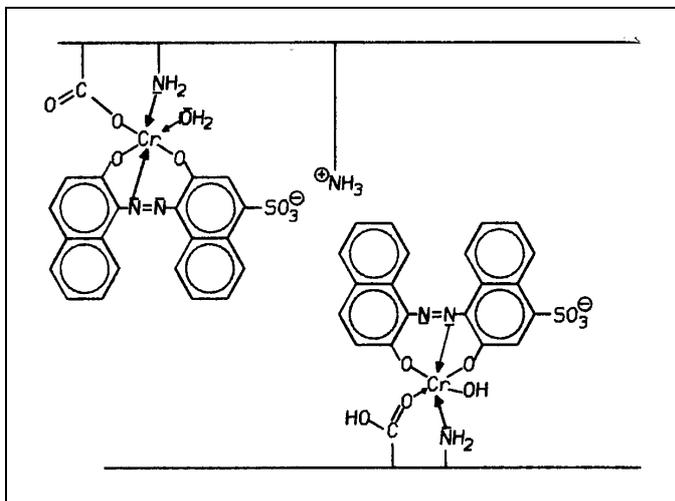
Figure 9.6: Representation of possible ionic and coordination bonds between wool and chrome dyes

The use of chrome dyes in *dyeing* processes requires the use of the following chemicals and auxiliaries:
- potassium and dichromate or chromate
- formic or acetic acid as pH regulators
- other organic acids such as tartaric and lactic acid. They are used to enhance the degree of conversion of Cr VI to Cr III
- sodium or ammonium sulphate.

Environmental issues

The ecological properties of chrome dyes are assessed under the following parameters. Table 9.5 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	
Organic halogens (AOX)	
Eco-toxicity	
Heavy metals	Chromium present in the final colorant is <u>not</u> contained in the molecule, being instead added as dichromate, or chromate salt during the dyeing process to allow dye fixation
Aromatic amines	
Unfixed colorant	
Effluent contamination by additives in the dye formulation	

Table 9.5: Overview of the ecological properties of chrome dyes

9.7   Naphtol dyes (azoic dyes developed on the fibre))

Applicability

Azoic dyes, also known as naphtol dyes, are used for cellulosic fibres (particularly cotton), but may also be applied to rayon, cellulose acetate, linen and sometimes polyester.

Properties

Azoic dyes have excellent wet fastness properties. Also good is light, chlorine and alkali fastness, while rubbing fastness is poor.

Chemical characteristics and general application conditions

From a chemical point of view naphtol dyes are very similar to azo dyes, the main difference being the absence of sulphonic solubilising groups.

They are made up of two chemically reactive compounds that are applied to the fabric in a two-stage process. The insoluble dye is synthetised directly in the fibre as the result of the coupling reaction between a diazotized base (developing agent) and a coupling component.

The coupling components are usually derivatives of the anilides of the 2-hydroxi-3-naphtoic acid (also called naphtol AS). These naphtols are available in powder form or in liquid form (in this case the solution also contains caustic soda, the naphtol concentration ranges between 30 % and 60 %).

Colour Index III ed.		Formula	Name of the commercial product
Coupling component n°	Chemical composition n°		
2	37505		Naftol AS (P,L)
4	37560		Naftol AS-BO (P,L)
5	37610		Naftol AS-G (P)
10	37510		Naftol AS-E (P)
11	37535		Naftol AS-RL (P)
12	37550		Naftol AS-ITR (P,L)
15	37600		Naftol AS-LB (P,L)
18	37520		Naftol AS-D (P,L)
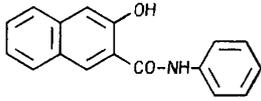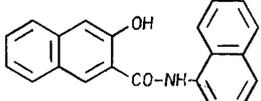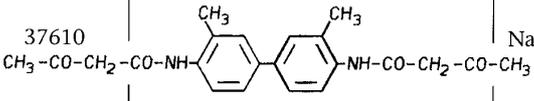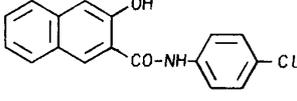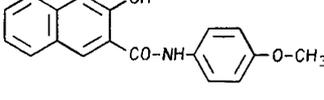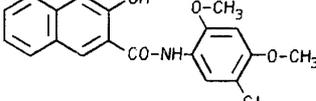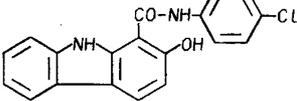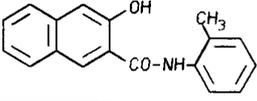
Figure 9.7: Examples of typical coupling components for naphtol dyes

Developing agents can be derivatives of aniline, toluidine, orto and meta anisidine, diphenyl amine. They are available as:
- free bases (fast colour bases)
- liquid bases (these formulations are aqueous dispersions of the aromatic amines, they are safer and simpler to apply than solid bases)
- fast colour salts (these are already diazotized diazonium compounds that are marketed in stabilised forms and do not need to be diazotized before use in dyeing: some examples are given in the figure below).

Colour Index		Formula
Diazo component n°	Chemical composition n°	
2	37005	3-chloroaniline (NH₂, Cl)
3	37010	dichloroaniline (NH₂, Cl, Cl)
6	37025	2-nitroaniline (NH₂, NO₂)
32	37090	chloro-methyl-aniline (NH₂, CH₃, Cl)
5	37125	methoxy-nitro-aniline (NH₂, OCH₃, NO₂)
41	37165	H₂N– ...–NH–CO–... (CH₃, OCH₃)
35	37255	H₂N–⟨⟩–NH–⟨⟩–OCH₃

Figure 9.8: Examples of typical developing agents (fast colour base) for naphtol dyes

C.I. Azoic Diazo component 5
stabilised as salt with
1,5 naphthalene disulphonic acid

$[O_2N$–...–$\overset{\oplus}{N}{\equiv}N|]$ HSO_3–...–$SO_3^{\ominus}$ (OCH₃)

C.I. Azoic Diazo component 10
stabilised as salt with
zinc chloride

$[Cl$–...–$\overset{\oplus}{N}{\equiv}N|]_2$ $ZnCl_4^{\ominus\ominus}$ (OCH₃)

C.I. Azoic Diazo component 34
stabilised as salt with
borontetrafluoride

$[O_2N$–...–$\overset{\oplus}{N}{\equiv}N|]$ $BF_4^{\ominus}$ (OCH₃)
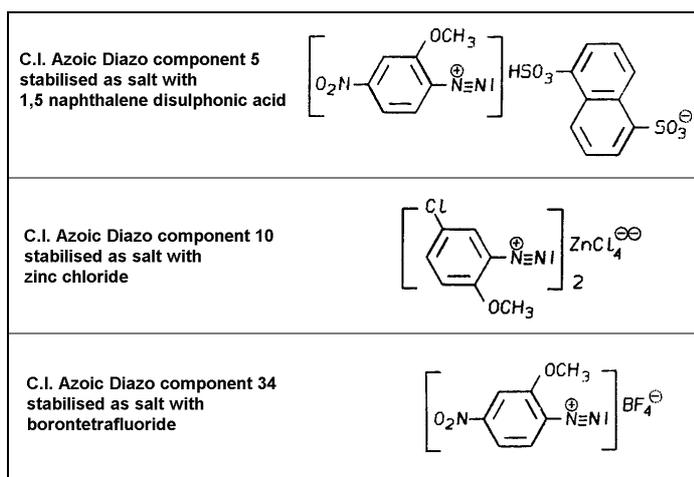
Figure 9.9: Examples of typical fast colour salts

Application of azoic colorants involves a number of steps:

- preparation of the naphtolate solution: naphtol is converted to the naphtolate form to be able to couple with the diazonium salt
- application of the naphtolate to the fibre
- preparation of the diazotized base: in order to make the coupling reaction possible, the base must first be diazotized in the cold, using sodium nitrite and hydrochloric acid (this step can be avoided when using fast colour salts)
- formation of the azoic dye into the fibre.

Environmental issues

The ecological properties of naphtol dyes are assessed under the following parameters. Table 9.6 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	
Organic halogens (AOX)	
Eco-toxicity	
Heavy metals	
Aromatic amines	Developing agents are all diazotisable amines or diamines or substituted anilines, toluidines, anisidines, azobenzenes or diphenylamines. Some of these amines and in particular, p-nitroaniline, chloroaniline and ß-naphtilamine are on the 1980 US EPA priority list as harmful pollutants and their use is forbidden.
Unfixed colorant	Degree of fixation in continuous dyeing processes ranges between 76 and 89 % and between 80 and 91 % in printing processes [EURATEX]
Effluent contamination by dispersants and additives in the dye	

Table 9.6: Overview of the ecological properties of naphtol dyes

9.8 Reactive dyes

Applicability

Reactive dyes are mainly used for dyeing cellulose fibres such as cotton and rayon, but are also sometimes used for wool, silk and polyamide.

Properties

They provide high wet fastness (better than the less expensive direct dyes). Chlorine fastness is slightly poorer than that of vat dyes, as is light fastness under severe conditions.

The range of available reactive dyes is wide and enables a large number of dyeing techniques to be used.

Chemical characteristics

Reactive dyes are unique in that they contain specific chemical groups capable of forming covalent links with the textile substrate.

The energy required to break this bond is similar to that required to degrade the substrate itself, thus accounting for the high wet fastness of these dyes.

Chemical structure of reactive dyes can be schematically represented by the following formula: Col-B-R, where:

- Col is the chromophore that is in general constituted by monoazoic, anthraquinone, phtalocianine and metal-complex compounds
- B is the linking group between the chromophore and the reactive group (-NH- group is the most common)
- R represents the reactive group.

Some typical examples of reactive systems for cellulose and wool or polyamide fibres are reported in the following tables.
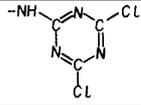
Anchor system	Denomination	Commercial name
	Dichloro-s-triazine (cold dyer)	Procion MX
	Amino-fluoro-s-triazine (warm dyer)	Cibacron F
	Trichloro-pyrimidine (hot dyer)	Cibacron T-E Dimaren X, Z
$-SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_3Na$	Beta-sulphate-ethyl-sulphone (warm dyer)	Remazol
$-SO_2\text{-}CH_2\text{-}CH_2\text{-}Cl$	Beta-chloroethylsulphone (warm dyer)	Remazol Druck
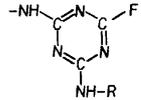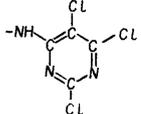
Table 9.7: Typical anchor systems for cellulose fibres
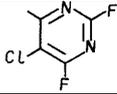
Anchor system	Denomination	Commercial name
	2,4-difluoro 5-chloro pyrimidine	Verofix Drimalan F
$-SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_3Na$	Beta-sulphate-ethyl-sulphone	Remazolan
$-SO_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_3H$	Sulphate-ethyl sulphonamide	Levafix

Table 9.8: Typical anchor systems for wool and polyamide fibres

The reactive groups of the colorant react with the amino groups of the fibre in the case of protein and polyamide fibres, and with the hydroxyl groups in the case of cellulose.

In both cases, depending on the anchor system, two reaction mechanisms are possible: a nucleophilic substitution mechanism or a nucleophylic addition mechanism.

Futhermore, anchor systems are characterised by their reactivity. Based on this, they are classified as hot, warm and cold dyers.

An important issue to consider when dealing with reactive dyes is the fact that two competing reactions are always involved in the colouring process:
1. hydrolysis: Dye + water → hydrolysed dye washed away after dyeing
2. alcoholysis: Dye + fibre → dye fixed on the fibre.

This fact has important consequences, especially in the case of cellulose fibres. In fact, the alkaline conditions in which reactive dyes react with cellulose fibres increase the rate of the hydrolysis reaction (undesired reaction).

As a result, a certain amount of unfixed hydrolised dye is always present at the end of the process.

Poor dye fixation has been a long-standing problem with reactive dyes in particular in batch dyeing, where a significant amount of salt is normally added to improve dye exhaustion (and therefore also dye fixation).

Dyeing cellulose fibres with reactive dyes may imply the use of the following *chemicals* and *auxiliaries*:
*   alkali (sodium carbonate, bicarbonate and caustic soda)
*   salt (mainly sodium chloride and sulphate)
*   urea (usually added to the padding liquor in continuous processes).

Reactive dyes are applied to wool or polyamide fibres under different conditions. In the case of *wool and polyamide fibres*, reactivity of the amino groups is considerably higher than that of hydroxyl groups in cellulose.

Levelling properties are often achieved with the use of speciality amphoteric levelling agents, which form complexes with the dye at low dyebath temperatures.

These complexes are absorbed onto the fibre surface in a more even manner than that of the dyestuff itself. They then break down as the dyeing temperature increases, allowing the dye to penetrate and react with the substrate.

Reactive dyes are generally applied at pH values of between 5 and 6, depending on depth of shade, in the presence of ammonium sulphate and the specialised levelling agents mentioned above.

In *cellulose printing*, moderately reactive dyes are generally employed (mainly mochlorotriazine systems). Highly reactive sulphoethyl sulphones are also used, but only in the two-phase process.

Printing with reactive dyes requires the use of:
*   thickening agents (mainly polyacrylates in combination with alginates)
*   urea
*   alkali (e.g. sodium carbonate and bicarbonate)
*   oxidising agents (mainly benzenesulphonic acid derivatives): they are used to prevent reduction of more sensitive dyes during steaming.

Environmental issues

The ecological properties of reactive dyes are assessed under the following parameters.

Table 9.9 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	Because both unfixed reactive dye and its hydrolysate are readily soluble they are difficult to eliminate in biological wastewater treatment plants
Organic halogens (AOX)	Many reactive dyes contain organic halogens. However, a distinction has to be made between halogens bonded to the chromophore and halogens bonded to the anchor because organic halogens present in the anchor are converted during dyeing into inorganic chloride. The amount of unfixed dye is likely to be largely hydrolysed in the presence of alkali. [BASF]
Eco-toxicity	
Heavy metals	Heavy metals can be present both as impurities from the production process (limits have been set by ETAD) and as an integral part of the chromophore. The latter concerns phthalocyanine dyes, which are still widely used especially for blue and turquoise shades (substitutes have not yet been found)
Aromatic amines	
Unfixed colorant	Generally poor (1) (see also discussion in Section 2.7.8). Efforts have been made to increase the level of fixation (some reactive dyes can reach >95 % of fixation)
Effluent contamination by dispersants and additives already in the dye	

Notes:
(1) [EURATEX] Fixation degree for:
-    cotton batch dyeing: 55 - 80 %
-    wool batch dyeing: 90 - 97 %
-    printing (general): 60 %

Table 9.9: Overview of the ecological properties of reactive dyes

9.9   Sulphur dyes

Applicability

Sulphur dyes are mainly used for cotton and rayon substrates. They may also be used for dyeing blends of cellulose and synthetic fibres, including polyamides and polyesters. They are occasionally used for dyeing silk. Apart from black shades, sulphur dyes play almost no part in textile printing.

Properties

Bleach and wash fastness properties are very good, while light fastness varies from moderate to good. Although they encompass a broad shade range, sulphur dyes are mostly used for dark shades because lighter shades have poor resistance to light and laundering. Sulphur dyes tend to be dull compared with other dye classes.

Chemical characteristics and general application conditions

Sulphur dyes are made up of high molecular weight compounds obtained by reaction of sulphur or sulphides with amines and phenols. Many colorants exist that contain sulphur in their molecule, but only dyestuffs which become soluble in water after reaction with sodium sulphide under alkaline conditions can be called sulphur dyes.

The exact chemical structure is not always known because these are mixtures of molecules of a high level of complexity. Amino derivatives, nitrobenzenes, nitro and aminobiphenyls, substituded phenols, substituted naphhalenes, condensed aromatic compounds, indophenols, azines, oxazine, thiazol, azine and thiazine rings can be part of these compounds. Sulphur dyes contain sulphur both as an integral part of the chromophore and in polysulphide side chains.

As has already been mentioned, sulphur dyes are insoluble in water, but after reduction under alkaline conditions they are converted into the leuco form, which is water-soluble and has high affinity for the fibre. After absorption into the fibre they are oxidised and converted to the original insoluble state.

Sulphur dyes are available in various modifications, which are classified under the following names:
- sulphur dyes - available as amorphous powders or dispersible pigments. Amorphous powders are insoluble or partially soluble in water and are brought into solution by boiling with sodium sulphide and water. Dispersible pigments can be used in this form for pad dyeing in presence of a dispersing agent. They can contain a certain amount of reducing agent already in the formulation and in this case are called "partly reduced pigments".
- leuco-sulphur dyes (ready-for-use dyes) - available in liquid form and contain already the reducing agent required for dyeing. Therefore they must simply be diluted with water before application. Low-sulphide types are also available on the market
- water-soluble sulphur dyes - available in the form of Bunte salts (Col-S-SO$_3$Na) obtained by treating the dye in its insoluble form (Col-S-S-Col) with sodium hydrosulphite. They can be dissolved in hot water, but they do not have affinity for the fibre. The addition of alkali and reducing agent makes them substantive for the fibre.

Sodium sulphide and sodium hydrogensulphyde are generally employed as reducing agents to bring into solution the dye (unless ready-for-use sulphur dyes are applied). Binary systems made of glucose and sodium dithionite (hydrosulphite) or thiourea dioxide are also used as alternative reducing agents for water-soluble dyes. With powder/liquid dispersions, only hydrosulphite is used. [UBA]

In all processes the dye is finally fixed on the substrate by oxidation. Nowadays, hydrogen peroxide or halogenated organic compounds such as bromate, iodate and chlorite are the most commonly used oxidising agents.

Apart from the above-mentioned reducing and oxidising agents, additional chemicals and auxiliaries required when dyeing with sulphur dyes are:
- alkali (mainly caustic soda)
- salt (sodium chloride and sulphate)
- dispersing agents: usually they are naphthalenesulphonic acid-formaldehyde condensates, ligninsulphonates and sulphonated oils
- complexing agents: EDTA and polyphosphates are used in some cases to prevent negative effects due to the presence of alkaline-earth ions.

Environmental issues

The ecological properties of sulphur dyes are assessed under the following parameters. Table 9.10 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	
Organic halogens (AOX)	Possible contamination from halogen-containing oxidising agents used
Eco-toxicity	
Heavy metals	
Aromatic amines	
Unfixed colorant	Degree of fixation ranges between 60 and 90 % in continuous dyeing and 65 - 95 % in printing [EURATEX]
Effluent contamination by additives in the dye formulation	Poorly biodegradable dispersants are present

Table 9.10: Overview of the ecological properties of sulphur dyes

9.10 Vat dyes

Applicability

Vat dyes are used most often in dyeing and printing of cotton and cellulose fibres. They can also be applied for dyeing polyamide and polyester blends with cellulose fibres.

Properties

Vat dyes have excellent fastness properties when properly selected and are often used for fabrics that will be subjected to severe washing and bleaching conditions (towelling, industrial and military uniforms, etc.). The range of colours is wide, but shades are generally dull.

Chemical characteristics and general application conditions

From a chemical point of view vat dyes can be distinguished into two groups: indigoid vat dyes and anthraquinoid dyes. Indigo dyes are almost exclusively used for dyeing warp yarn in the production of blue denim.

Like sulphur dyes, vat dyes are normally insoluble in water, but they become water-soluble and substantive for the fibre after reduction in alkaline conditions (vatting). They are then converted again to the original insoluble form by oxidation and in this way they remain fixed into the fibre.
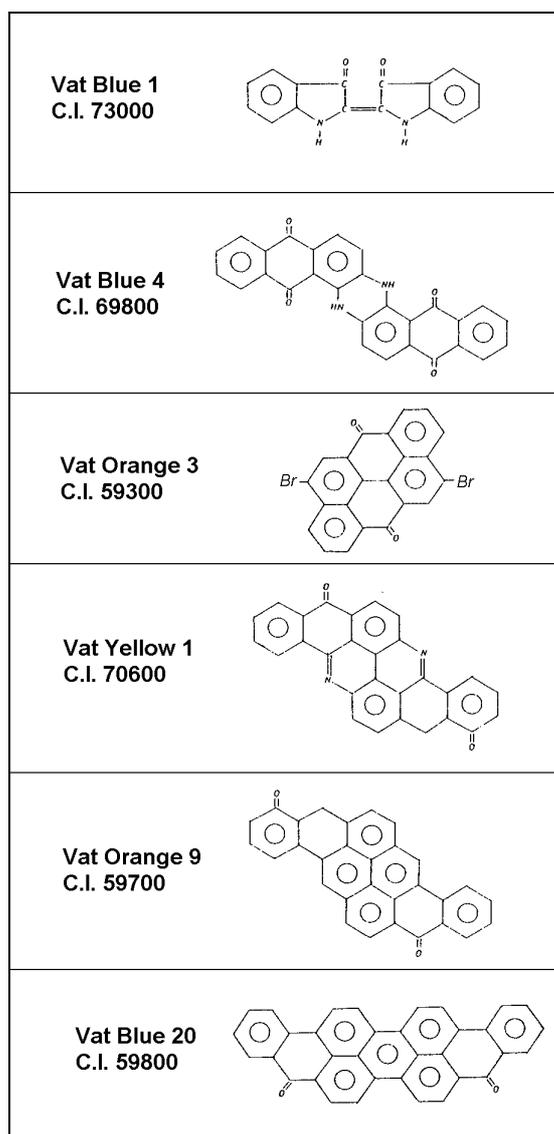
Figure 9.10: Examples of typical vat dyes

Vat dyes are preparations that basically consist of a vattable coloured pigment and a dispersing agent (mainly formaldehyde condensation products and ligninsulphonates). They are generally supplied in powder, granules and paste form.

A wide range of different techniques is used in colouring processes with vat dyes. Nevertheless, all processes involve three steps:
- vatting
- oxidation
- after-treatment.

The step in which the reduction of the dyestuff into its leuco-form takes place is called *vatting*. Vat dyes are generally more difficult to reduce than sulphur dyes. Various reducing agents are used. Sodium dithionite (hydrosulphite) is still the most widely employed although it has some limits. Sodium dithionite is consumed by reduction of the dye and also by reaction with atmospheric oxygen, therefore an excess of reducing agent has to be used and various techniques have been proposed to reduce these losses. In addition sodium dithionite cannot be used for high temperature or pad-steam dyeing processes because over-reduction can occur with sensitive dyes. In these application conditions and also for printing, sulphoxylic acid derivatives are normally preferred.

Thiourea dioxide is also sometimes used as a reducing agent, but a risk of over-reduction exists as its reduction potential is much higher than that of hydrosulphite. Furthermore the oxidation products of thiourea dioxide contribute to nitrogen and sulphur contamination of wastewater.

Following increasing environmental pressures, biodegradable sulphur-free organic reducing agents such as hydroxyacetone are now available. Their reducing effect, however, is weaker than that of hydrosulphite, so they cannot replace it in all applications. Nevertheless hydroxyacetone can be used in combination with hydrosulphite, thus reducing to a certain extent the sulphite load in the effluent.

After absorption by the fibre, the dye in its soluble leuco form is converted to the original pigment by *oxidation*. This process is carried out in the course of wet treatment (washing) by addition of oxidants such as hydrogen peroxide, perborate or 3-nitrobenzenesulphonic acid to the liquor.

The final step consists in *after-treating* the material in weakly alkaline liquor with a detergent at boiling temperature. This soap treatment is not only aimed at removing pigment particles, but also allows the crystallisation of amorphous dye particles, which gives the material the final shade and the fastness properties typical of vat dyes.

Vat dyeing conditions can vary widely in terms of temperature, amount of salt and alkali required, depending on the nature of the dye applied. Vat dyes are therefore divided into the following groups according to their affinity for the fibre and amount of alkali required for dyeing:
- IK dyes (I = Indanthren, K = cold) have low affinity, they are dyed at 20 – 30 ºC and require little alkali and salt to increase dye absorption
- IW dyes (W = warm) have higher affinity, they are dyed at 40 – 45 ºC with more alkali and little or no salt
- IN dyes (N = normal) are highly substantive and applied at 60 ºC and require much alkali, but no addition of salt.

The following *chemicals and auxiliaries* may be found in *dyeing* processes:
- sodium dithionite, thiourea dioxide and sulphoxilic acid derivatives as reducing agents
- caustic soda
- sodium sulphate
- polyacrylates and alginates as anti-migration agents in padding processes
- formaldehyde condensation products with naphthalenesulphonic acid and ligninsulphonates as dispersing agents
- surfactants (including ethoxylated fatty amines) and other components such as betaines, polyalkylenamines, polyvinylpyrrolidone as levelling agents
- hidrogen peroxide, perborate, 3-nitrobenzenesulphonic acid as oxidants
- soap.

The following *chemicals and auxiliaries* may be found in *printing* processes:
- thickening agents (starch esters with seed flour derivatives)
- reducing agents: various chemicals are used depending on the printing method (all-in or two-phase process), dye selected and steaming conditions. Sulphoxylic acid derivatives are the most common, but hydrosulphite can also be used (in the two-phase process when very short steaming time is required)
- alkali: potassium carbonate, sodium carbonate, sodium hydroxide
- oxidising agents (the same used for dyeing)
- soap.

Environmental issues

The ecological properties of vat dyes are assessed under the following parameters. Table 9.11 does not consider the environmental issues related to chemicals and auxiliaries employed in the dyeing process because these issues are dealt with in a specific annex.

Parameters of concern	Comments
Bio-eliminability	Vat dyes can be regarded to as highly eliminable due to their high degree of fixation and to the fact that they are water-insoluble
Organic halogens (AOX)	Possible contamination from halogen-containing oxidising agents used
Eco-toxicity	Since they are sparingly soluble they are not bio-available [BASF]
Heavy metals	Vat dyes contain heavy metal impurities (Cu, Fe, Mn, Ba and Pb) due to their production process (in some cases it is still difficult to keep these limits below the ETAD standards) [BASF]
Aromatic amines	
Unfixed colorant	Vat dyes show high exhaustion levels (70 - 95 % in continuous dyeing processes and 70 - 80 % in printing)
Effluent contamination by additives in the dye formulation	Dispersants are present in the dye formulation. As they are water-soluble and poorly degradable, they are found in the wastewater. According to [ULLMANN'S] new formaldehyde condensation products with higher elimination (>70 %) are already available and more readily eliminable substitutes are being developed.

Table 9.11: Overview of the ecological properties of vat dyes

9.11   Pigments

Pigments are widely used in printing processes (pigment printing).

Pigments are insoluble in water and organic solvents. Organic pigments are for a large part derived from benzoids. Inorganic pigments are derivatives of metals such as titanium, zinc, barium, lead, iron, molybdenum, antimony, zirconium, calcium, aluminium, magnesium, cadmium, chromium.

Parameters of concern	Comments
Bio-eliminability	?
Organic halogens (AOX)	?
Eco-toxicity	?
Heavy metals	?
Aromatic amines	?
Unfixed colorant	?
Effluent contamination by additives in the dye formulation	?

Table 9.12: Overview of the ecological properties of pigments

10 ANNEX III WET PROCESSES: MACHINERY AND TECHNIQUES

10.1 Loose fibre

10.1.1 Autoclave

Various types of machines are used for processing fibres in loose form. These include conical pan machines, pear shaped machines and radial flow machines. They are used for all the wet operations, that is, pretreatment, dyeing, application of finishing agents and washing.

In conical pan machines (Figure 10.1) the fibre is packed into a removable fibre carrier, which is located onto a central spigot in the base of the vessel. Liquor circulation is provided, via this connection, by an external pump. Associated pipework allows liquor to be circulated either from the base of the pack or from the top.

Pear shapes machines have a removable perforated base plate through which liquor is circulated via an impeller, returning to the dyeing vessel via a weir. Fibre is loaded directly into these machines and a further perforated plate is positioned on top. Liquor circulation packs the fibre into the base of the machine between the two plates. To unload the machine both plates are removed by crane and the fibre manually removed.

Radial flow machines are characterised by a fibre carrier, equipped with a central perforated column from which liquor flows across the pack to the perforated walls of the carrier.

Loose fibre is typically packed into these machines manually. Capacity varies between 200 - 300Kg, with a working volume equivalent to between 7 and 10 litres per Kg fibre. The low packing density in these machines allows liquor to circulate freely through the fibre pack at modest pressures, thus minimising mechanical damage to the fibre while ensuring level dyeing.

The bath is heated by closed steam coils in the base of the machine. In many cases the level of automation on these machines is low and temperature may be controlled manually with a simple steam valve. In other cases electro/pneumatic programmers or logic controllers may be installed to regulate time / temperature and control the direction of liquor circulation.

Autoclaves can be equipped for operation at higher pressure (this not the case when they are used for dyeing wool fibres).

Autoclaves of all designs may be fitted with an external holding tank, capable of accommodating at least the volume of the dyeing vessel. Such tanks are used to facilitate re-use of liquors in more than one dyeing. Occasionally more than one dyeing vessel may be connected to a common tank, allowing liquor to be shared between vessels. [ENCO]

The liquor ratio for loose fibre can vary between 1:4 to 1:12, depending on the type of machine, level of loading, type of fibre, etc.
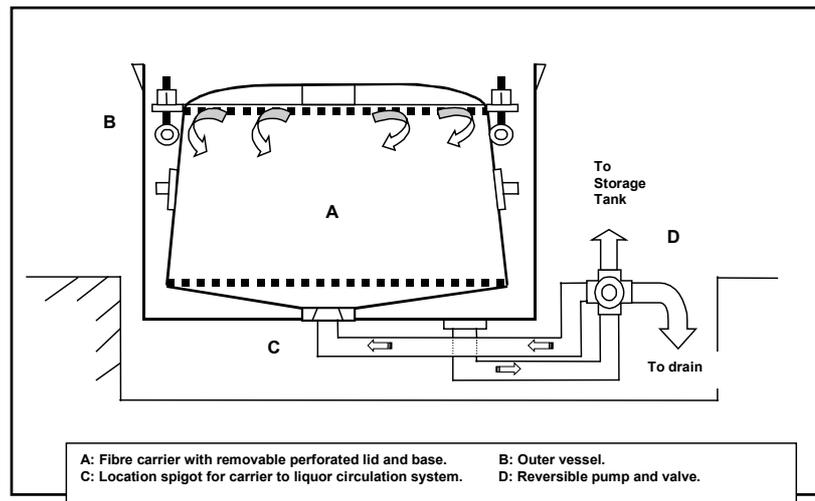
Figure 10.1: Schematic layout of a conical pan loose fibre dyeing machine [ENCO]

10.2   Yarn

Yarn can be processed either in hank form or in package. Different machines are used depending on the method chosen. They are used for all the wet operations, that is, pretreatment, dyeing, application of finishing agents and washing.

10.2.1 Hank dyeing machines

Hank dyeing machines are mostly of the single stick (Hussong) design, in which hanks are hung from the underside of the dyeing vessel lid on removable sticks. (Figure 10.2) The lid is lowered vertically onto the dyeing vessel, which consists of a simple box with a perforated false bottom. Liquor is circulated by a reversible impeller, located vertically in a weir chamber at one end of the machine. Heating is typically by closed steam coils beneath the false bottom and on smaller machines by live steam injection. Temperature control is provided by electro-mechanical or programmable logic controllers. These devices may also control/time the timing of chemical and dye additions and any required cooling cycles. Machine capacities vary from 10 kg sample machines to 1000 kg machines. These larger machines may be coupled together in pairs with interconnecting pipework in such a way that yarn loads of up to 4000 kg can be dyed while still retaining the flexibility to dye individual 1000 kg lots.

Variations of this design may utilise a horizontal circulation impeller passing through a sealing gland at the base of the weir chamber. Such machines invariably have a concave bottom, which is said to improve circulation and reduce fibre to liquor ratio by a small margin. [ENCO]

Liquor ratios of 1:15 are typical for these machines.

A: Lifting crane to raise lid.   B: Machine lid with hanks suspended on sticks.
C: Impeller housing, weir plate and motor to circulate dyeliquor.   D: Heating Coils.   E: Hanks
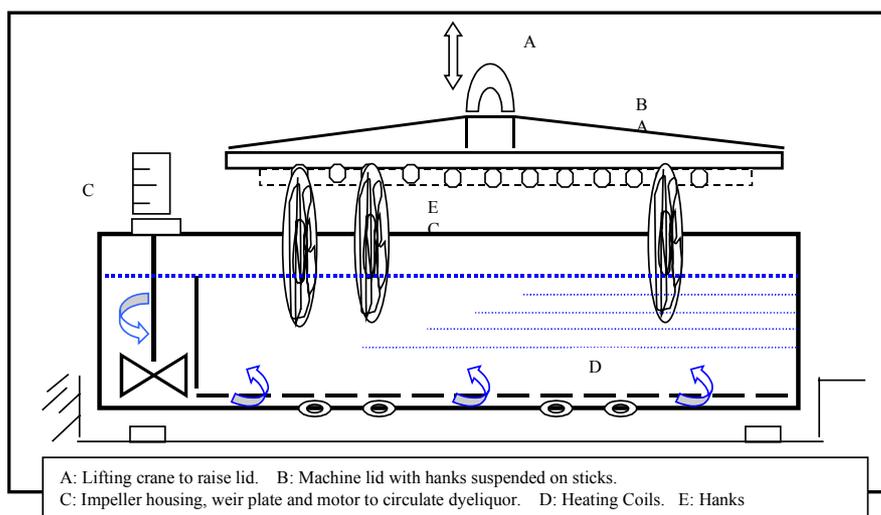
Figure 10.2: Schematic diagram of a Hussong type hank dying machine

10.2.2 Package dyeing machines

Three basic types of machine may be used for package dyeing wool yarns: horizontal or vertical spindle machines or tube type machines.

Horizontal spindle machines may be rectangular in design, similar to hank dyeing machines, but modified to take frames, onto which yarn packages are inserted horizontally; alternatively a horizontal autoclave into which is wheeled the carrier containing the yarn packages. Both types operate with high flow rate pumps, necessary to give good circulation of the dyeliquor. These machines are usually used for bulky yarns, which are wound onto soft packages, again to increase dye liquor penetration.

Vertical spindle machines are the most commonly used (see Figure 10.3). The packages may be press packed onto vertical carrier spindles to increase payload, assist in dye liquor circulation and minimise liquor to fibre ratio.

Tube type machines consist of a number of vertical or horizontal tubes into which package carriers are inserted, the tubes forming individual dyeing vessels linked by common pipework and circulation pumps. These machines are more flexible than the above types because individual tubes can be blanked off to vary the overall load capacity of the machine.

Fibre to liquor ratios employed in package dyeing are typically close to 12:1. Machines with capacities up to 500Kg are used in dyeing carpet yarns with the facility to link two or more machine together when dyeing larger single batches. [ENCO]
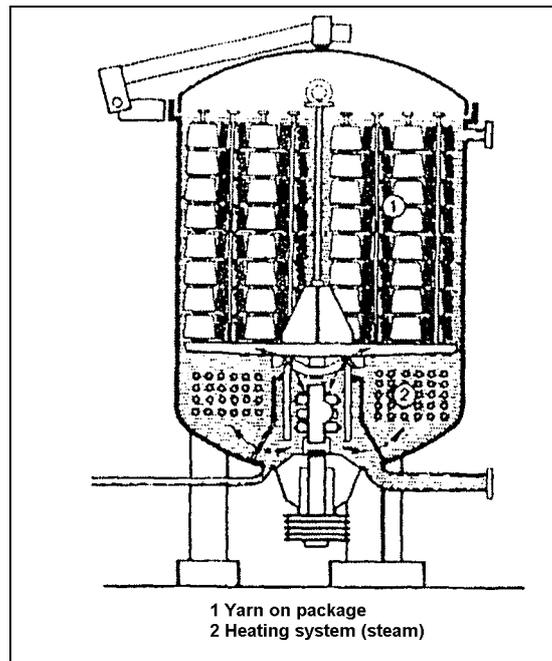
Figure 10.3: Schematic layout of a package dyeing machine

10.3 Fabric in rope form

Wet treatments on fabrics in rope form can be carried out both in batch and in continuous.

10.3.1 Batch processes

10.3.1.1 Winch beck (flow)

In the winch beck (see Figure 10.4), the bath stands still, while the fabric is kept in circulation by a reel positioned in the upper part of the machine. The winch draws the fabric via a guide roller out of the bath and returns it in folds into the bath. The development of synthetic fibres has lead to the production of pressurised machines (HT machines may reach 130 – 140 ºC.

The fabric in a batch is divided into pieces of equal length whose ends are sewn together to form endless loops. Usually there are up to 10 loops of fabric side by side on the winch, separated by guiding plates. [ULLMANN'S]

This machine is used mainly for dyeing carpets (they are usually dyed in full width).

Bath ratios are quite high (1:20 to 1:50), which makes this technique fairly expensive due to high water and energy consumption. Moreover, this equipment is not suitable for fabric prone to form crease marks.
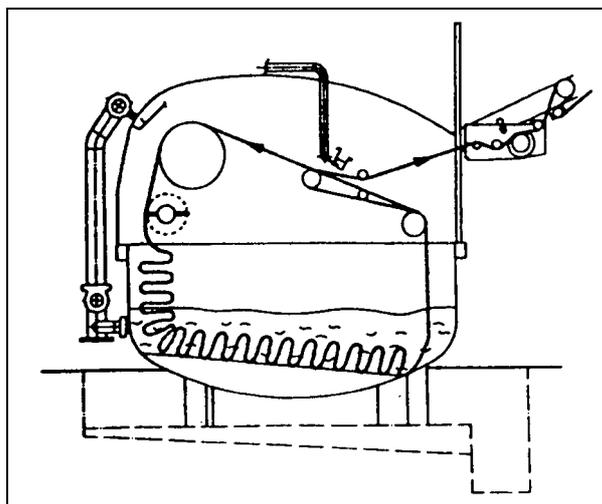
Figure 10.4: Schematic representation of a winch beck dyeing machine

10.3.1.2 Jet

Jet machines (see Figure 10.5) have been designed with the aim of eliminating some of the problems associated with the use of winch machines.

The reel is eliminated and the bath is kept in movement thanks to a strong jet of the bath itself, pumped through a nozzle. The liquor is pumped through a nozzle. The textile is also transported through the nozzle, being lifted up to by sliding, by means of a transportation device, or by floating.

Jets can usually be operated at high temperatures, so that they can be used also for dyeing polyester fibres.

Depending on the shape of the fabric storage area, the type of nozzle and its position (above or below the level of the bath) various types of jets exist.

Advantages of this machine are low consumption of water (typical liquor ratios range between 1:4 and 1:20) and short treatment time (e.g. short dyeing time). A disadvantage, however, is the high mechanical stress on the textile, caused by the speed difference between the bath and the fabric. For this reason jets are not suitable for some delicate fabrics.

1 Dyestuffs and auxiliaries feeding container
2 Heat exchanger
3 Pump for the circulation of the liquor
4 High pressure pipework
5 Dyeing drum
6 Winch
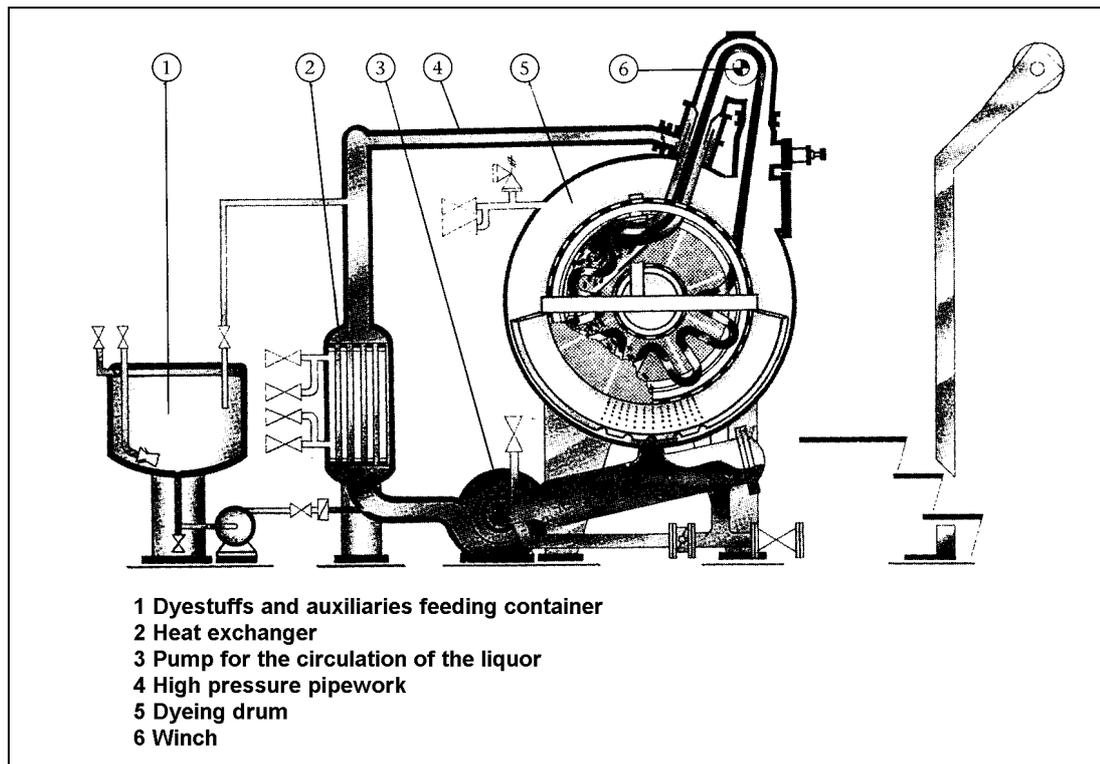
Figure 10.5: Schematic representation of a jet dyeing machine

10.3.1.3 Overflow

Overflows (see Figure 10.6) have been designed for delicate knitted and woven fabrics made of natural and synthetic fibres.

The main difference between jet and overflows machines stays in the fact that in jet machines the fabric is transported by the bath flowing at high speed through the nozzle, while with overflows the fabric is transported by the gravitational force of the liquor overflow.

A winch (usually not motor driven) is located in the upper part of the machine and the fabric hangs over it. A longer length of textile hangs from the exist side of the winch than from the inlet side. Gravitational forces pull the longer length of textile downward more strongly than the shorter. The fabric is therefore soaked in the bath without any tension (transportation is very gentle).

Different designs are available on the market and some of them can operate under pressure and consequently at higher temperatures.

Some machines can operate at liquor ratio between 1:3 and 1:8 (1:3 - 1:5 during the dyeing step and 1:8 during washing). Other models work with bath ratio between 1:10 and 1:12. [CORBANI]
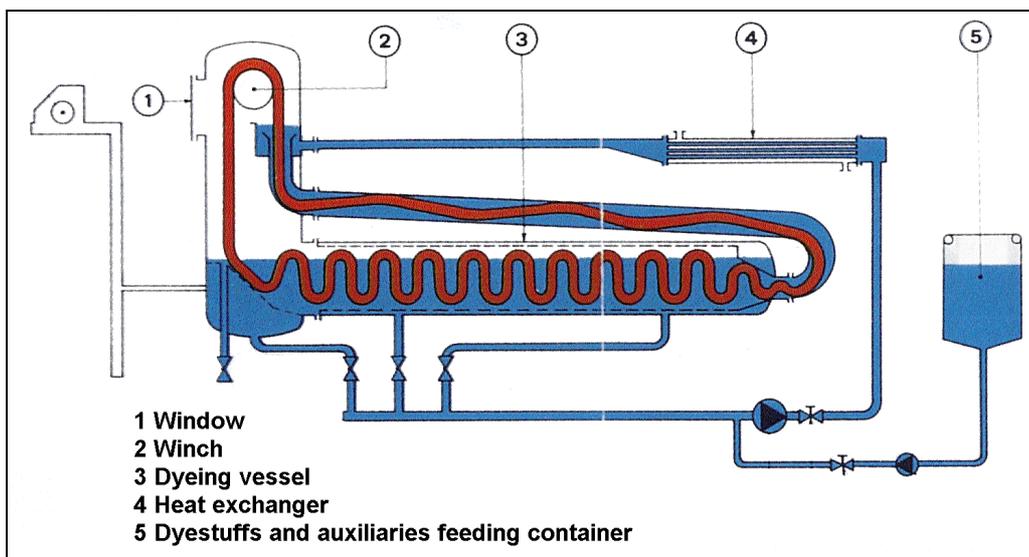
Figure 10.6: Schematic representation of an overflow dyeing machine

10.3.1.4 Air jet

The difference between air jet (see Figure 10.7) and jet machines is that in the former an air jet instead of a water jet keeps in circulation the fabric. The fabric passes into the storage area which contains a very small amount of free liquor. As a result, a reduction in water, energy and chemicals consumption can be achieved.

Because of the short liquor ratios achievable (from 2:1 to 4:1) the dye must be highly water-soluble.
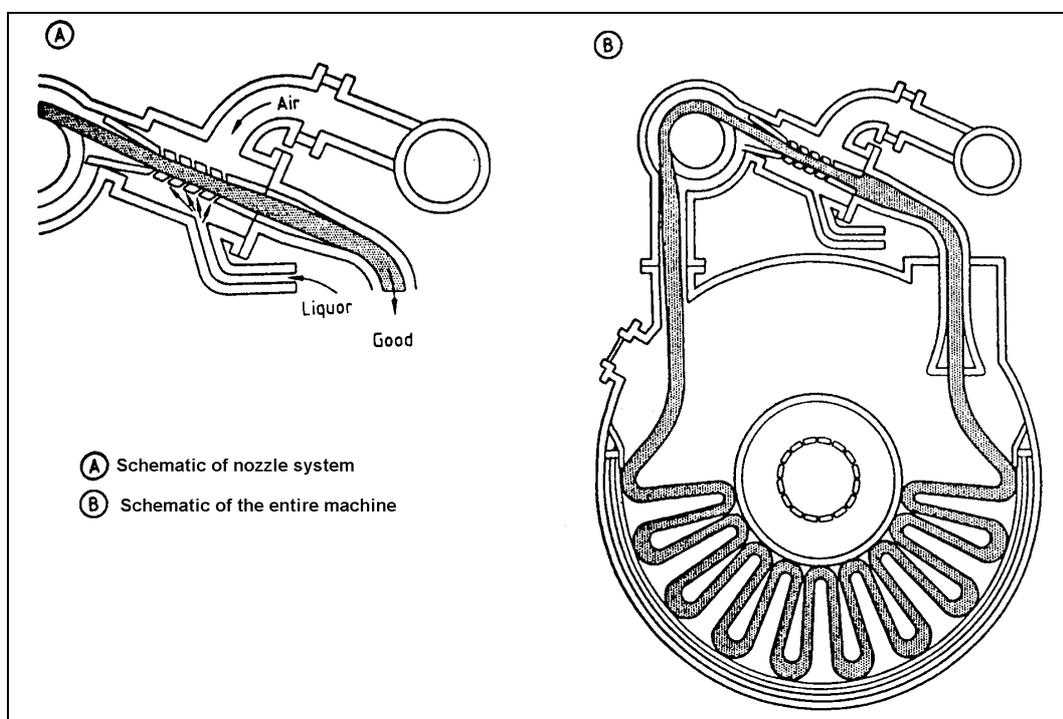

Figure 10.7: Schematic representation of jet dyeing machine

10.3.2 Continuous processes

Machines for treatment in continuous of fabrics in rope form are essentially composed of the following parts:
- a padding device for impregnating the fabric in rope form
- a storage area for the fixation of the chemicals applied
- a washing machine for fabric in rope form.

The padding device is composed of a long basin equipped with two or three rotating rollers at the inlet and another two at the outlet of it. The basin contains a concentrated solution of the chemicals and auxiliaries that have to be applied (desizing agents, bleaching agents, etc.). The fabric is pressed by the rotating rollers at the inlet in order to obtain a homogeneous absorption of the chemicals and the elimination of air. The other two rollers only squeeze the fabric. After squeezing the fabric keeps only a relatively low amount of bath. As a result high concentrations of the chemicals are needed, moreover the solutions must be adequately stabilised to avoid unwanted oxidation reactions, etc.

The storage area (also called reaction chamber) can have different shapes: one typical model is the J-Box. The J-Box is filled up by 1/3 with the treatment bath.

The main advantage of this technique is the high production capacity. On the other hand there is the risk of longitudinal creases, which can negatively affect the dyeing process. As a result this technique is mainly applied in case of white end products for pretreatment operations (e.g. bleaching).
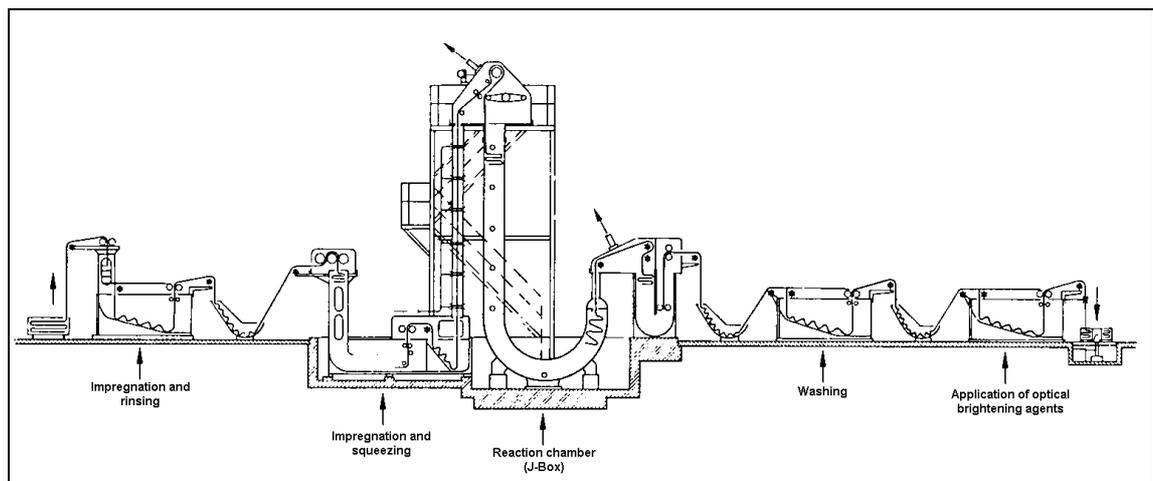

Figure 10.8: Example of continuous process for knitted fabric in rope form

10.4   Fabric in open-width

10.4.1 Batch processes

10.4.1.1 Beam

The fabric is wound in open-width on perforated cylinder called beam (see Figure 10.9). The fabric is stationary and the bath is pumped through the beam. The direction of the flow is normally from the inside to the outside of the roll of textile.

The ends of the beam are covered with metal sheets before the fabric is wound on, to prevent a short circuit of the liquor.

Beams can operate both under pressure and at atmospheric pressure.

These machines are suitable for pre-treatment operations like scouring and bleaching and also for dyeing of lightweight, wide and delicate goods. One disadvantage is represented by the risk of non-homogeneous penetration of chemicals and auxiliaries used for the treatment.


1 Fabric
2 Valve system for reversing direction of the flow
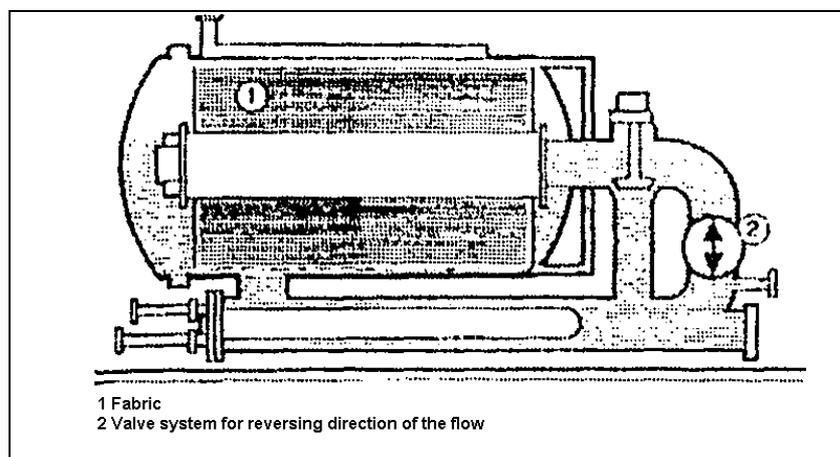
Figure 10.9: Schematic representation of a beam dyeing machine

10.4.1.2 Jigger

A jigger (see Figure 10.10) is composed of a trapezoidal tub containing the bath and two rolls on which the fabric is alternatively wound. In this type of machines the bath is stationary while the fabric is in motion. The fabric, initially wound on the first roll, flows through the bath and then is wound on the other one; the rotation is then reversed and the cycle continues. The fabric is led in its path by a few small guide rollers.

HT jiggers are also produced, allowing treatments at temperatures above 100 ºC. This type of machine is used not only for dyeing, but also for various wet treatments on fabrics in full width.

The main disadvantage of this system is the risk of non-homogeneity between the initial and final part of the piece. This is due to variations in feed speed and tension of the fabric, or temperature and chemicals concentration in the bath during the period of the treatment. However in modern jiggers speed and tension of the fabric is kept constant during the whole process.


1 Window
2 Fabric
3 Take up roll
4 let-off roll
5 Liquor
6 Guiding devices
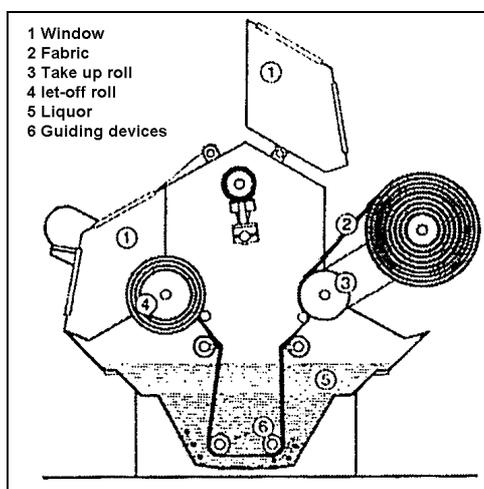
Figure 10.10: Schematic representation of a jigger

10.4.2 Semi-continuous and continuous processes

The following treatment steps are common to both semi-continuous and continuous processes:
- impregnation in a padding device
- storage/fixation, which can be carried out in different ways depending on the process applied (e.g. dry heat, steam)
- washing in continuous in open width.

The most widely used processes are the following:
- pad-batch
- pad-roll
- pad-jig
- pad-steam
- pad-dry
- thermosol.

They are briefly described in the following sections.

10.4.2.1 Padding machine for open-width fabric

Padding machines (foulards) are used to apply dyestuffs or other chemicals on fabric in open-width form. The fabric passes through the pad trough where it picks up the liquor. After leaving the pad trough, the fabric is squeezed between rubber rolls. The amount of liquor picked up depends mainly on the pressure produced by the two rolls, the speed at which the fabric is transported and the type of substrate. The level in the trough is automatically maintained to compensate for liquor picked up by the fabric. The liquor is kept in circulation to avoid differences in temperature and/or concentration. Different designs of foulards exist: some examples are shown in Figure 10.11.
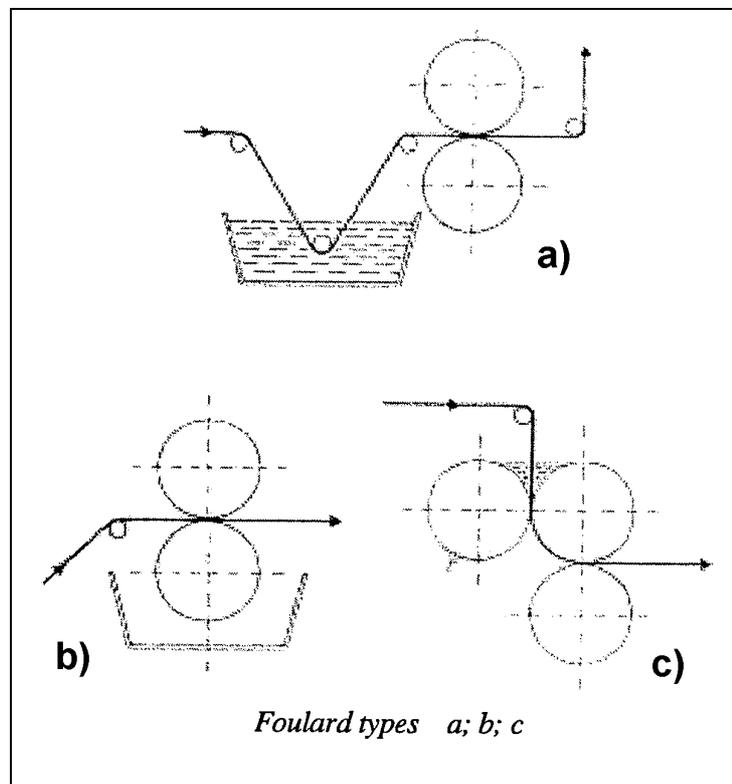

Foulard types   a; b; c

Figure 10.11: Foulard types

10.4.2.2 Pad-batch process (semi-continuous)

This process includes an impregnation step on a padding machine.

After being squeezed, the fabric is wound onto a roll and stored at room temperature. The roll is kept in slow rotation until the desired chemical processes (e.g. fixation of the dyestuffs, etc.) are complete. At the end the fabric is washed in an open-width washing machine.

This process is commonly used for pretreatment (e.g. desizing), dyeing (mainly with direct and reactive dyes). It is characterised by low water and energy consumption (about 50 – 80 % less than conventional systems) and good repeatability.
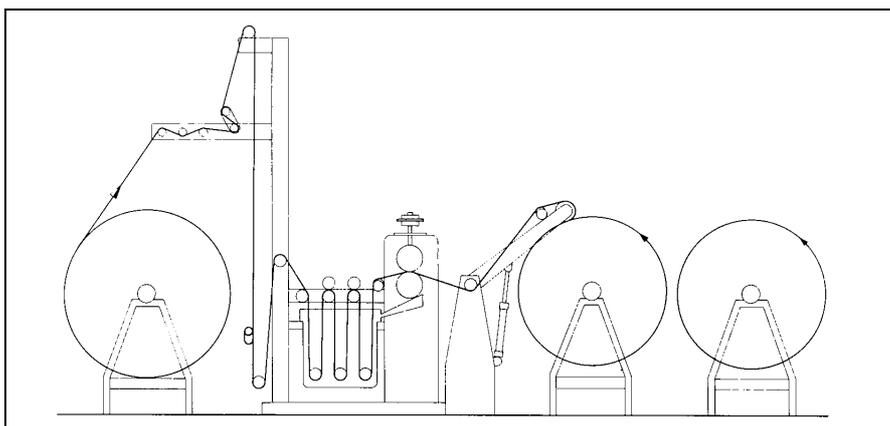

Figure 10.12: Schematic layout of a pad-batch plant

10.4.2.3 Pad-roll process (semi-continuous)

This process is similar to pad-batch, but in this case the fabric, after padding, passes through an infrared oven. It is than rolled and kept in slow rotation in a hot steam chamber until fixation, or other chemical processes are complete. The fabric is then washed in an open-width washing machine.

10.4.2.4 Pad-jig process (semi-continuous)

This process is generally used as a dyeing technique, mainly used for heavy weight fabrics with direct and reactive dyes.

In this process the fabric passes through a padding machine where it is impregnated with the dyeing bath, then the dyestuff is fixed on a jigger.

Sometimes the fabric can be dried in a hot-flue drier after padding, before entering the jigger.

The application of the dyestuff by padding allows for homogeneous dyeing and time saving if compared to traditional jigger dyeing processes.

10.4.2.5 Pad-steam process (continuous)

This technique is mainly used in for scouring woven fabric and dyeing. It is particularly suitable for the application of direct, vat, sulphur and reactive dyestuffs.

It includes the following steps:
- impregnation by padding
- steaming (at about 100 ºC)
- additional impregnation of the fabric with developing agents (e.g. reducing agents in vat or sulphur dyeing)
- washing and rinsing.

A) Padding of liquor (Bicoflex foulard) and air passage
B) Kiss padding of chemicals
C) Steaming and aftertreatment
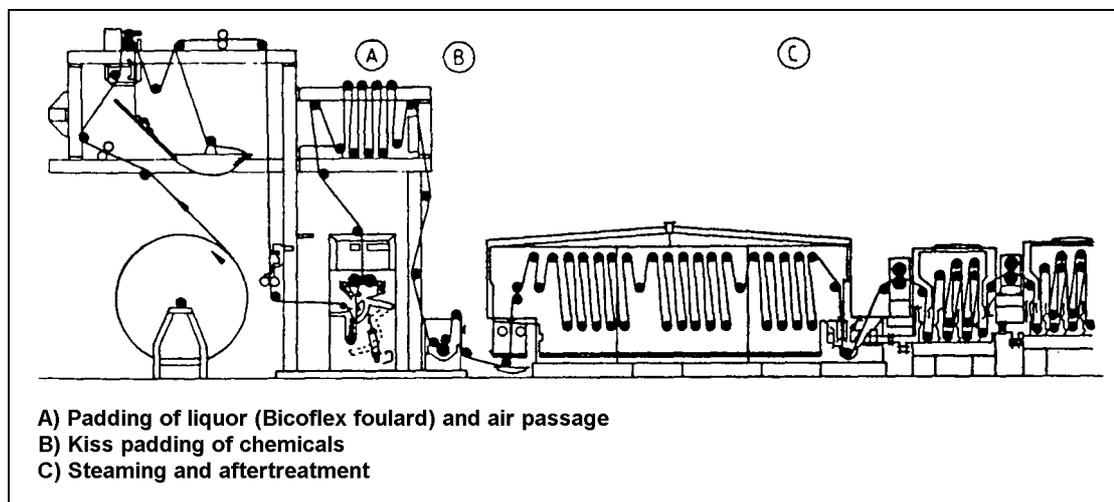
Figure 10.13: Schematic representation of a pad-steam plant (wet steam) for dyeing with vat dyes

10.4.2.6 Pad-dry process (continuous)

This process includes the following steps:
- impregnation by padding
- intermediate drying (optional)
- fixation in hot-flue
- washing.

10.4.2.7 Thermosol process (continuous)

This process is specific for dyeing with disperse dyestuffs polyester or cotton/polyester blends.

The process includes the following steps:
- impregnation in the dyeing liquor
- pre-drying in an infrared oven
- drying in hot-flue
- passage through a stenter frame for thermal fixation at 200 ºC of the disperse dyes to the PES.

An alkaline reductive after-treatment is then carried out or, in the case of cotton/polyester blends, the second dye is developed according to the procedure typical of its class, using in general pad-steam, pad-jig or pad-batch processes.

GLOSSARY

Adsorbable Organic Halogens (AOX)	A measure of the adsorbable organically bound halogens in water. The analytical test consists in adsorbing the organic substances contained in the water sample on activated charcoal (halogen-free). The charcoal is then eluted with sodium nitrate solution to completely remove chloride ions (non-organically bound halogen). Afterwards, the charcoal is burned in a stream of oxygen and the resultant hydrogen chloride is quantitatively determined. Only chlorine, bromine and iodine (not the ecologically important fluorine compounds) are determined with this analytical method. Bromine and iodine are calculated as Cl. The analytical values are expressed as AOX in: - mg Cl/l of water or - mg Cl/g of substance.

Aquatic toxicity

A measure of the effects of a given pollutant on aquatic life. The most common parameters are:

IC_{10} = inhibition concentration of bacterial growth (10 % inhibition). Concentrations above the IC_{10} value may strongly affect the efficiency of a biological treatment plant or even completely poison the activated sludge.

LC_{50} = lethal concentration (50 % mortality). It is used for fish and represents the water concentration at which a given substance causes the mortality of 50 % of the population.

EC_{50} = effect concentration (50 % effect). It is used for particularly sensitive organisms such as daphnia and algae.

The level of aquatic toxicity of a given pollutant is defined as follows:
- highly toxic: <0.1 mg/l
- very toxic: 0.1 - 1 mg/l
- toxic: 1.0 - 10 mg/l
- moderately toxic: 10 - 100 mg/l
- non toxic: >100 mg/l.

Biochemical Oxygen Demand (BOD)

A measure of the oxygen consumed by bacteria to biochemically oxidise organic substances present in water to carbon dioxide and water.

The higher the organic load, the larger the amount of oxygen consumed. As a result, with high organic concentrations in the effluent, the amount of oxygen in water may be reduced below acceptable levels for aquatic life.

BOD tests are carried out at 20 °C in dilute solution and the amount of oxygen consumed is determined after 5, 7 or, less commonly, 30 days. The corresponding parameters are called BOD_5, BOD_7 and BOD_{30}.

The analytical values are usually expressed in:
- mg O_2/l (effluent) or
- mg O_2/g (substance).

Biodegradability

A measure of the ability of an organic substance to be biologically oxidised by bacteria. It is measured by BOD tests (OECD tests 301 A to F) and relates to the biodegradation mechanisms taking place in biological waste water treatment works. It is usually expressed in % (of the substance).

Bioeliminability	A measure of the ability of an organic substance to be removed from the effluent as a consequence of all elimination mechanisms that can take place in a biological plant (including biodegradation). It is measured by the bio-elimination test OECD 302 B, which determines the total effect of all elimination mechanisms in a biological treatment plant: - biodegradation (measured over a long period - up to 28 days - in order to account for the biodegradation of substances that necessitate the development of specially acclimatised bacteria capable of digesting them) - adsorption on activated sludge - stripping of volatile substances - hydrolysis and precipitation processes It is usually expressed in % (of the substance).
Chemical Oxygen Demand (COD)	A measure of the amount of oxygen required to chemically oxidise organic and inorganic substances in water. COD tests are carried out at ca. 150 ºC in the presence of a strong oxidant (usually potassium dichromate). To evaluate the oxygen consumption, the amount of chromium VI reduced to chromium III is determined and the obtained value is converted into oxygen equivalent The analytical values are usually expressed in: - mg O_2/l (effluent) or - mg O_2/g (substance).
DDT	An organochlorine pesticide which has been banned in most European countries. The isomer used as pesticide is: p,p'-DDT 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane In the production process o,p'-DDT is also formed as a by-product. DDT and its metabolites, DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane) are persistent compounds which have demonstrated hormonal effects. In environmental samples, the concentration of DDT is often given as sDDT, which is the sum of DDT, DDE and DDD.
Finishing	This term can address both the sequence of wet treatments that are carried out to give the fibre the required colour and final properties, and any specific operation to apply functional finishes (easy-care, anti-felting, mothproofing agents, etc.).
Hazardous substances	Substances or groups of substances that have one or several dangerous properties such as toxicicity, persistence and bioaccumulability, or are classified as dangerous to humans or environment according to Directive 67/548 (Dangerous Substances Directive)
Make-up	Generic term used in the textile industry to name the different forms in which a textile material can exist. Examples are floc, yarn, woven and knitted fabric.
Nylon	Generic name for polyamide fibres.

Rayon	A generic name for man-made continuous filament fibres, obtained from regenerated cellulose. The term rayon is used for fibres produced by both cupra-ammonium and viscose processes.
Scouring	Removal of foreign impurities from textiles. In the case of wool, this term can address both the removal of the grease and dirt present on raw wool (wool scouring process) and the removal of spinning oils and residual contaminants from yarn or fabric in the wet treatments that are carried out before the dyeing process.
Texturised fibres	Filament yarns that have undergone a special treatement aimed at giving the fibre a greater volume and surface interest than the conventional yarn of the same fibre.
Top	A continuous untwisted strand or sliver of wool fibres.

Abbreviations and acronyms

Acronym/ abbreviation	Explanation
AC	Cellulose acetate
AC	Absorption coefficient
AE	Alcohol ethoxylates
AOX	Adsorbable organic halogens
APE	Alkyl phenol ethoxylates
APEO	Alkyl phenol ethoxylates
BAT	Best available techniques
BOD	Biochemical oxygen demand
BREF	BAT reference document
C.I.	Colour index
CMC	Carboximethyl cellulose
CO	Cotton
COD	Chemical oxygen demand
Conc.	Concentration
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CT	Cellulose triacetate
CU	Cupro
CV	Viscose
DAF	Dissolved air flotation
DTPA	Diethylenetriamine pentaacetate
DTPMP	Diethyletriamine penta(methylenephosphonic acid)
EDTA	Ethylenediamine tetraacetate
EDTMP	Ethylenediamine tetra(methylenephosphonic acid)
E-Fac	Emission factor
EL	Elastane
EO/PO	Ethylene oxide/propylene oxide (group of copolymers)
ETAD	Ecological and Toxicological Association of the Dyestuffs manufacturing industry
EUR	The euro, unit of european currency
EVA	Ethylene vinyl acetate
FR	Flame retardant
HC	Hydrocarbons
HCH	Hexachlorocyclohexane (pesticide)

HT	High temperature (process)
IGR	Insect growth regulators (group of pesticides)
IK	Indanthren cold (group of vat dyes)
IN	Indanthren normal (group of vat dyes)
IR	Infra red (light)
IW	Indanthren warm (group of vat dyes)
L.R.	Liquor ratio
NPE	Nonyl phenol ethoxylates
NRA	National Registration Authority (Australia)
NTA	Nitrilo triacetate
o.w.b	On the weight of the bath
o.w.f	On the weight of the fibre
OC	Organochlorines (group of pesticides)
OECD	Organisation for Economic Co-operation and Development
OP	Organophosphates (group of pesticides)
PA	Polyamide fibres
PAC	Polyacrylonitrile fibres
PCP	Pentacholoro phenol
PE	Polyethylene
PES	Polyester fibres
PP	Polypropylene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
Qww	Waste water flow
SBR	Styrene butadiene rubber
SI	Silk
SP	Synthetic pyrethroids (group of pesticides)
SS	Suspended solids
TEGEWA	Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V. (Industry Association)
TFI	Textile finishing industry
TOC	Total organic carbon
UF	Ultra filtration
US EPA	United States environmental protection agency
UV	Ultra violet (light)
VOC	Volatile organic compounds
WO	Wool
WW	Waste water
x-SBR	Carboxylated SBR

REFERENCES

1. B.O. Bateup, J. R. C., A.J. Poole, C. Skourtis and D.J. Westmoreland - CSIRO, Australia (1996). Effluent management. Top Tech '96.

2. BASF (1994). Products for Textile Finishing: Ecological Evaluation.

3. BASF (2000). BASF products for resin finishing.

4. CORBANI (1994). Nobilitazione dei Tessili.

5. CRIT-Prato (1999). IPPC - Italian Wool Textile Industry.

6. ECA/GuT (2000). Production Processes for Textile Floorcoverings - Draft 1.

7. ENco (2000). Best Available Techniques in Wool and Wool-blend Carpet Yarn Wet Processing.

8. EPA, U. (1995). Best Management Practices for Pollution Prevention in the Textile Industry.

9. EURATEX (2000). Textiles BAT Reference Document.

10. Graham Savage-NRA, A. (1998). The Residues Implications of Sheep Ectopasiticides, National Registration Autorithy for Agricultural and Veterinary Chemicals.

11. Interlaine (2000). Best Available Techniques in Wool Scouring.

12. RIZA (1998). Dutch notes on BAT for the textile and Carpet Industry, RIZA, Institute for Inland Water Management and Waste Water Treatment.

13. Schonberger (2000). Pollution Prevention and Waste Reduction in the Textile Industry.

14. Stewart, R. G. (1988). Wool Scouring and Allied Technology.

15. TEBODIN (1991). Technical and economic aspects of measures to reduce water pollution from the textile finishing industry.

16. TEGEWA (1987). Nomenclature of Textile Auxiliaries, Leather and Fur Auxiliaries, Paper Auxiliaries and Surfactants.

17. UBA (1994). Reduktion der Abwasserbelastung in der Textilindustrie, Schonberger, H.; Kaps, U.

18. UBA (2000). "Reduktion der Abwasserbelanstung in der Textilindustrie." Schonberger, H.

19. Ullmanns (2000). Ullmann's Encyclopedia of Industrial Chemistry.

20. UNEP (1994). The Textile Industry and the Environment.

21. VITO (1998). Best Available Techniques in the Textile Industry.