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1 Introduction

In order to comply with brand requirements and government regulations, suppliers of textile and leather products must be able to identify the potential negative impacts their chemical processes may have on the environment, workers’ health, and consumer safety. It can be a difficult and confusing task to quantify these impacts – especially for suppliers that “finish” textile and leather products and may not receive complete chemical information from their own suppliers.

This guidance document is intended to provide readers with an overview and background on the types of chemicals used in textile and leather goods manufacturing so that suppliers who make or finish textile and leather goods will have the necessary information to assess the likely environmental, workplace health, and consumer safety impacts of these products.

How to Use This Document

This document is organized into the following sections:

- 1: Introduction
- 2: Textile Raw Materials
- 3: Textile Chemicals and Auxiliaries
- 4: Production Processes
- 5: Role of Pesticides
- 6: Natural Leather Finishing
- 7: Artificial Leather Manufacture and Finish
- 8: Adhesives

After reading the introduction and background information contained in this section, readers may wish to go directly to the section of concern to them. For example, a natural leather goods finisher would make use of Section 6 and perhaps Section 8, whereas a textile finisher might make use of Sections 2 through 5 and Section 8. In each section, we will describe the technology involved, the types of chemicals used, and why and how they are used. We will also provide information about the impacts each process might have on the environment (energy use, air and water emissions), workplace health and safety concerns, and the potential for residue on the final consumer products.

This guidance document will be updated periodically. Information about the toxicological and ecological effects of the chemicals used in textile and leather products is constantly developing and regulators are adding chemicals to classification systems such as REACH or GHS. Where information may appear to be incomplete in certain sections, it will undoubtedly be updated in upcoming revisions.

Throughout the document, we have noted the chemical substances that might play an important role with respect to environmental emissions or for worker health and consumer safety in red font. If such substances will be used or generated in a process, we urge suppliers to refer to the material’s Safety Data Sheet to become familiar with its hazardous properties and the appropriate control measures.

1.1 Background on Textile Industry

When attempting to assess the environmental, worker health and consumer product safety impacts of textile finishing, it is easy to become overwhelmed by the large number of textile and chemical raw
materials that may be combined in hundreds or even thousands of processes. It is therefore important to begin with an understanding of the basic textile manufacturing process. In Figure 1.1, we see that two resources – textile raw materials (which may be natural or man-made) and chemical raw materials – are combined using energy (human, electric), water, and air to make a new product, the desired textile product. This combination also results in some wastes – in the form of heat, and air emissions (off gas), waste water, and solid wastes – that are now chemically changed, or loaded.

The impacts associated with the textile raw material are the result of the processing work that took place to make it useful to the finisher – the cleaning, spinning, dyeing, etc. that occurred before the textile raw material arrived at the finisher. These steps are described in Section 2.

The chemical raw material also has impacts that are the result of the property of the chemical itself or the by-products and impurities formed during its production.

These ecological or toxicological impacts or charges are released during the textile finishing process, but are mostly created by the raw material suppliers. A more or less small portion of all the chemical input remains on the final textile product or intermediate either intentionally (color, effect) or unintentionally (impurities, by-products or reaction products from the process).

Reducing Impacts. The impacts associated with textile and chemical raw materials may be reduced in several ways:

- The raw material supplier may substitute and minimize the use of certain substances.
- The finisher may optimize process technologies.
- The finisher may make use of end-of-pipe technologies to capture or remediate its discharges.

Case Study of Austrian Textile Industry. In order to understand the major sources of textile discharges and to provide a sense of the magnitude of the impacts and of the best opportunities to
reduce these impacts, we will look at a country-wide eco/toxicological survey made within the Austrian textile industry in 1997. Figure 1.2 describes the country’s textile production chain (total fiber consumption: 95,000 metric tons per year (61 % man-made fibers, 27 % cotton, 5 % wool; total production knitted/woven textiles: 79,000 metric tons per year). Figure 1.3 shows the input scheme for the total amounts used per year of chemical raw materials (in original trading form), all separated for organic and inorganic substances. This makes about 28,000 metric tons per year of input. Figure 1.4 represents the real total emissions to water and air in Austria, based on the pure organic and inorganic substances, which are about 16,000 metric tons per year.
Figure 1.3: Basic Scheme of Inputs to Textile Finishing Industry (Austria)

Total inputs: 28,000 tons/year (organics and inorganics)

- Fiber/yarn dyeing
  - 4550 t inorganics
  - 2045 t organics
  - 105 t organic detergents

- Approx 5400 t organics from raw materials

- Pre-treatment
  - 8435 t inorganics
  - 1348 t organic formulations

- Dyeing

- Printing
  - 730 t inorganics
  - 970 t organic formulations

- Finishing
  - 4183 t organics
The environmental releases associated with the major steps in textile product manufacturing that are depicted in Figure 1.4 are summarized in Table 1.1.

<table>
<thead>
<tr>
<th>Table 1.1: Environmental Releases from Austrian Textile Industry, 1997</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-treatment</strong></td>
</tr>
<tr>
<td><strong>Dyeing</strong></td>
</tr>
<tr>
<td><strong>Printing</strong></td>
</tr>
<tr>
<td><strong>Finishing</strong></td>
</tr>
</tbody>
</table>

This study resulted in the following findings, which are useful as background information for textile producers and finishers around the world:

- The quantity of inorganics (mainly salts) emitted is roughly equal to the quantity of organics emitted – both about 8000 metric tons/year, for a total of about 16,000 metric tons per year.

- **More than 90% of the organic input to the finishing process remains on the textile. More than 90% of the organic input to pre-treatment and dyeing is released to the environment.**

- 10% - 20% of all the individual organic chemical raw materials used make up 80% - 90% of the total amount used.

- Nearly 90% of the organic raw materials are discharged into waste water. The rest are discharged to the air and as solid waste.
Only about 10% of the organic textile auxiliaries (main component water) used are released to the environment.

The main material inputs to the European textile industry in the 1990s are listed in Table 1.2. Note that the thousands of special chemicals with potential toxicological and ecotoxicological properties are of the most concern from a consumer safety perspective, while they represent the smallest quantity of inputs to this industry.

<table>
<thead>
<tr>
<th>Substances</th>
<th>Inputs [metric tons/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts</td>
<td>200 – 250,000</td>
</tr>
<tr>
<td>Natural fiber by-products</td>
<td>50 – 100,000</td>
</tr>
<tr>
<td>Sizes (starch/derivatives dominantly, less polyacrylates and polyvinylalcohol)</td>
<td>80 – 100,000</td>
</tr>
<tr>
<td>Preparation oils (mostly mineral oils, less ester oils)</td>
<td>25 - 30,000</td>
</tr>
<tr>
<td>Tensides (dispersing agents, emulsifiers, detergents) (large variety)</td>
<td>20 - 25,000</td>
</tr>
<tr>
<td>Carbonic acids (mainly acetic acid)</td>
<td>15 - 20,000</td>
</tr>
<tr>
<td>Thickeners (starch derivatives)</td>
<td>10 - 15,000</td>
</tr>
<tr>
<td>Urea</td>
<td>5 – 10,000</td>
</tr>
<tr>
<td>Complexing agents</td>
<td>&lt; 5,000</td>
</tr>
<tr>
<td>Solvents</td>
<td>?</td>
</tr>
<tr>
<td>Thousands of special substances with potential eco/toxicological properties</td>
<td>&lt; 5,000</td>
</tr>
</tbody>
</table>

The European textile industry is based on about 15,000 more or less complex chemical formulations. The reader will note that dyestuffs are entirely missing from Table 1.2. Although very impressive in color, the amount of dyestuffs, in relation to the other substances, is not significant (< 1 % of the total inputs (in metric tons/year), so they are neglected here. However, dyes are intended to stay on the final textile products and therefore pose a potential consumer safety issue.

By far, the largest discharger to the environment is the textile raw material supplier. It is not easy to influence this supplier. The textile raw material is oftentimes not under selection control of the textile finisher because it is controlled instead by the fabric producer (e.g., weaver). The situation is much easier with the chemical raw material, over which the finisher has full control.

Since the environmental impacts associated with textile finishing materials may derive from several different sources, the different raw materials will be described in this document with respect to their:

- means of production;
- chemical composition;
- basic ecological and toxicological properties;
- impact on workplace, water, air, waste; and
- by-products and impurities.
This information is necessary to evaluate individual processes in terms of air and water emissions, workplace atmosphere, liquid and solid waste and even residuals on the finished textile product. While necessary, however, textile companies hardly ever receive “complete” information on textile raw materials and chemicals from suppliers.

**Example of “Complete” Information on an Individual Process – Flame Retardant for Cotton.** As an example, the typical information provided to a finisher regarding a flame retardant for cotton is included in the first two columns of Table 1.3, below. To evaluate the actual environmental impacts, however, some basic knowledge about the “real” composition of the flame retardant substance should be available. This is shown in the final column of Table 1.3. (Based on real analysis, the actual formulation contains about 500 separate chemical substances.) Additionally, the flame retardant user should have some information regarding how the system behaves depending on different process parameters – in this case:

- Reactivity of melamine resin with *phosphonate*
- Reactivity of this complex with cotton
- Release of all reaction by-products and original impurities and by-products of the components to the environment and the consumer

Equipped with the complete information, the textile finisher will reasonably be able to substitute materials, minimize impacts, and clean or remediate its environmental impacts.
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Typical Composition of Flame Retardant Formulation</th>
<th>Actual Composition of Substances Listed in Flame Retardant Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 g/l</td>
<td>Polysiloxane formulation</td>
<td>20 % Polysiloxane with chain distribution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 % Oligosiloxane, cyclic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 % Acetic acid, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 % Fatty alcohol, ethoxylate, by-products</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 % Glycerol, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 % Fatty amine, ethoxylate, by-products</td>
</tr>
<tr>
<td>20 g/l</td>
<td>Stearylurea formulation</td>
<td>20 % Methylolated stearylurea, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.7 % Ethanediol, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3 % Methanol, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 % Diisobutoxy methane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 % Isobutanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 % Formaldehyde</td>
</tr>
<tr>
<td>2 g/l</td>
<td>Phosphoric acid ester formulation</td>
<td>50 % Phosphoric acid butylester, technical</td>
</tr>
<tr>
<td>20 g/l</td>
<td>Melamine resin</td>
<td>50 % Trimethyl(methylol)melamine ether, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 % Ethanediol, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 % Toluene sulfonic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 % Formaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 % Inorganic salts</td>
</tr>
<tr>
<td>70 g/l</td>
<td>Dimethylol dihydroxy ethylene urea resin</td>
<td>70 % Dimethylol dihydroxy ethylene urea, resin, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 % Diethylene glycol, technical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 % Organic acid salts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 % Formaldehyde</td>
</tr>
<tr>
<td>25 g/l</td>
<td>Phosphoric acid</td>
<td>85 % Phosphoric acid, technical</td>
</tr>
<tr>
<td>400 g/l</td>
<td>Alkylphosphonic acid ester</td>
<td>75 % Dimethoxymethylphosphonopropion-amide, methylolated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 % Dimethylmethane phosphonic acid ester</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 % Phosphites, different qualities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 % Formaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 Acrylamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 Methylol acrylamide</td>
</tr>
<tr>
<td>458 g/l</td>
<td>Water</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.3: Flame Retardant Composition**
2 Textile Industry: Basic Raw Materials

A simplified textile finishing industry scheme is shown in Figure 2.1. As indicated in Section 1, in order to understand the environmental, worker health and consumer safety impacts of textile finishing, we will first need to examine the basic raw materials used within the textile finishing processes. This will help textile finishers establish priorities for reducing negative impacts associated with their products. These basic raw materials are:

- textile raw materials such as fibers, yarns and textiles
- chemical raw materials like chemicals, dyestuffs and auxiliaries.

2.1 Textile Raw Materials

The material flow in the textile finishing chain is shown in the very simplified scheme in Figure 2.2. In the following sub-sections, we will review first the natural raw materials and then the chemical raw materials involved in the material flow. We will discuss the chemistry and technology involved in making these materials, along with the potential environmental impacts, worker health concerns and consumer product safety implications.

Reminder: Those chemicals for which there may be significant concerns regarding environmental impacts, worker health, and consumer product residues are highlighted in red font. We urge suppliers to obtain the Safety Data Sheets for these materials in order to become familiar with their hazardous properties and the appropriate control measures.
2.2 Natural Fibers

2.2.1 Wool

Woolen textiles constitute around 5% - 7% of all finished textiles. The natural growth process of wool produces fiber with a range of physical properties, including fiber diameter, staple length, extent of crimp, color and luster. Fiber for any given end use is selected on the best balance of these properties and in many cases the final textile article will contain a blend of wool from different sources designed to achieve the highest cost/performance ratio. In broad terms, the long, fine fiber typically produced by Merino sheep will be processed via the worsted system into apparel products, while shorter, courser fiber types are typically processed into carpet yarns and hand knitting yarns. There are, however, many exceptions to these generalizations.

Raw wool typically contains a variety of inorganic and organic contaminants:

- Wool grease (lanolin) 2 – 25%
- Suint (dried perspiration) 2 – 12%
- Dirt (principally sand) 5 – 45%
- Vegetable matter 0.5 – 10%
- Wool fiber 40 – 90%
Fine wool from Merino sheep typically contains 13 % wool grease, while coarser wool contains on average 5 % grease.

Wool grease, suint salts and dirt are largely removed in the wool scouring process (see the separate section on wool scouring for more detail). Any remaining dirt and vegetable matter, together with short fiber fragments are removed either mechanically during carding or chemically by carbonizing. The resulting clean fiber typically contains less than 0.5 % residual wool grease.

Raw wool may also contain residues of chemicals arising from background environmental levels and from veterinary medicines used to protect sheep from ectoparasites such as the blowfly. These compounds may be insecticides, acaricides (kill ticks and mites) or insect growth regulators. The environmental consequences associated with the use of these materials in animal husbandry are well understood in major wool-producing countries, most of which have regulations to control their use and minimize residues at shearing.

Batching and spinning oils are applied for yarn production. Combed slivers are washed before spinning to remove combing oils. The washing of fabrics removes batching oils and impurities (e.g., wax) resulting from the weaving process.

In the presence of humidity and alkali at temperatures between 40 °C and 100 °C, small amounts of ammonia, hydrogen sulfide, sulfuric acid and their salts are released from wool. These chemicals are generally not released under dry heat conditions.

2.2.2 Cotton

Natural cotton fiber consists mainly of cellulose and some other components of varying composition as shown in Table 2.1:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>88 % - 96 %</td>
</tr>
<tr>
<td>Pectin substances</td>
<td>0.7 % - 1.2 %</td>
</tr>
<tr>
<td>Wax</td>
<td>0.4 % - 1.0 %</td>
</tr>
<tr>
<td>Proteins</td>
<td>1.1 % - 1.9 %</td>
</tr>
<tr>
<td>Ash</td>
<td>0.7 % - 1.6 %</td>
</tr>
<tr>
<td>Other organic components</td>
<td>0.5 % - 1.0 %</td>
</tr>
</tbody>
</table>

The organic material in natural cotton (pectin substances, proteins, etc. -- see Table 2.1 above) is released during pre-treatment processes and creates chemical oxygen demand (COD) in the waste water. Inorganic substances (salts of K, Na, Fe, etc.) are also removed from cotton in the pre-treatment processes.

To protect the cotton plants and fibers, considerable amounts of pesticides are used (around 18 % of world-wide pesticide consumption). Pentachlorophenol (PCP) is used as a preservation agent. Studies conducted in the 1990s on raw cotton from different countries shows that of pesticides tested, only very small amounts (below the
permissible values for food in Germany) could be detected. (See Section 5, Role of Pesticides.)

2.2.2.1 Spinning Auxiliaries

In the spinning process, specific auxiliaries (spinning oils) are applied (between 0.5 and 1 % by weight) to the cotton fibers in order to increase the gliding property and decrease the frictional resistance. Typical components are: pentaerythrit stearate (or -dioleate) and fatty alcohol phosphoric acid esters.

2.2.2.2 Sizing Agents

Sizing agents are textile auxiliaries that optimize the weaving process. Before weaving, sizing agents (in the form of water solutions or water dispersions) are applied to the yarns on the slasher. The sizing agent forms a protective film on the yarn. After weaving and before dyeing/finishing processes, the sized grey textiles must be desized (washed out) with hot water and auxiliaries.

The chemistry of sizing agents is described below:

Natural Products

Starch is the most common natural sizing agent; it is used in approximately 70 % of the European market for cotton. Starch can be derived from different substances, typically corn and potatoes. Starch is used mainly for cotton products and other natural fibers. For high-performance weaving mills (high speed of weaving, high quality products) starch by itself is not always suitable and is therefore used in blends with other sizing agents. Because starch is not (or only sparingly) water soluble, it must be degraded for desizing into water soluble sugars, which are then removed by washing before scouring. Starch therefore cannot be reused or recycled, and is responsible for most of the chemical oxygen demand/biological oxygen demand (COD/BOD) loading from finishing mills’ waste water discharges.

Synthetic Products

Synthetic sizing agents include polyvinyl alcohol (PVA; fully/partially saponified polyvinyl acetate), polyacrylate (acrylic acid based, ester based), polyester and vinyl acetate copolymerizates. Synthetic sizing agents are water soluble and can be washed out with surfactants, or with surfactants and alkali in the scouring phase.

Semi-Synthetic Products

These include modified starches (hydroxyethyl, hydroxypropyl, carboxymethyl, carbamate, phosphate), galactomannan derivatives and modified cellulose (carboxymethylcellulose).

The ecological properties of sizing agents are listed in Table 2.2 below.
### Table 2.2: Ecological Properties of Sizing Agents

<table>
<thead>
<tr>
<th>Product</th>
<th>COD [mg O$_2$/g]</th>
<th>BOD [mg O$_2$/g]</th>
<th>Biodegradability</th>
<th>Degree of Bioelimination* [%]</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ability to adsorb to sludge</td>
<td>+ low +++</td>
</tr>
<tr>
<td>Starch</td>
<td>900-1000</td>
<td>500-600</td>
<td>Good</td>
<td>95</td>
<td>(+++) high</td>
</tr>
<tr>
<td>Carboxymethylstarch</td>
<td>~950</td>
<td>-</td>
<td>Good (depends on degree of substitution)</td>
<td>90</td>
<td>++</td>
</tr>
<tr>
<td>Galaktomannan</td>
<td>1000-1150</td>
<td>400</td>
<td>Good</td>
<td>95</td>
<td>++</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
<td>800-1000</td>
<td>50-90</td>
<td>Poor</td>
<td>Moderate to Poor</td>
<td>++</td>
</tr>
<tr>
<td>Polycrlylate (acrylic acid based)</td>
<td>~1800</td>
<td>-</td>
<td>Poor</td>
<td>Poor</td>
<td>++</td>
</tr>
<tr>
<td>Polycrlylate (ester based)</td>
<td>1350-1650</td>
<td>&lt; 50</td>
<td>Poor</td>
<td>95</td>
<td>+++</td>
</tr>
<tr>
<td>Polyester</td>
<td>1600-1700</td>
<td>&lt; 50</td>
<td>Poor</td>
<td>Partial</td>
<td>+++ (for PES)</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>~1700</td>
<td>30-80 (not adapted sludge)</td>
<td>Good (adapted sludge)</td>
<td>Good</td>
<td>+++</td>
</tr>
</tbody>
</table>

In most cases, sizing is a mixture of the above-mentioned substances. The mixing might be carried out by the user or by the supplier.

Additional auxiliaries normally used in sizing mixtures include:

- lubricants, softeners, emulsifiers, anti-sticking agents (these are usually emulsified fatty acids, and fatty esters) (impart smoothness and low frictional properties to the yarn)
- defoamers (to decrease foam if the water is too soft)
- deliquescentss such as urea (for better wash-out effects)

Auxiliaries influence the aquatic toxicity and BOD of sizing agents.

The amount of size pick-up needed on the yarns and the type of the sizing agent depends on the yarn type (CO, CO/PES), yarn titer, etc., the type of the weaving machine (weft insertion rate, etc.) and the sizing process. Therefore size pick-up of warp yarns varies in a wide range (5% - 15%). Practically all sizing agents have to be protected against bacteria-induced decomposition and are therefore treated with preservatives like chlorinated phenols, ortho-phenylphenol, isothiazolinones, etc. Poorly de-sized materials might, therefore, contain residual biocides.
2.2.3 Silk

Silk is produced by the silkworm, *Bombyx mori*. The filament can be unwound directly from the cocoon. The length of the thread (1.0 – 3.5 dtex) is in the range of 700 to 1500 m. The silk thread is composed of two fibroin filaments wrapped with sericine (silk gum). Silk is a protein fiber, like wool. However, silk contains less cystine (sulfur-containing amino acid). Silk is hygroscopic (moisture content: 9 - 11 %). It is necessary to partially or completely remove the sericine, natural oils, and organic impurities to prepare a silk yarn for dyeing and to prepare silk fabrics for dyeing and printing.

2.2.4 Flax

Flax is a bast fiber, that is, a part of the plant stem. The fiber is isolated from the flax stem in several different steps. After cutting, the flax is retted (dew retting, water retting, enzymatic, microbiotic, steam or chemical retting) to dissolve away much of the cellular tissues and pectins surrounding the fiber and facilitate its separation from the stem. Pectinic substances and hemicellulose are degraded in this step. Rovings are produced by further mechanical treatment. Spinning is carried out using dry spinning or wet spinning technologies.

2.3 Man-Made Fibers

2.3.1 Polyester (PET, Polyethylene terephthalate)

The largest quantity of man-made fibers are those made of polyethylene terephthalate (PET). Polyester fibers consist of at least 85 % of an ester made from ethylene glycol and terephthalic acid.

Polycondensation occurs in a vacuum at around 280 °C with catalysts (e.g., Sb-, Ge-, Ti-derivates like antimony trioxide in the range of a few 100 ppm). The polymer contains 1 - 3 %, by mass, of di- and trimers.

To avoid thermal, thermo-oxidative or hydrolytical degradation, the polymer contains special additives such as:

- Stabilizers (phosphates, phosphonates, phosphinic acid [0.02 – 0.2 %])
- Antioxidants (sterically hindered phenols [0.05 – 0.2 %])
- UV-stabilizers (benzotriazole, hydroxybenzophenones)

Environmental impacts result from oligomers and applied primary and secondary preparation systems, as well as from antimony trioxide. Antimony trioxide can also be found in the final textile products and therefore is a consumer safety consideration.

2.3.2 Polyamides (PA)

2.3.2.1 Polyamide 6.6 (PA 6.6)

PA 6.6 is produced by thermal polycondensation of equimolecular amounts of adipic acid and 1,6-hexamethylene diamine (oxygen-free atmosphere) at 200 - 280 °C. The equilibrium condensate contains small amounts of monomers and cyclic dimers (total extractable amount: 2 % [herein: 96 % cyclic dimer]).
2.3.2.2 Polyamide 6 (PA 6)

PA 6 is made of $\varepsilon$-caprolactam. The reaction starts with the acid-catalyzed hydrolytical opening of $\varepsilon$-caprolactam to $\varepsilon$-aminocaproic acid. There is a temperature-dependent equilibrium condensate at 250 °C, which contains 89 % (by mass) linear polyamide; 8.5 % (by mass) caprolactam; and 2.5 % (by mass) higher cyclic amides. The caprolactam content can be reduced to 0.2 % by extraction with hot water. During the melting process of the fiber production, the caprolactam content rises again to about 5 %, which will be partially emitted during following thermal treatments.

Textile fibers made of polyamide contain phenolic antioxidants (e.g., amine salts of 3,5-dialkyl-4-hydroxyphenylcarbonic acids). There are environmental impacts resulting from monomers (oligomers) and from applied primary and secondary preparation systems. Caprolactam should be considered from a consumer safety perspective.

2.3.3 Polyacrylonitrile (PAN)

Polyacrylonitrile fibers contain at least 85 % polymerized acrylonitrile. Most of the PAN fibers contain ternary copolymers with 89 % - 85 % acrylonitrile, 4 % - 10 % non-ionogen comonomers and 0.5 % - 1 % ionic comonomers with sulfo or sulfato groups. PAN polymers are mostly produced by suspension polymerization in water. The polymerization is initiated by water-soluble reduction-oxidation (redox) systems.

N,N-dimethylformamide (DMF) is used as a solvent for the dry spinning process. For the wet spinning process, DMF as well as N,N-dimethylacetamide (DMAc), dimethyl sulfoxide and aqueous solutions of inorganic salts or acids are used. Residual solvent and salts are washed out in hot water in the after-treatment.

Environmental impacts from PAN fibers result mainly from residual solvent contents (0.2 % - 2 %) and applied primary and secondary preparation systems. The amount of residual monomers, such as acrylonitrile, is < 1 ppm and more or less negligible.

2.3.4 Polypropylene (PP)

Polypropylene is an addition polymer produced from “propene” (propylene – C₃) in the presence of catalysts. The orientation of the tertiary methyl group on each monomer unit on the chain determines the properties. Isotactic PP (all methyl groups have the same orientation) have the most useful properties for textile fibers. Isotactic PP tends to crystallize under certain conditions, which has noticeable effects on the end product. PP is highly sensitive to oxidation in the presence of heat with air, metals or UV radiation. To prevent this, antioxidant additives are used. Typically a combination of primary antioxidants (hindered phenolics are the most common) and secondary antioxidants or “peroxide decomposers” (phosphites are the most common) are used to inhibit oxidation. An acid scavenger (usually calcium or zinc stearate) is also necessary. Given the locations of cadmium and zinc in the Periodic Table of the Elements, there may always be some cadmium impurities.

During the extrusion process, some low molecular weight aliphatics (C₅ – C₁₅) and volatile additives are emitted into the air, requiring special ventilation precautions.
2.3.5 Polyurethane (PU)

Polyurethane polymers are formed by reacting at least two isocyanate functional groups with at least two alcohol groups in the presence of a catalyst (e.g., tertiary amines such as dimethylcyclohexylamine, and organometallic salts such as dibutyltin dilaurate). Dibutyltin dilaurate always contains impurities of tributyltin monolaurate. The first essential component of a polyurethane polymer is the isocyanate. Molecules that contain two isocyanate groups are called diisocyanates. These molecules are also referred to as monomers or monomer units, since they themselves are used to produce polymeric isocyanates that contain three or more isocyanate functional groups. Isocyanates can aromatic compounds such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI), or aliphatic compounds such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI).

The second essential component of a polyurethane polymer is the polyol. Molecules that contain two hydroxyl groups are called diols, those with three hydroxyl groups are called triols, etc. In practice, polyols are distinguished from short-chain or low-molecular-weight glycol chain extenders and cross linkers such as ethylene glycol (EG), 1,4-butandiol (BDO), diethylene glycol (DEG), glycerine, and trimethylol propane (TMP). Polyols are polymers in their own right. They are formed by free radical addition of propylene oxide (PO) or ethylene oxide (EO) onto a hydroxyl- or amine-containing initiator, or by polyesterification of a di-acid (e.g., adipic acid) with glycols, such as ethylene glycol or dipropylene glycol (DPG). Polyols extended with PO or EO are polyether polyols. Polyols formed by polyesterification are polyester polyols.

2.3.6 Elastane (EL)

Elastane fibers are made of at least 85% polyurethane (PU). Their characteristic properties are based on alternately long, “soft,” low-melting, flexible segments and relatively short, “hard,” high-melting segments with strong hydrogen bonds.

Elastane fibers are produced by dry spinning with N,N-dimethylacetamide as the solvent. The residual solvent content in the fiber is < 1%.

Additives help reduce the high adhesiveness of elastane fibers and guarantee sufficient gliding properties during processing. The composition of these additives is 95% silicone oils and 5% surfactants.

2.3.7 Viscose (CV)

Viscose fibers are made of alkaline solutions of cellulose xanthogenate, in which carbon disulfide is the solvent. The spinning solution coagulates in acid baths containing sulfuric acid, sodium sulfate and zinc sulfate.

The environmental impacts associated with viscose production relate to the applied primary and secondary preparation systems.

2.3.8 Cupro (CU)

Cellulose (wood pulp) can also be dissolved in an aqueous solution of ammonia and copper sulfate. Cupro fibers are produced in a wet spinning process followed by a washing step (to wash out copper salts).
2.3.9 Acetate (CA)

Acetate fibers are cellulose derivatives (cellulose esters). Cellulose (wood pulp) is treated with glacial acetic acid and acetic anhydride, together with catalysts (sulfuric acid, zinc chloride) to produce cellulose triacetate. Hydrolytic treatment (saponification), in which 2 – 2.5 of the cellulosic OH-groups are esterified, produces diacetate. Fibers from diacetate and triacetate are generated in a dry spinning process. (Using acetone as the solvent in the spinning process produces diacetate fibers; using methylene chloride produces triacetate fibers.

2.4 Preparation Systems

Lubricants play an important role in fabric manufacture; any mechanical operation will employ lubricants to avoid friction damage to textile materials. Directly after the spinning beam and quenching ducts on the fiber production line, the man-made fibers are prepared with spin finishes; these are considered the primary preparation systems and consist of 0.3 – 0.8 % fatty acid esters. These systems must provide sufficient moisture content in the fibers to guarantee perfect bobbin winding as well as smoothness for further processing (see Figure 2.4).

The production of man-made fibers is a physical conversion of linear polymers with high molecular weights into thin fibers. To accomplish this, the unoriented molecular chains have to be fixed parallel to the fiber axis after spinning (i.e., drawing) and released from internal tensions by thermal treatment (i.e., heat setting). The fibers can then be texturized to give them the appearance, structure and feel of natural fibers.
2.4.1 Drawing

Varying the velocity of the drawing-off of the thread in the spinning process leads to an increase of molecular chain orientation and crystallinity of the fiber structure. This process is responsible for good textile technological characteristics in the fibers/yarns. Fiber characteristics like tensile strength, elongation at break, shrinkage, etc. can be influenced by this process.

2.4.2 Heat Setting

Heat-setting processes also influence the orientation and crystallinity of the macromolecules. Internal, “frozen” tensions due to the stretch-spinning process -- mostly in amorphous areas -- must be removed to avoid shrinkage or creasing in the following thermal processing steps.

2.4.3 Texturizing

In contrast to natural fibers, man-made fibers have a smooth surface and no crimp. To allow for further processing and improved textile characteristics like voluminosity, increased elongation and heat retentivity, different methods are used to texturize the fibers. The thermoplastic properties of the fibers are exploited to achieve an artificial crimp.

2.4.4 Preparation Auxiliaries

In the above-mentioned fiber preparation steps, as well as the preparation steps that follow (see Figure 2.4), man-made fibers require special auxiliary chemicals (“add-ons”) such as coning oils, batching oils, spinning oils etc. These will be picked up by different types of fibers/yarns in differing amounts. Some characteristic add-on pick-up levels are shown in Table 2.3, below:

<table>
<thead>
<tr>
<th>Preparation System</th>
<th>Fiber/Yarn</th>
<th>Add-On</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin finish</td>
<td>Staple fibers</td>
<td>0.3 %</td>
</tr>
<tr>
<td></td>
<td>Flat filaments</td>
<td>0.8 %</td>
</tr>
<tr>
<td>Coning oil</td>
<td>Texturized filaments</td>
<td>1.5 % - 5.0 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(average: 2 - 3 %; max.: 14 %)</td>
</tr>
<tr>
<td>Batching oil</td>
<td>Dyed fibers/yarns</td>
<td>3 % - 6 %</td>
</tr>
<tr>
<td>Twisting oil</td>
<td>Staple fiber yarns</td>
<td>0.1 % - 2.0 %</td>
</tr>
</tbody>
</table>

Figure 2.4 shows the application points, as well as the characteristic add-on levels for the fiber preparation systems.
2.5 Preparation Systems Chemistry

“Preparation systems” is a collective term for all the auxiliaries used for fiber production and processing, from the single fiber/yarn to the ready-made fabric. These auxiliaries prepare the fibers/yarns for the best performance on the textile machines.

Preparation systems are a combination of different substances, which perform the following functions:

- Greasing the fiber surface
- Maintaining cohesion of the fibers in the fiber bundle
- Protecting against electrostatic charge

Depending on the processing step and the kind of application, the preparation systems have different names in the textile chain. Their composition differs only in the amounts of the different components. The preparation is applied by the fiber producer and must be (a) uniformly distributed on the fiber surface and (b) washed out before finishing. To meet these requirements, preparations are oil/water type emulsions.

The main components of preparation systems are:

- Lubricants (40 % - 70 %)
- Antistatic agents (20 % - 40 %)
- Emulsifiers (5 % - 15 %)
- Additives (1% - 5%)
Additives may include any of the following:

- Agents for the compactness of the thread
- Wetting agents
- Bactericides
- Corrosion inhibitors

The type of preparation system used depends upon the fiber production and fiber processing technologies, as well as fiber-specific properties and the fabric process. Preparations must not splash, evaporate, migrate and/or spoil dyeing.

2.5.1 Lubricants

The most commonly used lubricants are described in the sub-sections below. Often the specific requirements for a lubricant cannot be achieved by one component alone; in this case, mixtures of these lubricants are used.

2.5.1.1 Mineral Oils

Highly raffinated mineral oils of “white oil quality” are used. These are mostly paraffin mixtures of hydrocarbons (C_{12} - C_{40}, boiling range 220 °C - 550 °C). The vapor pressure diagrams of these alkanes at heat-setting temperature of 180 °C show that a considerable amount is in a gaseous state and should therefore be considered when determining air emissions.

Due to increasing spinning and texturizing velocities, contact temperatures between fibers and metallic components may increase to 600 °C. In this temperature range, the stability of mineral oils is exceeded. They will evaporate and be released into the air; some will partly decompose, raising concerns about potential workplace air concentrations of products of decomposition.

Hydrocarbons have very low biodegradability, which is a disadvantage in terms of their environmental impact.

An advantage for preparations based on mineral oils is the low price. Currently, this type of preparation has the highest market share. Some sources of these mineral oil-based preparations may be contaminated with polycyclic aromatic hydrocarbons (PAHs).

2.5.1.2 Ester Oils

Ester oils are esters from fatty acids (lauryl acid – stearyl acid) with alcohols (butanol - stearyl alcohol) or polyols.

Compared to mineral oils, the ester oils are thermally stable, biodegradable and emulsifiable. At high temperatures, thermal cracking may lead, for example, to residues and condensation products in the texturizing heater.

2.5.1.3 EO/PO Products:

EO/PO products are adducts from fatty alcohols/acids and ethylene oxide (EO) or propylene oxide (PO).

RCH_2O(CH_2CH_2O)_xH \quad x = 10 - 20
These alkylene polyglycol ethers are used as texturizing preparations because they are thermally stable. On the other hand, their biodegradability is quite low. EO/PO products are also used as emulsifiers, depending on molecular weight and viscosity.

2.5.2 Antistatic Agents

One basic function of preparation systems is to avoid static charges. The following substances are important antistatic agents:

**Non-ionic Surfactants**
- Fatty acid ethoxylates or fatty acid polyglycol esters
- Fatty or oxoalcohol ethoxylates
- Triglyceride (e.g., castor oil) ethoxylates
- Fatty acid monoalkyglycol esters

**Anionic Surfactants**
- Phosphoric acid salts, based on ethoxylated or non-ethoxylated fatty or oxoalcohols
- Alkylsulfonate salts
- Sarcoside salts

**Cationic Surfactants**
- Tetraalkylammonium chlorides or -ethosulfates or -methosulfates
- Fatty imidazolium salts

In general, non-ionic or anionic antistatic agents are used, because cationic surfactants can spoil the dye process that may follow, due to their inefficient washability.

It is best for the antistatic agent to remain on the outside of the fiber; otherwise it may impact the fiber’s behavior in future steps or even impact the fiber’s stability. The antistatic agent diffuses into the fiber’s interior in the case of the relatively hydrophilic fiber PA and the relatively porous fiber PAN. This effect can also be noticed during long storage.

2.5.3 Emulsifiers

Emulsifiers and wetting agents are added to the preparation system in order to disperse oils in a very fine way and achieve stable emulsions for wetting the fibers. The emulsifier components are anionic substances such as soaps and sulfonated products or non-ionic substances such as ethylene oxide condensation products.

It is important, for the washability of the fibers, to know the properties of the emulsifiers. Low ethoxylated surfactants are most commonly used as emulsifiers. The best temperature for the washing process is therefore less than 50 °C; at higher temperatures, the emulsions are broken. In the same way, the tensides used in the washing process have to be made consistent with the emulsifier.

2.5.4 Additives

“Additives” is the collective term for the following substances, which are only used in small amounts in preparation systems.
Agents to facilitate compactness of the thread

- Sarcosides
- Polyacrylates

Wetting agents (for uniform distribution of the emulsion)

- Silicones

Anti-splash agents (responsible for adhesion of the preparation on the fiber surface to avoid splashing during processing)

- Polyethoxylates

Preservatives (bactericides)

- Imidazoles
- Halogenated fatty acid amides

Corrosion inhibitors (protection for machine components)

- Fatty acid soaps
- Sarcosides

2.6 Batching Oils

Batching oils function in the same way as the preparation systems. In order to dye or bleach the fibers or yarns, the preparation add-ons must first be removed. To process the dyed or bleached fiber/yarn further, the surface has to be lubricated again and electrostatic charges have to be reduced. Batching oils are also used in the spinning of dyed and bleached cotton. It is especially important to add batching oils to reduce oligomer migration when processing PET products.

The batching oil is normally applied after dyeing or bleaching, in the last rinsing bath. The concentration of the batching oils in the bath is around 3%. The amount of batching oil taken up by the fiber (i.e., the “exhaust degree”) is quite low for PET and PA (10% - 30%), but quite high for CO and PAN (> 80%).

The chemical composition of batching oils is very similar to the composition of preparation systems described above.

2.7 Spinning Oils, Twisting Oils, Coning Oils

Spinning oils are applied on staple fibers for the yarn spinning process to reduce both fiber/fiber friction as well as fiber/metal friction, especially during carding. The properties and chemical composition of spinning oils are very similar to those of the preparation systems. Twisting oils are applied during the twisting process; coning oils are used in texturizing processes (see Table 2.3).

2.8 Fabric Processing Preparations

Fabrics can be produced by weaving, knitting or using non-woven techniques. For all these processing steps, the specific auxiliaries/preparation systems have been applied on the fibers/yarns in earlier, preparatory steps; there is no need for any additional auxiliaries.

Special oils are used to grease knitting needles; these consist of raffinated mineral oils (0.5% - 1%).
3 Textile Chemicals and Auxiliaries

In this section, we will briefly describe the composition of textile chemicals and auxiliaries, why they are used, how they are used, and the potential for air emissions, waste water discharges, workplace health/safety concerns, and the potential for residue on final consumer product.

Note: Fabric Finishing vs. Garment Finishing. In the “How Applied” section of each table, we discuss how the textile chemicals and auxiliaries are applied to fabrics. The same chemicals are used if garment finishing is performed, but they are nearly always applied using an exhaust process (versus a padding process). As a consequence, garment finishing (e.g., with jeans manufacture) typically results in more waste water discharges of textile chemicals and auxiliaries. Fabric finishing, often a padding process, typically results in more air emissions of these chemicals.

3.1 Desizing Agents

| Composition                                                                 | Typically amylases (enzymatic desizing), persulfates (oxidative desizing), glycols and tensides
|                                                                            | Desizing without auxiliaries is also possible. |
| Use                                                                        | Desizing agents are used to solubilize or degrade the sizing agent so it may be washed out. |
| How Applied                                                                | Pad-steam, pad-batch and continuous (e.g., jigger) processes may be used to apply desizing agents to fabric. With enzymatic desizing, pad-steam is applied only for big lots and with enzymes stable under steam conditions. |
| Environmental Impacts                                                      | Up to 100% of these agents may be discharged to waste water; all substances are highly biodegradable. Air emissions are negligible. |
| Workplace Health/Safety Concerns                                           | There is some hazard of respiratory sensitization with amylases. |
| Consumer Safety Concerns                                                   | None expected. |

3.2 Mercerizing Agents

| Composition                                                                 | The process is carried out with strong alkali (caustic soda) together with surfactants. Normally alkylsulfates are used. As by-products, they contain alkylalcohols or -diols. They contain phosphoric acid esters like tributylphosphates as anti-foaming agents. |
| Use                                                                        | Mercerizing agents increase textile strength and give fabric a shiny, silky appearance. |
| How Applied                                                                | Mercerizing agents may be applied to fabrics using several different techniques, including (1) under tension at cold temperatures and (2) hot stretching at temperatures close to the boiling point followed by cooling to ambient temperature |
and washing under tension. To ensure homogeneous penetration of fabric by mercerizing agents, wetting agents may be used (especially at ambient temperatures).

<table>
<thead>
<tr>
<th>Environmental Impacts</th>
<th>Negligible air emissions. Active substances and by-products are released to the waste water. The biodegradability is quite good.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Workplace Health/Safety Concerns</td>
<td>Negligible impact on workplace air.</td>
</tr>
<tr>
<td>Consumer Safety Concerns</td>
<td>None expected.</td>
</tr>
</tbody>
</table>

### 3.3 Scouring Agents, Washing Agents

#### Composition

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>Sodium palmitate, sodium stearate, sulfated oils, alkylarylsulfonates, dialkylsulfosuccinates, sulfated alkanolamides, sulfated alkylphenolpolyglycols</td>
</tr>
<tr>
<td>Cationic</td>
<td>Alkylaminammonium derivatives, benzylidimethylalkylammonium chloride, cetyl pyridinium chloride</td>
</tr>
<tr>
<td>Amphoteric</td>
<td>Amino compounds combined with carboxylic, sulfate or sulfonic acid groups</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Alkylphenol ethoxylates (see comments below in Section 3.3.1), and/or fatty alcohol-, fatty acid- or fatty amine-ethoxylates</td>
</tr>
</tbody>
</table>

Below is a list of the main surfactants used in the textile industry (anionic and non-ionic tensides are normally used for washing/scouring):

- **Anionic**: Sodium palmitate, sodium stearate, sulfated oils, alkylarylsulfonates, dialkylsulfosuccinates, sulfated alkanolamides, sulfated alkylphenolpolyglycols
- **Cationic**: Alkylaminammonium derivatives, benzylidimethylalkylammonium chloride, cetyl pyridinium chloride
- **Amphoteric**: Amino compounds combined with carboxylic, sulfate or sulfonic acid groups
- **Non-ionic**: Alkylphenol ethoxylates (see comments below in Section 3.3.1), and/or fatty alcohol-, fatty acid- or fatty amine-ethoxylates

Synthetic materials are washed without caustic soda, but instead with anionic or nonionic detergents (see above).

#### Use

Scouring and washing agents are used to remove oils and other auxiliaries from the fabric once they are no longer needed.

#### How Applied

For yarns and fibers, scouring is usually done as a batch process. Fabrics are scoured in continuous mode, using a pad-steam process.

#### Environmental Impacts

The surfactants are discharged in the waste water. If APEOs have been used, measurable
concentrations of a mixture of APEO and its biodegradation product, alkylphenol, will be present in waste water discharges (see Section 3.1.1, below). Air emissions are negligible. Residual amounts of ethylene oxides, glycols, and monomers do not develop sufficiently high gaseous pressures in the aqueous phase to become airborne.

<table>
<thead>
<tr>
<th>Workplace Health/Safety Concerns</th>
<th>Negligible impact on workplace air.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumer Safety Concerns</td>
<td>In general, none expected. However, concentrations of APEOs used in wool and leather scouring may result in appreciable residues in textiles and leather. Home laundering of garments with these residues results in APEO discharges to the municipal waste water treatment plant. See Section 3.3.1, below.</td>
</tr>
</tbody>
</table>

### 3.3.1 About Alkylphenol Ethoxylates (APEOs)

APEOs have been used (and in some areas, continue to be used) as very effective surfactants for scouring of wool and leather. They are also used more broadly in dyestuff formulation as an emulsifier or dispersing agent.

APEOs belong to the group of nonionic surfactants; these consist of a polar (hydrophilic) part and a nonpolar (hydrophobic) part. In APEOs, the hydrophilic group is a polyethoxylate chain with varying ethoxylation degrees (number of ethoxylate (EO) units = 1-40). The hydrophobic region is provided by alkylphenols (APs) in which the branched hydrocarbon chains most commonly contain eight (i.e., octylphenol) or nine (i.e., nonylphenol) carbon atoms. Alkylphenols are known, weak endocrine disruptors; APEOs are toxic to fish.

Environmental Impacts. The majority of APEOs are used in aqueous solutions; therefore, they are discharged into municipal and industrial waste waters which enter sewage treatment plants. During the different steps of sewage treatment, a complex biodegradation process of APEOs takes place, leading to the formation of several (less biodegradable) metabolites. The degradation products 4-alkylphenol diethoxylate (AP2EO), 4-alkylphenol monoethoxylate (AP1EO), [(4-alkylphenoxy) ethoxy] acetic acid (AP2EC), (4-alkylphenoxy) acetic acid (AP1EC), and 4-alkylphenols (formed by shortening of the hydrophilic ethoxy chain) are persistent, strongly lipophilic, and more toxic than the parent compounds. The release of these highly toxic compounds via secondary effluents or sewage sludge could be harmful to the aquatic or terrestrial environment.

Due to considerable concern about the use of APEOs, they have been extensively replaced in laundry detergents in a number of countries.

The discussion about nonylphenol (NP) in the environment has recently revived because of its estrogenic activity. It has been identified in studies as inducing the proliferation of MCF7 human breast tumor cells and reducing testicular size and daily sperm production in male rats.
## 3.4 Dry Cleaning Chemicals

| Composition                                                                 | A variety of chemicals are applied (also for removing of spots from fabrics and garments and machine cleaning). These include:  
|                                                                            |  
|                                                                            |   - Ethanol, acetic acid ester, etc.  
|                                                                            |   - Terpenes like d-limonene  
|                                                                            |   - Chlorinated hydrocarbons as perchloroethylene, dichloromethane, trichloroethylene, carbon tetrachloride, etc.  
|                                                                            |   - Surfactants, carbonic acids and other auxiliaries  
|                                                                            | Perchloroethylene is normally used in dry cleaning. |
| Use                                                                        | Dry cleaning agents are used to remove unwanted auxiliaries and any spots from fabrics. |
| How Applied                                                                | Dry-cleaning agents may be applied in a discontinuous mode in rope form in a tumbler (knitted fabrics) and continuously in full width (woven and knitted fabric). |
| Environmental Impacts                                                      | Some of the organic solvents are emitted into the air; organic halide emission limit values must be observed. Some of the solvents are discharged in waste water, where they are fairly biodegradable. |
| Workplace Health/Safety Concerns                                           | Workplace emissions of the solvents are a concern. D-Limonene is classified as a sensitizer and is being evaluated for possible carcinogenic effects. The chlorinated hydrocarbons used have toxic and possibly carcinogenic effects. Occupational exposure limits must be observed. |
| Consumer Safety Concerns                                                   | Garments made of synthetics and synthetic blends may retain between 0.1 to 0.5% of residual perchloroethylene—whether the perchloroethylene is used in manufacturing dry cleaning or when dry cleaned after purchase by the consumer. |

## 3.5 Bleaching Agents

### 3.5.1 Inorganic Bleaching Agents

| Composition                                                                 | Inorganic bleaching agents are mostly oxidizing substances such as hydrogen peroxide (predominantly) and hypochlorite/chlorite. However, some reductive substances are used as well, such as natrium dithionite (predominantly). |
|                                                                            |  
| Use                                                                        | The reductive substances are used to reduce surplus oxidizing agents as well for reductive bleaching processes (e.g., on wool, polyamide). |
### How Applied

A wide range of bleaching processes may be used, including cold-batch, bleaching under steaming conditions, pad-batch, and continuous mode.

### Environmental Impacts

Air emissions are not a concern because the vapor pressures of the components are quite low (with the exception of ClO₂ in chlorine bleaching). Air emissions following drying processes are also negligible.

Waste water discharges are a concern with bleaching agents, for a number of reasons. Hypochlorite or chlorite results in adsorbable organic halide (AOX) discharges in textile waste water and associated COD levels.

If waste water from different peroxide-containing processes is combined with chloride-containing waste water (NaCl from dyeing, printing, MgCl₂ from finishing), inorganic chlorides can be oxidized to their oxygen-active formation (chlorites/hypochlorites). These generate AOX, inexplicable for the “peroxide bleacher,” who bleaches without chlorites. This, in turn, leads to COD levels at the sewage plant and associated fees.

Even without the interaction with chloride-containing waste water, peroxide-containing waste water may yield a “virtual COD” under the COD test conditions. (The test uses dichromate to oxidize all carbon to CO₂. The consumed oxygen equivalent gives the COD value. Since dichromate is a stronger oxidizer than peroxide, the peroxide will be reduced, consuming oxygen from the dichromate and producing a COD value.)

### Workplace Health/Safety Concerns

Workplace air emissions of acetic acid, peracetic acid, formic acid, H₂O₂, and chlorodioxide may be of concern. Observe occupational exposure limits.

Warning: Hydrogen peroxide reacts with acetic acid to form peroxyacetic acid, which has mutagenic properties. Also the explosion risk has to be considered for concentrated formulations.

### Consumer Safety Concerns

None expected.

### 3.6 Stabilizers

#### Composition

Stabilizers are complex forming organic substances, such as:
- polycarboxylic acids
- phosphonates
- aminocarboxylic acids (EDTA/DETPA)

#### Use

Stabilizers are typically used to complex insoluble metals so that they become soluble and will not be deposited on fabrics, thereby avoiding dye quality issues.

#### How Applied

A wide range of processes may be used, including cold-batch, application under steaming conditions, pad-batch, and continuous mode.
Environmental Impacts

EDTA (ethylene diamine tetraacetic acid) is a problem in waste water discharge because of its low biodegradability and the fact that it remobilizes heavy metals from sludges. Phosphonates have very strong P-C-binding and are therefore not biodegradable (under either aerobic or anaerobic conditions). Photocatalytic degradation is observed, however. The rate at which phosphonates form complexes with heavy metals is quite high, resulting in only very small amounts of free heavy metal concentrations in the effluent. Such phosphonates will largely bind to sludge, which limits the re-use potential of the sludge, but also means that only very small quantities of phosphonates are discharged to receiving water. Polycarbonic acids can be easily degraded and cause no problems with respect to reusing sludge.

Workplace Health/Safety Concerns

None expected.

Consumer Safety Concerns

None expected.

### 3.7 Optical Brighteners

<table>
<thead>
<tr>
<th>Composition</th>
<th>Stilbene derivates. Formulation auxiliaries are dispersants and glycols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use</td>
<td>Optical brighteners are often applied when bleaching is not sufficient to achieve the required level of whiteness in a fabric.</td>
</tr>
<tr>
<td>How Applied</td>
<td>A padding process is typically used to apply optical brighteners.</td>
</tr>
<tr>
<td>Environmental Impacts</td>
<td>Because of the small application amounts, optical brighteners are expected to have negligible impact.</td>
</tr>
<tr>
<td>Workplace Health/Safety Concerns</td>
<td>None beyond use of normal workplace protections.</td>
</tr>
<tr>
<td>Consumer Safety Concerns</td>
<td>None expected.</td>
</tr>
</tbody>
</table>

### 3.8 Dyes (Colorants)

#### 3.8.1 Classification of Dyes (Colorants) -- Overview

Colorants used in the textile industry can first be divided into dyestuffs (soluble materials) and pigments (insoluble materials). Secondly, colorants can be organized according to their application technologies -- reactive dyestuffs, disperse dyestuffs, vat dyestuffs, mordant dyestuffs, acid/basic dyestuffs, direct dyestuffs, metal-complex dyestuffs and pigments.

Lastly, dyes may be classified according to their chemical composition (azo, anthraquinone, sulfur, triphenylmethane, indigoid, phthalocyanine, etc.) or according to how they perform in the dyeing processes.
Most of the colorants used in the textile industry are soluble dyestuffs. The clear majority of these are azo dyes (70-80%). Most of the pigments on the market are azo pigments, followed next by phthalocyanines.

Nearly all the dyestuff classes described in this guidance document are currently in use in the textile industry and cannot readily be replaced, as each one has its own particular benefits when compared to others. For example, when dyeing cellulose, direct and reactive dyestuffs are commonly used. Reactive dyestuffs allow bright shades and their performance is excellent. However, direct dyestuffs are sometimes used to dye cellulose (even though their color fastness is much worse than that of reactive dyestuffs) because direct dyes involve the easiest process at a low cost.

Table 3.1 shows the different types of dyestuffs applied to various fabric types.

<table>
<thead>
<tr>
<th>CO</th>
<th>WO</th>
<th>LI</th>
<th>SI</th>
<th>CV</th>
<th>CA</th>
<th>PA</th>
<th>PES</th>
<th>PAC</th>
<th>Polyacrylonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>Wool</td>
<td>Flax</td>
<td>Sisal</td>
<td>Viscose</td>
<td>Cellulose acetate</td>
<td>Polyamide</td>
<td>Polyester</td>
<td>Polyacrylonitrile</td>
<td></td>
</tr>
<tr>
<td>Acid (Anionic)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mordant (chrome)</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basic (Cationic)</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal complex</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct</td>
<td>X</td>
<td>X (blends)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vat</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insoluble azoic</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disperse</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.8.2 Basic or Cationic Dyestuffs

Basic (or cationic) dyestuffs are used to obtain bright colors, typically on polyacrylonitrile fibers. Color fastness on polyacrylonitrile fibers is excellent. However, when applied to cellulose, basic dyestuffs have poor color fastness to light and rubbing.

Basic dyestuffs can be dissolved in water, but acetic acid yields better results. They are first dissolved in acetic acid and then mixed with hot water in order to avoid aggregation of dyestuff molecules. For information on environmental impacts, see Section 3.8.12.

3.8.3 Acid or Anionic Dyestuffs

Acid (or anionic) dyestuffs are used to dye protein, polyamide and modified polyacrylonitrile fibers. Color fastness to light and to washing ranges from poor to very good, depending upon the chemical structure of the dyestuff.

Acid dyestuffs are easily dissolved in water. The dye bath in which they are dissolved has an acid pH. For information on environmental impacts, see Section 3.8.12.
3.8.4 Mordant dyestuffs

Mordant dyestuffs can be classified as acid dyes, but because of the technology with which they are applied, they are a stand-alone category of dyes. The dyestuff molecules do not contain chromium, however chromium is present in the salt used to fix the dye onto the fibers. Commonly used salts in this process are: potassium dichromate, potassium chromate and sodium dichromate.

Mordant dyestuffs are used to dye protein and polyamide fibers. A chromium salt is mixed into the dye bath to fix the dyestuff to the fiber. Color fastness to light and to washing is excellent.

The environmental impact associated with chromium depends on its oxidation state. In its hexavalent form, chromium is 100 to 1000 times more toxic than the most common trivalent compounds. Chromium III exhibits low acute toxicity, while chromium VI is acutely toxic and has been shown to be carcinogenic in animals.

Due to high effectiveness and excellent dye bath exhaustion properties, chromium-containing dyes impose relatively small environmental impacts through effluent water. Chromium VI is only used (and is difficult to replace) as a mordant for dyeing wool. During the dyeing process, chromium VI is reduced to chromium III if the process is under control. If dye houses control dyestuff amount and pH exactly when using mordant dyes, they can even meet the strict German legislation criteria for waste water of 0.5 ppm of total chromium in the effluent.

For more information on environmental impacts, see Section 3.8.12.

3.8.5 Metal Complex Dyes

Metal complex dyes are composed of a metallic atom to which one or more dyestuff molecules are bonded. These dyes are typically used on protein and polyamide fibers.

Metal complex dyes 1:1 (designates one dyestuff molecule bonded to the metallic atom) are applied in strongly acidic solutions. Metal complex dyes 1:2 (designates two dyestuff molecules bonded to the metallic atom) are applied in neutral or weakly acidic solution (pH 5 - 6.5).

Metal complex dyes sometimes use chromium III for the metallic atom. The environmental impact associated with chromium depends on its oxidation state. Chromium III exhibits low acute toxicity, while chromium VI is acutely toxic and has been shown to be carcinogenic in animals. Due to high effectiveness and excellent dye bath exhaustion properties, chromium-containing dyes impose relatively small environmental impacts through effluent water. If dye houses control dyestuff amount when using metal complex dyes, they can even meet the strict German legislation criteria for waste water of 0.5 ppm of total chromium in the effluent.

For more information on environmental impacts, see Section 3.8.12.

3.8.6 Direct Dyes

Direct dyes are mainly used to dye cellulose substrates and, like anionic dyestuffs, direct dyes have acid characteristics. Color fastness to washing is poor, while fastness to light ranges from poor to excellent. Direct dyes are sometimes used to dye protein fibers (especially in blends).
Direct dyes are applied to cellulose-based fibers directly without mordant auxiliaries. For information on environmental impacts, see Section 3.8.12.

3.8.7 Vat Dyes

Vat dyes are mainly used for cellulose fibers. Sometimes they are used on protein and polyamide fibers. For information on environmental impacts, see Section 3.8.12.

3.8.8 Sulfur Dyes

Sulfur dyes are composed of amino and phenolic structures bound to sulfur compounds, and have high molecular weights. Many other dyes contain sulfur in their molecules, but only dyes which are insoluble in water and soluble by sodium sulfide in an alkaline environment belong to this class. Their exact composition is not always known because they are made up of complex substances.

Sulfur dyes are normally used on cellulose fibers, especially cotton. They do not yield bright shades on cellulose, but are low cost and provide good color fastness to washing. Fastness to light ranges from poor to excellent.

For information on environmental impacts, see Section 3.8.12.

3.8.9 Naphthol Dyes

Naphthol dyes are insoluble azo dyes synthesized from two compounds on the fiber itself (mainly cotton); therefore they are also called developing dyestuffs. Fibers are treated with diazo components (so-called free bases and diazonium salts) and coupling components (mainly derived from beta-Naphthol), which react to yield the azo chromophore (that part of the molecule responsible for its color).

Naphthol dyestuffs are insoluble in water, and therefore fastness to washing is good. On the other hand, fastness to rubbing is poor because these dyes deposit a pigment structure on the fiber. Fastness to light normally reaches high values and bright shades can be achieved. Naphthol dyes are used mostly to obtain orange, red and magenta colors. A special group of disperse/developing dyestuffs -- the dispersion diazo dyes -- are used to dye polyester.

About 70 % to 80 % of the dyes used nowadays belong to the azo dyes groups. Under reductive conditions, these dyes may produce amines, some of which are carcinogenic. A list of carcinogenic amines into which azo dyes can cleave is shown in Table 3.2 below.

While some countries have banned the sale of textile dyes that may form carcinogenic amines, more than 100 azo dyes with the potential to form carcinogenic amines are still available on the world market. For information on environmental impacts, see Section 3.8.12.
### Table 3.2: Carcinogenic Amines (CAS numbers)

<table>
<thead>
<tr>
<th></th>
<th>Carcinogenic Amines</th>
<th>CAS numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-aminodiphenyl (92-67-1)</td>
<td>13 3,3'-dimethyl-4,4'-diaminodiphenylmethane (838-88-0)</td>
</tr>
<tr>
<td>2</td>
<td>Benzidine (92-87-5)</td>
<td>14 2-methoxy-5-methylaniline (120-71-8)</td>
</tr>
<tr>
<td>3</td>
<td>4-chloro-o-toluidine (95-69-2)</td>
<td>15 4,4'-methylene-bis-(2-chloraniline) (101-14-4)</td>
</tr>
<tr>
<td>4</td>
<td>2-naphthylamine (91-59-8)</td>
<td>16 4,4'-oxydianiline (101-80-4)</td>
</tr>
<tr>
<td>5</td>
<td>p-chloroaniline (106-47-8)</td>
<td>17 4,4'-thiodianiline (139-65-1)</td>
</tr>
<tr>
<td>6</td>
<td>2,4-diaminoanisol (615-05-4)</td>
<td>18 o-toluidine (95-53-4)</td>
</tr>
<tr>
<td>7</td>
<td>4,4'-diaminodiphenylmethane (101-77-9)</td>
<td>19 2,4-toluenediamine (TDA) (95-80-7)</td>
</tr>
<tr>
<td>8</td>
<td>3,3'-dichlorobenzidine (91-94-1)</td>
<td>20 2,4,5-trimethylaniline (137-17-7)</td>
</tr>
<tr>
<td>9</td>
<td>3,3'-dimethoxybenzidine (119-90-4)</td>
<td>21 o-aminoazotoluene (97-56-3)</td>
</tr>
<tr>
<td>10</td>
<td>3,3'-dimethylbenzidine (119-93-7)</td>
<td>22 2-amino-4-nitrotoluene (99-55-8)</td>
</tr>
<tr>
<td>11</td>
<td>4-aminoazobenzene (60-09-3)</td>
<td>23 o-anisidine (90-04-0)</td>
</tr>
<tr>
<td>12</td>
<td>2,4-xylidine (95-68-1)</td>
<td>24 2,6-xylidene (87-62-7)</td>
</tr>
</tbody>
</table>

### 3.8.10 Reactive Dyes

Reactive dyes make use of a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The chromophores used are mainly azoic, anthraquinonic or metal complex molecules. Turquoise and navy blue shades are usually copper or nickel complexes of phthalocyanines. Fiber reactive dyes have largely replaced direct, azoic and vat dyes in dyeing cellulose fibers. Some kinds are also suitable for polyamide and protein fibers. Reactive dyes form covalent chemical bonds with the fiber, giving excellent fastness properties.

The dyestuff molecule is composed of two segments -- the reactive part and the chromophore. The reactive part may be any of several kinds of molecules -- e.g., vinylsulfone, chlorotriazine, fluoropyrimidine, chloropyrimidine, chlorofluoropyrimidine. The most commonly used is the vinylsulfone reactive molecule. Bi-functional reactive dyes have higher reactivity properties and flexibility with regard to varied process parameters. These are composed of two different reactive groups (one is typically a vinyl sulfone). Fixation values increase up to 85 to 90 % with the use of bi-functional reactive dyes.

Reactive dyes are easily soluble in water, but they have good fastness properties (except to chlorine attack) because of the strong chemical bond. Bright shades may be achieved.
Reactive dyes may contain high percentages (by weight) of halogens, which usually leave the molecule after it has formed a covalent bond with the fiber and end up as salts in the dye bath or in the rinsing bath. For information on environmental impacts, see Section 3.8.12.

3.8.11 Disperse Dyes

Disperse dyes are composed of organic compounds which are not water soluble but can be dispersed in water with the aid of specific auxiliaries.

Disperse dyes are often used for polyester, acetate and polyamide fibers. Fastness to light is generally quite good, while fastness to washing depends on the structure of the fiber to which the dye is applied.

Disperse dyes can be applied to the fiber by different technologies:

- Direct application of water dispersion aided by carrier substances at temperatures below 100 °C
- Direct application above 100 °C
- Application by solubilizing the dye in the fiber at high temperatures (e.g., Thermosol process).

Disperse dyes may have a sensitizing (allergenic) effect. Table 3.3 lists dyes which may cause sensitization. Apart from skin irritation, respiratory or nasal problems and itching of the eyes can occur.

For information on environmental impacts, see Section 3.8.12.

<table>
<thead>
<tr>
<th>Chemical type</th>
<th>Color-Index-Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthraquinone</td>
<td>Disperse Red 11, 15</td>
</tr>
<tr>
<td></td>
<td>Disperse Blue 1, 3, 7, 26, 35</td>
</tr>
<tr>
<td>Azo Dyes</td>
<td>Disperse red 1, 17</td>
</tr>
<tr>
<td></td>
<td>Disperse Blue 102, 124</td>
</tr>
<tr>
<td></td>
<td>Disperse Orange 1, 3, 76</td>
</tr>
<tr>
<td>Nitro Dyes</td>
<td>Disperse Yellow 1, 9</td>
</tr>
<tr>
<td>Methine</td>
<td>Disperse Yellow 39, 49</td>
</tr>
<tr>
<td>Quinoline</td>
<td>Disperse Yellow 54, 64</td>
</tr>
<tr>
<td>Triphenylmethane</td>
<td>Acid Violet 17</td>
</tr>
<tr>
<td>Others</td>
<td>Chromate</td>
</tr>
</tbody>
</table>

3.8.12 Environmental Impacts of Dyestuffs

One of the major causes of pollution in dyeing is associated with the unfixed dye which is consequently discharged in waste water. Table 3.4 lists the degree of fixation of types of dyes across three dye processes (continuous dyeing, printing, and batch dyeing).
## Table 3.4: Average Exhaustion Levels

<table>
<thead>
<tr>
<th>Type of dye</th>
<th>Process</th>
<th>Degree of fixation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse</td>
<td>C</td>
<td>88 – 99</td>
</tr>
<tr>
<td>Disperse</td>
<td>P</td>
<td>91 – 99</td>
</tr>
<tr>
<td>Direct</td>
<td>B</td>
<td>64 – 96</td>
</tr>
<tr>
<td>Reactive – wool</td>
<td>B</td>
<td>90 – 97</td>
</tr>
<tr>
<td>Reactive – cotton</td>
<td>B</td>
<td>55 – 80</td>
</tr>
<tr>
<td>Reactive – general</td>
<td>B</td>
<td>55 – 95</td>
</tr>
<tr>
<td>Reactive – general</td>
<td>P</td>
<td>60</td>
</tr>
<tr>
<td>Vat</td>
<td>C</td>
<td>70 – 95</td>
</tr>
<tr>
<td>Vat</td>
<td>P</td>
<td>70 – 80</td>
</tr>
<tr>
<td>Sulfur</td>
<td>C</td>
<td>60 – 90</td>
</tr>
<tr>
<td>Sulfur</td>
<td>P</td>
<td>65 – 95</td>
</tr>
<tr>
<td>Acid – one SO$_3^-$ group</td>
<td>B</td>
<td>85 – 93</td>
</tr>
<tr>
<td>Acid -&gt;1 SO$_3^-$ groups</td>
<td>B</td>
<td>85 – 98</td>
</tr>
<tr>
<td>Basic (Cationic)</td>
<td>B</td>
<td>96 – 100</td>
</tr>
<tr>
<td>Azoic (naphthol)</td>
<td>C</td>
<td>76 – 89</td>
</tr>
<tr>
<td>Azoic (naphthol)</td>
<td>P</td>
<td>80 – 91</td>
</tr>
<tr>
<td>Metal complex</td>
<td>B</td>
<td>82 – 98</td>
</tr>
<tr>
<td>Pigment</td>
<td>C</td>
<td>≈100</td>
</tr>
<tr>
<td>Pigment</td>
<td>P</td>
<td>≈100</td>
</tr>
</tbody>
</table>

Continuous dyeing results in lower discharge rates than batch dyeing because of the smaller liquor ratio. Discharge rates for printing are similar to those for continuous dyeing.

Dyestuffs that are not totally exhausted or fixed onto the fiber, or recycled, are consequently discharged in the waste water effluent. These have a high visual impact, and depending upon the make-up of the dyestuffs may have any of the following: a high load of organic compounds (usually expressed in high values for COD and BOD), high values of AOX (adsorbable organic halides) and heavy metals such as copper, zinc, chromium, and nickel which are toxic to the environment. Because dyestuffs are designed to be stable in textiles, they are normally not readily biodegradable under aerobic conditions. Note, as well, that a dyestuff formulation contains approximately 30% pure dyestuff; therefore the majority of the formulation consists of non-biodegradable dispersing agents (e.g., naphthalene sulfonic acid condensation products) and standardizing agents.
Modern dyes and brightening agents are large, organic chromophoric molecules which are difficult to break down and oxidize at a very slow rate, and some -- particularly hydrolyzed reactive dyes and certain acid dyes -- are not readily adsorbed by activated sludge in the waste water treatment process.

Other causes of pollution relate to the use of auxiliaries which are added before or during dyeing to allow and/or improve the dyeing process (see Section 3.8). These auxiliaries may contribute to the eutrophication of the surface waters by increasing concentrations of phosphorus and nitrogen.

### 3.9 Dyeing Auxiliaries

| Composition | The following inorganic basic substances are found in textile dyeing industry:  
| | • Sodium chloride  
| | • Silicic acid, silicates  
| | • Sulfites, sulfides, thiosulfates  
| | • Sulfates  
| | • Dichromates  
| | • Phosphates, borates  
| | The following organic substances are found in textile dyeing industry:  
| | • Acetic acid, acetates  
| | • Formic acid  
| | A list of active substances of dyeing auxiliaries found in the textile finishing industry follows, in Table 3.5. |
| Use | The most common dyeing auxiliaries are leveling agents, used to improve the uniform distribution of the dye in the fabric. Wetting, penetrating, de-aerating agents; dispersing agents, acid donors, antifoaming agents, and carriers are all also used as dyeing auxiliaries. |
| How Applied | Auxiliaries are applied with the dyes in exhaust baths or in a padding process (pigment dyeing). The main application mode for dyeing and dyestuff application is padding – this has the advantage of well-defined pickup, smaller energy consumption, and less waste water. |
| Environmental Impacts | Many acids are neutralized during dyeing/rinsing and released to effluent as their corresponding salts. Nearly all organic active substances are released to the waste water. Some are fairly biodegradable and others are not, however the substances are eliminated by waste water treatment (adsorption to activated sludge, etc.). The biological decomposition products of the well-known APEOs |
| Workplace Health/Safety Concerns | Due to the low vapor pressure of the substances in the dye bath, emissions to air are low but should still be watched in workplace air. In pigment dyeing, these substances are released in higher quantities to the air during drying. Components such as phthalates or aromatic esters (e.g., as carrier systems, leveling agents or penetration accelerators) and odor-intensive acids (acetic acid, formic acid) can be released in drying or finishing and have to be taken into consideration in terms of workplace air. Carrier systems that improve the dyeability of polyester (e.g., in dyeing of wool/polyester blends) have the potential for off gassing in drying and finishing steps. They contain emulsifiers (10 % - 30 %), solvents (0 % - 10 %) and active substances such as:
- Alkylphthalimides
- Benzoic acid esters /-ethers including benzyl chloride as impurity
- Chlorobenzenes and -toluenes
- Diphenyl
- Phthalic acid esters
- Aromatic hydrocarbons including toluene and benzene
Observe occupational exposure limits. |
| Consumer Safety Concerns | The above substances can also be found in relatively high residual concentrations in textile products, depending on the related process quality and/or after-scouring and/or drying efficiency. |
| **alkylphenol ethoxylates** in waste water treatment are toxic to fish and have recently been identified as a weak endocrine disruptor (alkylphenol). |
### Table 3.5: Active Substances of Dyeing Auxiliaries Found in Textile Finishing Industry

<table>
<thead>
<tr>
<th>Substance</th>
<th>Degree of Biodegradability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty alcohol ethoxylates</td>
<td>Readily biodegradable</td>
</tr>
<tr>
<td>Alkylphenol ethoxylates</td>
<td>Only primary biodegradation, toxic metabolites</td>
</tr>
<tr>
<td>Fatty amino ethoxylates</td>
<td>Not readily biodegradable</td>
</tr>
<tr>
<td>Naphthalene sulfonic acid-condensation products</td>
<td>(Almost) not biodegradable</td>
</tr>
<tr>
<td>Dyeing accelerators (carriers, leveling agents)</td>
<td>Varies greatly</td>
</tr>
<tr>
<td>Polymer dispersions/polyamides</td>
<td>Not readily biodegradable, eliminable (may adsorb to sludge)</td>
</tr>
<tr>
<td>Sulfates/sulfonates</td>
<td>Only somewhat biodegradable</td>
</tr>
<tr>
<td>Phosphate esters</td>
<td>Readily biodegradable</td>
</tr>
<tr>
<td>Polyamine compounds</td>
<td>Eliminable (may adsorb to sludge)</td>
</tr>
<tr>
<td>Carbonic acid, esters, alcohols, fatty amides</td>
<td>Readily biodegradable</td>
</tr>
</tbody>
</table>

### 3.10 Printing Auxiliaries

#### 3.10.1 Pigment (Padding) Printing

| Composition                                      | For pigment printing, inorganic and organic pigments are used as colorants. In addition, thickening agents, binders, plasticizers, fitting agents, emulsifiers may all be incorporated into the pigment paste. |
| Use                                              | Pigment printing is used to apply a specific color pattern to a fabric. |
| How Applied                                      | Pigment printing uses a pad-like process. Pigment paste is applied to the fabric surface in a defined pattern and then dries on the fabric in an oven. Volatile components are released as air emissions, but thickeners, binders, crosslinkers and dye pigments stay on the fabric. (See Section 4.6.2.2.) |
| Environmental Impacts                           | There are quite high amounts (an average of 10%) of hydrocarbons in the pigment binders used in white spirit printing. These are typically released in air emissions and they include:  

- aliphatic hydrocarbons ($C_{10} - C_{20}$)  
- monomers as acrylates, vinyl acetates, styrene |
| Workplace Health/Safety Concerns | Due to the variety of chemicals used, the occupational exposure limit values for the workplace must be evaluated for the following:

- Formaldehyde
- Acrylates
- Vinyl acetate
- Styrene
- Acrylonitrile
- Acrylamide
- 1,3-butadiene
- 2-vinyl cyclohexene
- 2-phenylcyclohexene
- 2-cyanocyclohexene
- Benzene
- Hydrocarbons, alcohols
- Sulfur dioxide
- Ammonia
- Dust |

| Consumer Safety Concerns | When fabric undergoes pigment printing, all of the (organic or inorganic) pigments remain on the fabric. All of the above-mentioned pigment binders can also remain in various residual concentrations in the printed textile products. As mentioned above, when binder systems are based on polyacrylates, polyurethanes or PVC, there is a risk of finding diisocyanates, acrylates and vinyl chloride on the textile products.

Note: In all cases where polyurethanes are used as a binder, there is a high risk of false positive findings, usually for the aromatic amines 2,4 TDA and MDA. This is a result of the structure of... |
polyurethanes (which are mainly based on the disocyanates 2,4- and 2,6-TDI as well as MDI -- check the global RSL for exact identification). These polyurethanes always contain a certain amount of oligomers, which can be extracted from the coating film. Under the given analytical conditions for detection of aromatic amines from azo colorants, it is unavoidable that from these oligomers, first the disocyanates and next the corresponding amines will be formed, especially when using the GC/MS detection method.

This can also happen when pigment printing on polyurethane-based fabrics, such as all kinds of elastic materials usually based on fibers as Elasthane™ (DuPont) or Dorlastan® (Bayer) but also from generic (“no-name”) materials.

### 3.10.2 Non-Pigment Printing Processes

| Composition | The same dyestuffs used for dyeing processes can be used for non-pigment printing (see Section 3.7, above). Dyestuff printing auxiliaries include thickening agents, solubilizing agents, acid donors, defoamers, printing oils, after treatment agents, oxidizing agents, and reducing agents. |
| Use | Non-pigment printing processes use dyestuffs applied in patterns to achieve specific effects on fabrics. |
| How Applied | Dyestuffs are printed onto fabric and then cured in a drying oven; a washing step then follows. Auxiliaries are applied with dyestuff in a one-step or two-step (pad-dry-pad-steam) dyestuff printing process. As a consequence, all the above non-volatile materials are discharged to waste water. |
| Environmental Impacts | The environmental impacts associated with dyestuff printing result from the chemicals discharged into the waste water. These include: |
| | - Urea (hydrotrropic agent, formaldehyde binder) (contributes to nitrogen content in treatment plants) |
| | - Inorganic salts |
| | - Sulfates, sulfites (e.g., reducing agents) |
| | - Polymers (binder for pigment printing) |
| | - Polysaccharides (thickener) |
| | - Glycerin/polyols (frost protection agent/maintains sharp contours) |
| | - Emulsifiers |
| | - Polyvinyl alcohols (used as printing blanket) |
adhesive) (Poor biodegradability and low elimination at low temperatures (< 15 °C) in treatment plants must be considered.)

• Nitrobenzene sulfonic acid (reduced to aminobenzene sulfonate) (maintain sharp contours) (Good degree of biodegradability)
• Aliphatic hydrocarbons (e.g., pigment printing binders, thickeners and white spirit printing)

### Workplace Health/Safety Concerns

Due to the variety of chemicals used, the occupational exposure limit values for the workplace must be evaluated for the following:

- Formaldehyde
- Acrylates
- Vinyl acetate
- Styrene
- Acrylonitrile
- Acrylamide
- 1,3-butadiene
- 2-vinyl cyclohexene
- 2-phenylcyclohexene
- 2-cyanocyclohexene
- Benzene
- Hydrocarbons, alcohols
- Sulfur dioxide
- Ammonia
- Dust

### Consumer Safety Concerns

None expected.

#### 3.10.3 Coating Agents

##### 3.10.3.1 Overview of Environmental Impacts of Coating Agents

Coating processes, applied in a padding process, are likely to have a minimal impact on waste water discharges. Attention should be focused instead on impacts from coating agents to exhaust air pollution, workplace health and safety levels and consumer safety. Where halogenated polymers are used, there may be brief, pronounced discharges of AOX. The impact of phthalate discharges must be considered because of their carcinogenic, teratogenic, and hormone-disturbing effects.

##### 3.10.3.2 Overview of Consumer Safety Concerns with Coating Agents

All of the substances listed under “Composition” in the sub-sections below will also remain in the coating film depending on its thickness, the volatility of the substance, and the drying efficiency of the oven. Residual concentrations on the fabric in the 0.1 to 1 % range are possible if, for example, solvents like DMF, DMAc or NMP are involved.
### 3.10.3.3 Coating Powders

<table>
<thead>
<tr>
<th>Composition</th>
<th>Coating powders may consist of polyethylene and comparables, polyamide 6, polyamide 6.6, copolyamides, polyester, polyurethane, polyvinyl chloride, polytetrafluoroethylene and comparables.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use</td>
<td>Coating powders are typically used on textile components used for garment construction; they are not necessarily visible to the consumer.</td>
</tr>
<tr>
<td>How Applied</td>
<td>Powder coating is applied using some type of sprayer; it is fixed to the textile component in a drying oven.</td>
</tr>
<tr>
<td>Environmental Impacts</td>
<td>Polyamide 6 and/or co-polyamides are air emissions of concern. The residual monomer (\varepsilon)-caprolactam (irritating, odor intensive) is released at usual process temperatures. Emission limit values are exceeded in the raw off-gas and at times they can only fall below these values by use of exhaust air cleaning. See also Section 3.10.3.1.</td>
</tr>
<tr>
<td>Workplace Health/Safety Concerns</td>
<td>When using coating powders, the potential for dust explosions and for dust emissions into the workplace and into exhaust air exhaust air must be considered. Especially where powder is circulated during processing, it is important to be aware of the potential for fine dust accumulation. Workplace concentrations of (\varepsilon)-caprolactam have to be considered, especially because inhalation of gaseous caprolactam may cause respiratory disorders. All polyamides based on lactames (e.g., lauryl lactame) can cause similar effects. Special care has to be taken with powders based on perfluorinated alkenes like PTFE (polytetrafluoroethylene) or higher relatives. Sinter temperatures &gt; 380 °C will release small amounts of highly toxic mixtures of substances to the exhaust air and workplace air (e.g., perfluoroisobutylene, organic fluoro-radical-compounds), which may cause reversible flu symptoms (fluoropolymer fever) and other, more serious health effects. All powders can release softeners (normally phthalates). At this time higher molecular types like dinonyl- or didecyl-, dodecylphthalates are preferred, which at the moment are not considered to be as problematic as diethylhexyl-, dibutyl-, benzylbutylphthalate. If using PVC powders with directly heated stenters, be aware of the potential for dioxins and vinyl chloride to be formed.</td>
</tr>
</tbody>
</table>
Observe occupational exposure limits.

| Consumer Safety Concerns | See Section 3.10.3.2. |

### 3.10.3.4 Water-Based Coating

| Composition | Water-based coating pastes include the substances above in “coating powders” and the polymer dispersions and melamine resins described in the two tables below, as well as formulation auxiliaries such as:
|             | • dispersing agents (surfactants, alkylphenol ethoxylates)
|             | • solubilizing agents (glycols, n-methylpyrrolidone, mineral oils)
|             | • foaming agents (mineral oils, fatty acids, fatty acid ammonia salts)
|             | • softeners (phthalates as DBP, BPP, DEHP, DNP, DIMP etc., sulfonamides)
|             | • thickeners (polyacrylates), ammonia (50 % in water) |

| Use | Water-based coating pastes are used to provide fabrics with a desired texture or appearance (e.g., shine). |

| How Applied | Coating pastes are made to adhere to fabric using heat and pressure (e.g., rollers, a knife); the fabric is then passed through an oven to cure and remove volatile solvents before cooling. |

| Environmental Impacts | Environmental impacts from the aqueous formulations result predominantly (except PA 6) from the formulation auxiliaries. These are mainly:  
|                       | • Surfactants (fatty alcohols/acids/amines)  
|                       | • Emulsifiers (glycols, oligols)  
|                       | • Dispersants (alkylphenols, gycol ethers)  
|                       | • Hydrotropic agents (aliphatic hydrocarbons)  
|                       | • Solvents (n-methylpyrrolidone, etc.)  
|                       | • Foaming agents (fatty acids/salts, ammonia)  
|                       | • Softeners/plasticizers (phthalates, sulfonamides/esters, acrylic acid, acrylates)  
|                       | • Thickeners (aliphatic hydrocarbons, benzene, ammonia)  
|                       | The raw off-gas emissions from coating pastes typically will exceed exhaust air limit values; air emission controls are likely to be needed.  
|                       | See also Section 3.10.3.1. |

| Workplace | Occupational exposure limits must be monitored for both the active substance and the formulation |
Water-based coatings may also include **polymer dispersions**.

<table>
<thead>
<tr>
<th>Health/Safety Concerns</th>
<th>auxiliaries.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumer Safety Concerns</td>
<td>See Section 3.10.3.2.</td>
</tr>
</tbody>
</table>

Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Polymer dispersions are made from:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• poly(meth) acrylate (butyl, ethyl, methyl, etc.)</td>
</tr>
<tr>
<td></td>
<td>• polyacrylic acid</td>
</tr>
<tr>
<td></td>
<td>• polyacrylonitrile</td>
</tr>
<tr>
<td></td>
<td>• polyacrylamide</td>
</tr>
<tr>
<td></td>
<td>• poly 1,3-butadiene</td>
</tr>
<tr>
<td></td>
<td>• polystyrene</td>
</tr>
<tr>
<td></td>
<td>• polyurethane (isocyanate)</td>
</tr>
<tr>
<td></td>
<td>• polyvinyl chloride and comparables</td>
</tr>
<tr>
<td></td>
<td>• polyvinyl acetate</td>
</tr>
<tr>
<td></td>
<td>• copolymers of the above-mentioned polymers</td>
</tr>
</tbody>
</table>

Environmental Impacts

<table>
<thead>
<tr>
<th>Environmental Impacts</th>
<th>Potential for slight exceedances of air emission limit values and workplace air levels mostly as a result of formulation auxiliaries – especially the dispersants.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>See also Section 3.10.3.1.</td>
</tr>
</tbody>
</table>

Workplace Health/Safety Concerns

<table>
<thead>
<tr>
<th>Workplace Health/Safety Concerns</th>
<th>Of most concern are emissions that arise from incomplete reactions of monomers when processing (see Table 3.6 below):</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Acrylates as acrylic acid, butyl acrylate, ethyl acrylate, methyl acrylate, ethylhexyl acrylate and vinyl acetate. These are often sensitizers; therefore the workplace emissions have to be carefully monitored. In most cases, the finisher is not aware of the potential for these emissions because, due to its low concentration, the auxiliary is not required to be included in the product information.</td>
</tr>
<tr>
<td></td>
<td>• Carcinogenic monomers like acrylonitrile, vinyl chloride, acrylamide, 1,3-butadiene and 2-vinyl cyclohexene. Acrylamide has neurotoxic characteristics, as well.</td>
</tr>
<tr>
<td></td>
<td>Occupational exposure limits must be observed.</td>
</tr>
<tr>
<td></td>
<td>Exceeding the emission limit values is not a particular concern with these substances since monomers are held in the coating film matrix and some amount will be emitted in the coating area to the room air. However, some of these monomers are quite odor intensive. This issue</td>
</tr>
</tbody>
</table>
can be resolved by installing evaporation equipment and/or exhaust air ventilation, if necessary. Also in this case a residual monomer reduction program should be implemented.

**Consumer Safety Concerns**

Residual (carcinogenic) monomer content is the primary concern.
See Section 3.10.3.2.

<table>
<thead>
<tr>
<th>Table 3.6: Common Residual Monomer Contents in Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acrylates</strong></td>
</tr>
<tr>
<td><strong>Vinyl acetates</strong></td>
</tr>
<tr>
<td><strong>Carcinogenic monomers</strong></td>
</tr>
</tbody>
</table>

Water-based coatings may also contain **melamine resins**:

**Composition**
Melamine resins are produced by reaction of melamine with formaldehyde and subsequent etherification with (mostly) methanol in an aqueous medium. Due to the hexa-functionality of melamine, a variety of compounds is possible. The products contain only 50 % - 70 % of the resin and are of technical quality. Normally they contain considerable amounts of free formaldehyde and methanol.

New developments contain only less than 1 % formaldehyde due to the addition of formaldehyde catchers like diethylene glycol or higher glycols.

**Environmental Impacts**
A good working exhaust air scrubber can solve the problem of formaldehyde emissions. New melamine resins are being developed with less formaldehyde, which will help.

**Workplace Health/Safety Concerns**
Note: Never catalyze melamine resin-based formulas with hydrochloric acid or metal chlorides; the extremely carcinogenic substance bischloromethyl ether (BCME) will be formed. Detection of BCME is difficult and the industrial room air standard (for the chemical industry) is around < 0.5 ppb. The potential for BCME formation should be considered even when simply storing formaldehyde and simple hydrochloric acid in the laboratory. Observe occupational exposure limits.

**Consumer Safety Concerns**
Residual formaldehyde and methanol is the primary consumer safety concern.
See Section 3.10.3.2.
### 3.10.3.1 Solvent Coatings

<table>
<thead>
<tr>
<th><strong>Composition</strong></th>
<th>These products are not widespread in the Western textile finishing industry; however these are widely used in Asian textile finishing plants. Solvents such as NMP, DMF, DMAc, and toluene are very common.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Use</strong></td>
<td>Solvent-based coating pastes are used to provide fabrics with a desired texture or appearance (e.g., shine).</td>
</tr>
<tr>
<td><strong>How Applied</strong></td>
<td>Coating pastes are made to adhere to fabric using heat and pressure (e.g., rollers, a knife); the fabric is then passed through an oven to cure and remove volatile solvents before cooling.</td>
</tr>
<tr>
<td><strong>Environmental Impacts</strong></td>
<td>Application of these auxiliaries automatically requires exhaust air cleaning equipment (based on thermal incineration or adsorption on active carbon) and reuse, as well as efficient, state-of-the art workplace air ventilation.</td>
</tr>
<tr>
<td><strong>Workplace Health/Safety Concerns</strong></td>
<td>Observe established occupational exposure limits for all volatile components of finishing recipes. See also Section 3.10.3.1.</td>
</tr>
<tr>
<td><strong>Consumer Safety Concerns</strong></td>
<td>Textile products coated using this technology are at high risk of containing residual solvent loads in the 0.1 to 2 % range. See also Section 3.10.3.2.</td>
</tr>
</tbody>
</table>

### 3.10.4 Biocides

| **Composition** | The active ingredients in biocides are many and diverse. Widespread are:  
- zinc organic compounds (be careful of cadmium impurities)  
- organotin compounds  
- (di)-chlorophen(ester)(compounds)  
- benzimidazole-derivates  
- benzothiazole  
- triclosane  
- isothiazolinones  
- silver compounds |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Use</strong></td>
<td>Biocides are used in textiles to provide hygienic finishes where that is required – e.g., in undergarments and socks. Biocides are also used in small amounts as preservation agents in native printing thickeners, finishing and sizing agents (“in-can” preservation). Currently, the following types of biocides are in widespread use:</td>
</tr>
</tbody>
</table>
### How Applied

Biocides are applied within a finishing recipe.

### Environmental Impacts

Potential air emissions from formulating auxiliaries like hydrotropic agents, softeners, etc. include:
- alcohols, glycols
- phthalates
- esters, carbonic acids

Care must be taken to apply biocides as directed in the Safety Data Sheet or technical manual. Residual amounts of biocides must always be disposed of separately and according to hazardous waste regulations. Should residual amounts be directly discharged to wastewater, there is a high risk that these biocides would kill the waste water treatment plant bacteria required for the biological treatment step.

Some of the above-mentioned biocide ingredients have extremely high boiling points (or are solid in original form). Due to water vapor volatility, however, these ingredients become air emissions during the drying process.

### Workplace Health/Safety Concerns

Due to their intended biocidal effect, these chemicals also have human toxicological effects. Special care must be taken with regard to the skin sensitizing properties of most of the biocides.

Observe occupational exposure limits.

### Consumer Safety Concerns

Most of the biocides mentioned above are strong or medium skin sensitizers. Depending upon how much biocide remains on the garment or intended effect of biocide, this may be a concern.

---

### 3.10.5 Antistatics

<table>
<thead>
<tr>
<th>Composition</th>
<th>Antistatics are mostly quaternary ammonium compounds (polycondensates) and phosphoric acid (partial) esters such as tributylphosphates.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use</td>
<td>Antistatic agents are used to make the surface of fabrics slightly conductive in order to reduce or eliminate the buildup of static electricity. Before applying antistatics, it’s important for finishers to consider that the fabric they are working with may already have antistatics in it (e.g., a residue of a lubricant containing surfactants); otherwise, there is the potential to apply a conflicting surfactant.</td>
</tr>
</tbody>
</table>
Antistatic agents are typically incorporated in the textile finishing recipe, using a pad process for fabrics or exhaust process for garments.

Quaternary ammonium compounds have high aquatic toxicity. High amounts of AOX (percent range) can result from incomplete quarternization and include chemicals such as epichlorohydrin or chloromethane.

Phosphoric acid esters tend to release non-reacted alcohols during drying in the stenter (mostly n-butanol, which is very odor intensive), along with the phosphoric acid ester itself. Observe established occupational exposure limits for all volatile components of finishing recipes.

Some of the phosphoric acid esters are known strong skin sensitizers.

Commonly used flame retardants include the following:
- Inorganic flame retardants
- Flame retardants based on Sb₂O₃
- P-organic, reactive
- P-organic, non-reactive
- P-organic, halogenated
- Others

Flame retardants are used to prevent or slow fabrics from igniting when exposed to flames.

Flame retardants are applied to the fabric, then dried and heat set. Only in the case of a phosphor-organic flame retardant is application followed up with a washing process. Reactive, phosphor-organic flame retardant agents are often applied together with melamine resins as cross-linking agents. Small amounts of methanol and formaldehyde are hereby released. As a result of the required after-application washing process in these instances, quite high amounts of phosphonates are released to the waste water.

The following are expected as air emissions:
- Phosphonates
- Methanol
- Formaldehyde
- Glycols etc.
- Chloroparaffins

Antimony trioxide is not an emittant, but
mechanical abrasion (cutting, scrubbing, scratching, etc.) can occur, releasing dried pastes or dusts containing antimony trioxide. Because of their poor biodegradability, toxicity, and AOX significance, flame retardant residues should be disposed of separately (or recycled), according to hazardous waste regulations.

| Workplace Health/Safety Concerns | Flame retardants based on antimony trioxide always contain halogenated organic synergists. Normally these are  
- decabromo- and/or pentabromodiphenyl ether  
- hexabromocyclododecane  
- chloroparaffins and/or PVC  
Due to the danger of dioxin formation and other adverse effects, the above-mentioned diphenylethers should be substituted. Non-reactive, phosphor-organic flame retardant agents release volatile components like glycols, alcohols, glycol ether etc. or parts of the active substances. Inorganic flame retardant agents can release ammonia at high process temperatures (> 150 °C). Formaldehyde is a problem with reactive phospho-organic flame retardants, but can be controlled with room ventilation. When processing with antimony trioxide containing-agents, special care should be taken with regard to dust emissions associated with dried pastes. Antimony trioxide is carcinogenic and contains (depending on quality) up to 0.04 % arsenic trioxide. Observe established occupational exposure limits for all volatile components of finishing recipes. |

| Consumer Safety Concerns | All the above-listed substances will also remain in the flame retardant finish film depending on its thickness, the volatility of the substance, and the drying efficiency of the oven. |

### 3.10.7 Hydrophobic/Oleophobic Agents

#### 3.10.7.1 Fluorochemical Repellants

| Composition | These fluoro chemicals or fluorocarbon resins are supplied as formulations to the textile finisher. They include the fluoropolymer as active agent; together with emulsifiers (as fatty alcohol-, fatty amine-, fatty acid ethoxylates or fatty amine-based quaternary ammonium salts [quads] and |
possibly alkylphenol ethoxylates in no-name formulations); and other additives, by-products or impurities from fluoropolymer manufacturing which are often solvents such as:

- acetic acid esters (e.g., butyl/ethylacetate
- ketones (e.g., methyl ethyl ketone and methylisobutyl ketone)
- glycols (e.g., ethylene glycol, propylene glycol etc.)
- glycol ethers (e.g., dipropylene glycol, diethylene glycol, tripropylene glycols and their various methyl ethers or acetates)
  (Caution: Many of these glycol ethers are known or suspected reproductive toxins.)

There is an ongoing discussion about certain hazardous residuals from production of fluoropolymers such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) as well as perfluorinated telomers and sulfonates (possible precursors of PFOA/PFOS). PFOS has nearly been eliminated since the related manufacturing technology – electrofluorination – has been phased out. (Fluorochemicals manufactured in China may still be based on PFOS.) PFOA residuals today are in the range of < 10 ppb.

C8-based telomerization technology (which results in PFOA formation) has been gradually substituted by C6 technology, which is unable to cause a PFOS/PFOA issue. However, perfluorohexanoic acid (PFHA) may be found, but also at < 10 ppb. Residual C6-based telomers are measurable in a lower percent range (0.1 to 0.5 %). Such telomers can be telomer alcohols, -iodides, -alkenes and acrylates.

The fluoro chemicals are used in combination with a formula for fabric finishing. Important components are extenders/crosslinkers/boosters such as melamine resins and/or blocked di/polyisocyanates, which give the fabric permanent fastness to washing and cleaning. Well-defined process conditions are needed to ensure that these crosslinkers react sufficiently to avoid any consumer safety risks from residual isocyanates and the corresponding amines.

**Use**

Fluoropolymers are used in textile finishing to create oleophobic and hydrophobic effects (soil release, water and oil repellency).

**How Applied**

Fluoropolymers are usually applied in combination with other finishing auxiliaries by a
### Environmental Impacts

Emissions from finishing processes with fluorochemicals are normally attributed to residual solvent contents as well as organics split off from the extenders (ketones, oximes, alcohols, pyrazoles). 2-Butaneoxime, a major emittant, is a suspected carcinogen. Bis-alkyltins (typically as dibutyl fatty acid compounds) are often used as catalysts. Tributyltin derivatives are always contaminants of these catalysts and are of more concern, from a toxicological perspective.

Alkylphenol ethoxylates, used as possible emulsifiers, are toxic to fish and have recently been identified as weak endocrine disruptors (alkylphenol). (See Section 3.3.1.) Another group of emulsifiers, the quads (quaternary ammonium salts of fatty amines and alkylchlorides), show similar aquatic toxicity.

Overall, the waste water impact from such fluorochemical finishing processes (as in general for all finishing processes) can be viewed as low, because padding processes used in finishing contribute very little to waste water discharges (a few liters per day).

### Workplace Health/Safety Concerns

Observe established occupational exposure limits for fluorochemicals and all volatile components of finishing recipes (as described above under environmental impacts).

### Consumer Safety Concerns

As described above (under “Composition”), well-defined process conditions are necessary to ensure that the crosslinkers/bootstrap/extenders react sufficiently so that they do not result in any consumer safety risks (from residual isocyanates and other substances).

#### 3.10.7.2 Paraffin-Metal-Salt Formulations

<table>
<thead>
<tr>
<th>Composition</th>
<th>Beside paraffins (approximately 25 %), these products contain approximately 5 % - 10 % zirconium (IV), and/or chromium(III)-fatty acid (acetic acid) complexes. The average amount of these metals is around 2 %.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use</td>
<td>These agents are used to provide fabrics with a water-repellent surface.</td>
</tr>
<tr>
<td>How Applied</td>
<td>These are applied by the pad-cure-dry process, often together with cross-linking agents in the presence of a catalyst.</td>
</tr>
<tr>
<td>Environmental Impacts</td>
<td>Metals that may be discharged into waste water include:</td>
</tr>
</tbody>
</table>

In relation to other inputs resulting from pre-treatment, dyeing, printing as well as waste water treatment, discharged amounts of these metals are quite negligible. However, it is still important to dispose of (or recycle) residual amounts of these formulations separately according to hazardous waste regulations because metal concentrations can, in some cases, be very high.

### Workplace Health/Safety Concerns
Observe established occupational exposure limits.

### Consumer Safety Concerns
Heavy metals like chromium, zirconium and tin in their inorganic or organic forms may always have the potential to cause some consumer health risks.

#### 3.10.7.3 Silicone Repellants

<table>
<thead>
<tr>
<th>Composition</th>
<th>These formulations typically consist of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Polysiloxane-active substances (dimethylpolysiloxane (amino), modified dimethylpolysiloxane)</td>
</tr>
<tr>
<td></td>
<td>• Emulsifiers</td>
</tr>
<tr>
<td></td>
<td>• Hydrotropic agents (glycols, glycol ether(acetate))</td>
</tr>
<tr>
<td></td>
<td>• Water</td>
</tr>
</tbody>
</table>

| Use         | These agents are used to provide fabrics with a water-repellant surface. (These are being considered as alternatives for fluorochemicals.) |

| How Applied | These are applied by the pad-cure-dry process, often together with cross-linking agents in the presence of a catalyst. |

| Environmental Impacts | In the case of modified polysiloxanes, these products contain releasable cyclic dimethysiloxanes like D4-siloxane which is a suspected carcinogen. Depending on the drying and curing conditions, these substances can be released in the exhaust air. |
|                      | Observe established occupational exposure limits for all volatile components of finishing recipes. |

| Workplace Health/Safety Concerns | |

| Consumer Safety Concerns | Residual concentrations of D4-siloxanes are normally low if formulation and drying processes are conducted properly. |
### 3.10.7.4 Fatty Modified Melamine Resins

<table>
<thead>
<tr>
<th><strong>Composition</strong></th>
<th>Melamine resins are modified with fatty acids, alcohols or amines to their fatty modified variations.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Use</strong></td>
<td>These agents are used to provide fabrics with a water-repellant surface.</td>
</tr>
<tr>
<td><strong>How Applied</strong></td>
<td>These are applied by the pad-cure-dry process, often together with cross-linking agents in the presence of a catalyst.</td>
</tr>
<tr>
<td><strong>Environmental Impacts</strong></td>
<td>Depending on the extent of reaction or finishing parameters such as temperature used in heat treatment, different amounts of formaldehyde and/or aliphatic alcohols can be released to the exhaust air. These products often contain paraffin. Observe established occupational exposure limits for all volatile components of finishing recipes.</td>
</tr>
<tr>
<td><strong>Workplace Health/Safety Concerns</strong></td>
<td>Skin sensitization may be a concern if there are high concentrations of formaldehyde in the residual formulation on the garment.</td>
</tr>
</tbody>
</table>

### 3.10.8 Easy-Care Agents

<table>
<thead>
<tr>
<th><strong>Composition</strong></th>
<th>A variety of easy-care agents are in use; these are listed in Table 3.7 below, along with the air emissions of concern.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Use</strong></td>
<td>Easy-care agents are typically used to reduce wrinkling and shrinkage when fabrics are laundered.</td>
</tr>
<tr>
<td><strong>How Applied</strong></td>
<td>These are applied by the pad-cure-dry process, often together with cross-linking agents in the presence of a catalyst.</td>
</tr>
<tr>
<td><strong>Environmental Impacts</strong></td>
<td>Currently, the use of low formaldehyde or formaldehyde-free cross-linkers means that emission limit values are rarely exceeded for formaldehyde associated with application of easy-care agents. See Table 3.7 for a list of potential air emissions associated with easy-care agents. The active substances in easy-care agents have very low biodegradability. Therefore, it is important to collect residues and dispose of them according to hazardous waste regulations rather than discharging to waste water.</td>
</tr>
<tr>
<td><strong>Workplace Health/Safety Concerns</strong></td>
<td>If melamine resins are used, it is important to monitor workplace air for formaldehyde emissions. Observe established occupational exposure limits for all volatile components of.</td>
</tr>
</tbody>
</table>
Consumer Safety Concerns
The product should always be carefully checked for formaldehyde residues.

Table 3.7: Easy-Care Agents and Associated Air Emissions

<table>
<thead>
<tr>
<th>Easy-Care Agents</th>
<th>Air Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine resins</td>
<td>Methanol</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>Low formaldehyde cross-linkers</td>
<td>Methanol/diols</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>Formaldehyde-rich cross-linkers</td>
<td>Alcohols</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>Catalysts</td>
<td>NH₄/Mg/Zn-salts</td>
</tr>
<tr>
<td>Formaldehyde-free cross-linkers</td>
<td>Organic substances</td>
</tr>
<tr>
<td>Polyethylene dispersions</td>
<td>Organic substances</td>
</tr>
<tr>
<td>Silicone-emulsions</td>
<td>Siloxanes</td>
</tr>
<tr>
<td></td>
<td>Alcohols</td>
</tr>
<tr>
<td>Silicic acid esters, polymers</td>
<td>Solvents, general</td>
</tr>
</tbody>
</table>

3.10.9 Non-Slip Agents

Polysilicic acid formulations are typically used as non-slip agents. During application, generally no waste water, exhaust air or working place charges will occur. Typically, only about 5% of formulation residues are discharged to waste water; these consist largely of biodegradable surfactants and acetic acid; therefore the impact to waste water is minimal.

3.10.10 Softeners

**Composition**
- Fatty acid esters, -amides, -condensates based on diethylene triamine, ethylene diamine and various ethanolamines
- Amino-modified silicones based on D₄-siloxane
- Quaternary ammonia compounds
- Paraffin/polyethylene
- Fatty sulfonates
- Betaine derivatives
- Phthalates (butyl, octyl) – only if hydrophobic softeners are used

**Use**
Softeners are mainly used to give a soft handle to
How Applied

Most softeners are applied in the fabric finishing treatment, using a pad-dry-cure process, but can also be applied in exhaust processes. (Garment finishing has to be an exhaust process.) Fatty sulfonates are applied by exhaust methods as crease-free agents.

Environmental Impacts

Emissions occur from an average of 2 % volatile carbolic acids, alcohols, aliphatic hydrocarbons and silicones.

The active substances in most softeners are only slightly biodegradable, but are fairly eliminable (adsorb to sludge). Therefore, the impact to waste water of residual amounts of softeners is relatively low.

When fatty sulfonates are used, high amounts are released to the waste water; however, these are highly biodegradable.

Workplace Health/Safety Concerns

Negligible

Consumer Safety Concerns

None expected.

3.10.11 Summary

From a global perspective, we expect that about 5000 chemical substances are used to manufacture about 15,000 colorants and other active ingredients; these are distributed in far more than 100,000 formulations (i.e., textile auxiliaries) to the global textile industry. Many of them have an adverse eco/toxicological profile.

4 PRODUCTION PROCESSES

In this section, we will briefly describe the steps and technology involved in textile production. Where information is available, we will provide some data on resource consumption (water, thermal energy, electricity, etc.) associated with the processes.

4.1 Yarn Production

Almost all textile apparel products are made from spun yarns of 100% natural fibers, 100% man-made staple fibers or blends. Only a few apparel products (e.g., smooth sportswear) are made of filament yarns.

The two most important overall types of yarns are single and twisted yarns. Twisted yarns are obtained by twisting together two or more single yarns.

4.2 Wool Spinning

Spinning is the process by which fibers are transformed into yarn suitable for the textile industry. Spinning requires electricity only for the textile machinery, but some businesses install an air
conditioning system in order to increase the machinery performance and improve the quality of the yarn, thereby increasing electricity consumption.

Spinning oils and lubricants are used to protect the yarn and the fibers during processing, and such substances are present on the fiber after processing; moreover they produce oil mists in the working environment.

Fiber particles are dispersed in the atmosphere during opening, carding, combing, drawing, twisting and spinning operations. The fiber dust problem is minimized by use of extractors and filtration. In the carding process of the worsted and woolen spinning systems, approximately 15 %– 35 % of the initial weight of the wool is rejected as carding wastes. In addition, in the worsted system, approximately 6.5 %– 11 % of the wool fibers is rejected as wool noils in the combing stage.

### 4.2.1 Worsted and Semi-Worsted Spinning

In worsted spinning, higher-quality and longer fibers (generally speaking) are processed into a fine yarn. First the fibers are paralleled in a combing machine and then they are drawn and spun. In the wool sector, ring spinning is widely used.

Worsted spinning can be split up into the following sub-phases:

- Blending
- Oiling
- Carding (disentangling and intimate mixing of the fibers)
- Combing (paralleling the fibers and separating short fibers from the others; short fibers are rejected as noils, while long fibers go forward to make the wool “top”)
- Top finishing (not always performed; finishing processes on top are blending and dyeing)
- Drawing (regularizing and reducing the thickness of the material)
- Spinning (forming a yarn of the required thickness and number of turns of twist; ring spinning frame or rotor spinning frame are adopted)
- Twisting (if required; see description below)
- Winding (transferring single or twisted yarn onto cones for weaving or knitting purposes)

Two different spinning technologies exist: ring and open end (rotor) spinning:

- In **ring spinning**, a frame twist is inserted into the yarn using a revolving traveler; the yarn is wound onto a tube since the rotational speed of the package is greater than that of the traveler.
- In **rotor spinning**, a high-speed rotor is used to collect and twist individual fibers into yarn; on entering the rapidly rotating rotor, the fibers are distributed around its circumference and temporarily held there by centrifugal force.
Table 4.1: Resource Consumption in Worsted Spinning

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.2 – 3.2</td>
<td>l/kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>~ 1.7</td>
<td>kWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>~ 3.7</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>Oil and lubricants</td>
<td>10 – 15</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

In the woolen system, fibers are processed that are too short for the worsted system. Woolen spinning depends upon three different spinning technologies: self-acting, ring and open end. Ring spinning has higher performance, while self-acting spinning is more versatile.

The woolen spinning system can be divided into the following phases:

- Blending
- Oiling
- Carding
- Spinning (forms a yarn of the required thickness and number of turns of twist; ring spinning frame or rotor spinning frame are adopted)
- Twisting (if required; see description below)
- Winding (transferring single or twisted yarn on to cones for weaving or knitting purposes)

Table 4.2: Resource Consumption in Woolen Spinning

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>~ 0.14</td>
<td>l/kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>~ 0.16</td>
<td>kWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>~ 0.015</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>Oils and lubricants</td>
<td>~ 40</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

4.2.2 Cotton Spinning

The cotton spinning system is generally used for cotton and man-made fibers, which can be blended during spinning. The average length of fibers processed in the cotton spinning is 40 mm or less.

The cotton spinning system can be divided into the following sub-phases:

- Opening (of tufts)
- Mixing and blending (of tufts, cleaning of cotton)
- Cleaning (of thrash and cotton dust)
- Carding (intermixing fibers to produce a continuous web, which is formed into a rope-like strand of fibers known as a sliver)
- Drawing (taking a number of slivers and drawing them into a smaller strand of fibers known as drawn sliver)
- Roving (only for ring spinning – the drawn sliver is further drawn into a smaller strand of fibers and some twist is inserted)
- Spinning (forms a yarn of the required thickness and number of turns of twist; ring spinning frame or rotor spinning frame are adopted)
- Twisting (if required; see description below)
- Winding (transferring single or twisted yarn onto cones for weaving or knitting purposes)

### Table 4.3: Resource Consumption in Cotton Spinning (Electricity)

<table>
<thead>
<tr>
<th>Process</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opening</td>
<td>~ 0.3</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Blending and combing</td>
<td>~ 0.1</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Carding</td>
<td>0.2 – 0.3</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Drawing</td>
<td>&lt; 0.1</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Roving (only ring spinning)</td>
<td>0.2 – 0.3</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Spinning</td>
<td>0.6 – 2.8</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Winding</td>
<td>0.2 – 0.6</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Total consumption for process</td>
<td>1.7 – 4.5</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Consumption for air conditioning and lighting</td>
<td>0.2 – 0.7</td>
<td>kWh/kg yarn</td>
</tr>
<tr>
<td>Total electrical consumption</td>
<td>1.9 – 5.2</td>
<td>kWh/kg yarn</td>
</tr>
</tbody>
</table>

The environmental impact associated with cotton spinning is negligible when compared to other textile processes; however there are significant material losses in cotton spinning as reported in the following table.

### Table 4.4: Average Material Losses in Cotton Spinning

<table>
<thead>
<tr>
<th>Process</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opening</td>
<td>~ 50</td>
<td>g/kg raw cotton</td>
</tr>
<tr>
<td>Carding</td>
<td>~ 40</td>
<td>g/kg raw cotton</td>
</tr>
<tr>
<td>Combing</td>
<td>~ 150</td>
<td>g/kg raw cotton</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>~ 100</td>
<td>g/kg raw cotton</td>
</tr>
<tr>
<td>Total loss</td>
<td>~ 340</td>
<td>g/kg raw cotton</td>
</tr>
</tbody>
</table>
4.2.3 Continuous Filament Synthetic Yarns

Filament yarns are either monofilament or multifilament. Because filament yarns are endless, it is not necessary to insert a twist to keep the fibers from breaking. Filament yarn are commonly produced by the man-made fiber manufacturer. Filament yarns of most synthetic fibers can be either flat or texturized.

4.2.3.1 Texturizing

Only thermoplastic synthetic fibers can be texturized (polyacrylonitrile fibers are not thermoplastic). Texturizing increases the covering power or apparent volume of continuous filament yarns (of man-made fibers), so that their appearance resembles that of natural spun yarn. Texturizing increases the volume of the filament fibers by 200 – 300%. A number of processes can be used for yarn texturizing, including torsional crimping, edge crimping, compression crimping and air texturing. Texturizing is a thermo-mechanical process, consuming electrical and thermal energy. In most cases, texturizing is done by the fiber manufacturer, although some yarn manufacturers perform the process themselves.

Emissions of low molecular fractions of the polymer or spin finishes, lubricants and other additives may be a major occupational health and environmental problem if the texturizing machines are not sufficiently sealed.

| Table 4.5: Resource Consumption in Texturizing |
|-------------------------------|-----------|----------|
| Inputs                        | Quantity  | Units    |
| Electricity                   | N.A.      | kWh/kg   |
| Thermal energy                | 3.2 – 7.6 | MJ/kg yarn |

4.2.3.2 Twisting

Twisting is a purely mechanical process, in which two or more threads are coupled by inserting torsion to the yarn and winding it on cones or other supports. By twisting, the mechanical performances of yarn are increased, and particular effects are obtained. This process requires only small quantities of electricity and its environmental impact is negligible except for the applied twisting oils.

4.3 Fabric Production

Fabric production consists of a series of processes that convert yarns into a bi-dimensional structure. Most common fabric production methods are weaving and knitting, but other techniques have been developed, such as the non-wovens sector.

In weaving, a series of yarns are wound on a beam (warping), and then are interlaced with a yarn carried by a shuttle in a loom. In modern looms, in order to increase speed and productivity, shuttles have been replaced by air jets, rapier weaving, projectiles and water jets.

In knitting, the fabric is produced by moving needles which alternately interlace the yarns which are wound on cones. Several kinds of knitting machines exist (circular, flat, warp, and weft knitting).
Non-wovens are textile products that are not produced by traditional textile methods (spinning, weaving, or knitting). They consist of a layer of fibers which have been assembled together by various other techniques.

4.3.1 Woven textiles

4.3.1.1 Warping

Warping is a process by which yarn is prepared for weaving. Yarn in the form of cone packages is placed in a predetermined order, side by side on a beam. No water and no thermal energy are consumed; electric consumption depends on the specific machinery used and the kind of fiber. Small quantities of fiber dust are emitted as a result of this process. Environmental impacts due to warping are negligible when compared to other textile processes.

Table 4.6: Resource Consumption in Warping (Electricity)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>5 – 10</td>
<td>kWh/t</td>
</tr>
</tbody>
</table>

4.3.1.2 Sizing

Yarn is usually sized after warping, in order to lubricate and protect it during the weaving process. The sizing process itself generates waste in the form of end-of-run bath drops and wash-down water (cleaning). This process also consumes water, steam and electricity. It may emit traces of some of the chemicals used, or breakdown products, and lint or fly. Some environmental impact on waste water will occur when the sizing machine is cleaned down periodically. However, the real waste water impact associated with sizes occurs in subsequent wet processing, particularly in desizing.

Table 4.7: Resource Consumption in Sizing

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2 – 3</td>
<td>l/kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.1 – 0.2</td>
<td>kWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>2 – 15</td>
<td>MJ/kg</td>
</tr>
</tbody>
</table>

4.3.1.3 Weaving

Weaving is the process by which yarns are assembled into a fabric. Other processes (such as warping, threading and sizing) are done before weaving; these may generally be called “preparation for weaving” (see previous subsections).

Loom technology has a large impact on the process performance. Electricity is only required for the process itself; thermal energy is used for heating in the cold season. Lubricants and oils are used to lubricate the loom, but in particular cases they may contaminate the fabric, too. The environmental impact
associated with weaving is negligible (with the exception of noise and vibrations) when compared to other textile processes.

Table 4.8: Resource Consumption in Weaving

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>0.6–3.3</td>
<td>kWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>0.1–0.6</td>
<td>MJ/kg</td>
</tr>
</tbody>
</table>

Note that the wide ranges of consumption estimates are due to different machinery, different materials processed, and other factors.

4.3.2 Knitted Textiles

4.3.2.1 Waxing

All yarns processed on knitting machines must be waxed during winding in order to reduce the friction of yarn against mechanical parts of the machines during the subsequent processes. Winding machines, therefore, have an integrated device that distributes wax uniformly on the yarn. Misuse of large quantities of wax may raise the friction coefficient and may also damage the knitting machine.

4.3.2.2 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 machine technology and on the speed of the needles, and the value ranges between 0.5 % and 0.1 % of the weight of the fabric.

The environmental impacts related to knitting include fiber dust emissions, oil and wax content on the final fabric, and the by-product wastes (losses).

Table 4.9: Resource Consumption in Knitting (Electricity)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>~1</td>
<td>kWh/kg</td>
</tr>
</tbody>
</table>

4.3.3 Non-Woven Textiles

Non-wovens may be regarded as fabrics constructed of fibers held together by bonding or the interlocking of fibers or both, accomplished by mechanical, chemical, thermal and/or solvent means. The history of nonwovens began in the 1930s, and the raw materials used were mainly cotton waste fibers. The development of man-made fibers and bonding agents increased the significance of this segment of the textile industry.

The processing and manufacturing of non-woven fabrics varies with the fibers, methods of laying the fibers, and the bonding agents used. Fibers include cotton, wool, acetate, viscose, polyamide, polyester, polyacrylonitrile, polypropylene, polyethylene and combination fibers. Fibers are in staple form, and normally don’t consist of recovery...
materials. Raw goods are processed through a series of opening, conditioning and blending operations. Layers of webs of fibers are then formed. Fiber adhesion is accomplished by fiber friction, heat, and the addition of a bonding agent.

Non-wovens differentiate depending on the technology used to form the web and to bond it. Because each bonding method confers peculiar characteristics to the product, the intended use of the fabric must be known before processing.

Non-wovens may therefore be classified as:

- **Mechanically Bound Non-wovens.** In this case, fibers are intertwined together by a series of needles which cross the fiber layer perpendicularly. Otherwise, fibers may be sewn using another kind of sewing yarn.

- **Chemically Bound Non-wovens.** Several chemicals may be used, such as water-soluble polymers, synthetic polymers, and resins. After impregnation with the chemical agent, the fiber layers must be dried.

- **Thermally Bound Non-wovens.** If thermoplastic fibers are present in the layer, fibers are bound together with heat and compression. High temperature must be reached in order to soften the thermoplastic fibers.

### 4.4 Pre-treatment Processes

Pre-treatment and dyeing processes can be carried out at various stages of the textile production – for example, when the material is in fiber form (before spinning), as spun yarns, after the material has been woven or knitted, or, in the case of apparel, in garment form after cutting and sewing.

Most fabrics which will be dyed, printed or finished must first be prepared; denim and some yarn-dyed fabrics are exceptions to this rule. Pre-treatment is a crucial process to every subsequent treatment in the textile mill, both for quality and for environmental performance. A poor pre-treatment process creates faults that are only revealed by subsequent operations, causing off-quality production, finishing and dyeing reworks, and finally excess pollution. It is generally believed that a high proportion of the faults in textile coloration can be traced to faulty pre-treatment. Pre-treatment is therefore a key factor for right-first-time production.

The main goals of pre-treatment processes are to:

- Clean the material of all the substances fixed onto the fiber during the plant's natural growth or during transformation processes (especially spinning, winding, weaving, knitting, etc.)

- Improve the absorption capacity and hydrophility of the fiber for the application of dyestuffs, auxiliaries, and other chemicals

- Improve texture and fabric handling

- Relax unequal tensions in the fibrous material

- Produce an acceptable degree of whiteness for use as undyed fabric and the required brightness of shade to the subsequently dyed fabric.

Most mills can use uniform pre-treatment processes for the entire range of products they produce. Pre-treatment therefore constitutes the process with the highest volume in a mill.

Pre-treatment can be operated batchwise or continuous, in open-width or rope form. The choice depends upon fabric quality and the amount to be processed. Although continuous pre-treatment is usually economically and environmentally advantageous (provides better segregation for water
recycling), some mills still prefer to pre-treat goods batchwise on dyeing machines because of factors related to continuous processes, including:

- Complexity in scheduling and handling (especially coordination between pre-treatment and dyeing to avoid wet goods sitting around for a long time)
- High capital costs
- Capacity required for high productivity of knit pre-treatment equipment, whereas knit operations often have a low volume

All or only some of the various pre-treatment processes may be required and they can be applied either as separate stages or sometimes as combined stages -- especially desizing and scouring, or scouring and bleaching.

In the following sections, different pre-treatment steps are described in detail for synthetic materials, wool, cotton, flax and silk.

### 4.4.1 Pre-treatment of Synthetic Material

Most of the environmental impacts in textile finishing are the result of processing steps that occurred earlier in the textile chain. Preparations used in the textile chain remain on the fiber, yarn, and fabric – in amounts and chemical formulas that may be unknown to the finisher. For this reason, the following sections are devoted to the kinds of emissions likely to be associated with synthetic fibers.

#### 4.4.1.1 Fiber-Specific Emissions

Emission-relevant substances from man-made fibers derive from polyamide 6 and polyacrylonitrile: $\varepsilon$-caprolactam and dimethylformamide (DMF).

$\varepsilon$-caprolactam is the monomer used for the PA 6 production. The equilibrium condensate contains approximately 8.5 % $\varepsilon$-caprolactam and approximately 2.5 % - 4 % cyclic amides depending on the water content.

Studies on the release of caprolactam by thermal treatment show that depending on fiber fineness, the caprolactam-content in fibers is approximately 0.2 % – 0.8 %. During thermal treatment at 190 °C (heat setting temperature for PA 6), approximately 50 % will be emitted to the air, with corresponding emission factors of:

- $2 \text{ g} - 4 \text{ g caprolactam/kg textile} = 100 \text{ mg} - 200 \text{ mg caprolactam/m}^3 = 50 \text{ mg} - 100 \text{ mg C}$  
  (Air/textile ratio: 20 m$^3$/kg textile).

Polyacrylonitrile contains residual DMF (app. < 0.5 %), which can be emitted during thermal treatment with corresponding emission factors of:

- $1.4 \text{ g organic C/kg textile} = 70 \text{ mg organic C/m}^3$ (air/textile ratio: 20 m$^3$/kg textile)

Both fiber-specific substances can be reduced by washing and dyeing to 10 % - 20 %.
4.4.1.2 Emissions due to Preparation Systems

In addition to the fiber-specific emissions, there are emissions from the preparation systems used for processing. PA 6 as well as PAC fibers share only < 20% of the man-made fiber production. The applied amount of these auxiliaries for all man-made fibers is around 2%. This relationship shows that the source for the main emissions are these products.

Around 80% are released to the waste water. But there is more need to reduce the visible and smelly exhaust air (20% are released to the air).

In particular, the heat setting process for grey fabrics leads to high charges of exhaust air in textile finishing industry. Heat setting of grey fabrics means the thermal treatment of fabrics in a stenter with no further washing. For technical reasons some fabrics cannot be processed without further heat setting -- especially warp knit fabrics or very fine fabrics. Otherwise the fabrics do not get the required dimensional stability. Another aspect to heat set fine grey materials is the cost factor. Especially for these fabrics the washing process must be done very carefully and slowly, which is very cost intensive.

4.4.1.3 Release of Preparations by Heat Setting of Grey Fabrics

During heat setting, specific fiber properties are permanently fixed. We have to differentiate between long dwell times at lower temperatures in the presence of swelling agents (e.g., water vapor at 100° - 135 °C) and temperatures near the fiber softening point. In this case only short dwell times (5 s – 30 s) are allowed. The elastic properties and dimensional stability are especially influenced by heat setting.

Heat setting first occurs by fiber production and last by making up. Thermal treatments of man-made fibers are conducted under specific conditions throughout all processing steps. Fabric heat setting is done in a stenter. Fine woven and knitted fabrics must be heat set before finishing to prevent drafting and selvedge curling. Knitwear has to be heat set before finishing to achieve dimensional stability and the non-creasing effect.

In addition to these technological advantages of grey fabric heat setting, there are economical advantages. Washing or using end-of-pipe technologies are cost intensive.

The average add-on of preparation systems is approximately 2%. Based on this assumption, results for the dominantly used mineral oils in an exhaust air emission for grey fabric heat setting of:

- Approximately 8 g organic C/kg textile = 400 mg C/m³
  (Air/textile ratio: 20 m³/kg textile)

Similarly, for fatty acid esters, the estimate is:

- Approximately 4 g organic C/kg textile = 200 mg C/m³
  (Air/textile ratio: 20 m³/kg textile).
4.4.1.4 Release of Preparations by Washing

Pre-treatment prepares the grey fabric for subsequent dyeing/finishing processes. It ensures that all additives applied to the fiber/yarn/fabric during production are removed.

Preparations, batching oils, etc. for man-made fibers are generally easy to emulsify and can be removed in cold water. Quality and quantity of the emulsifiers are mostly unknown to the finisher. Due to increased friction or shearing strength, emulsions are often broken, losing their emulsifying effect and leaving the oily components on the fiber surface. For this reason, the finisher has to experiment to get an optimum washing efficiency.

Washing efficiency is influenced by the following factors:

- Temperature
- Dwell time
- Surfactant
- Liquor exchange/fresh water flow
- Number of washing compartments
- Fabric weight and fabric density

Washing machines are now optimized for washing efficiency and water consumption. Processing parameters can be easily regulated and continuity is guaranteed.

4.4.1.5 Examples of Air Emissions and Waste Water Discharges Resulting from Preparations

Complete, accurate and thorough exchange of information in the textile chain is very important to achieve good results at the end of the chain. The environmental impact of pre-treatment, in terms of waste water, is high because of the large amount of applied preparations, as the following examples show.

Heat setting of grey fabrics/release to exhaust air:

Assumption: Preparations consist of 50 % - 80 % of mineral oils. The residual content is mainly fatty ethoxylates.

Add-on: 5 % $\Rightarrow$ 50 g prep./kg textile $\Rightarrow$ 40 g mineral oil/kg textile

70 % will emit to air

$\Rightarrow$ 28 g mineral oil/kg textile
$\Rightarrow$ 23 g organic C/kg textile
$\Rightarrow$ 1150 mg C/m³ (air/textile ratio: 20 m³/kg textile)
Washing process/release to waste water:

Add-on: 5 % ⇒ 50 g prep./kg textile

Washing efficiency: 65 % ⇒ 33 g prep./kg textile

⇒ 26 g mineral oil/kg textile

+ 7 g fatty ethoxylates/kg textile

Average COD: 100 g/kg textile

4.4.2 Pre-treatment of Wool

4.4.2.1 Raw Wool Scouring

Note: Detailed information on raw wool scouring is provided in a document on the wool industry authored by T. Shaw (1999).

Raw wool must be scoured to remove soil, grease, and suint. Typically, this is done using water, detergent, and alkali, but solvent scouring may also be performed to remove water-insoluble oils (see Section 4.4.2.2, following).

The scouring effluent is strongly alkaline, and a significant portion of BOD and COD loads in textile manufacturing waste water discharges arises from scouring processes. The alkali breaks down natural oils and surfactants and suspends impurities in the bath. If an APEO has been used (e.g., OPEO, NPEO) as a surfactant (see Section 3.x), it breaks down in the waste water to yield even more toxic metabolites: alkylphenol, which is recognized to be a weak endocrine disruptor in humans and other animals; and polyethoxylates. APEO should be replaced with alcohol ethoxylates or other readily biodegradable, nontoxic surfactant.

4.4.2.2 Raw Wool Solvent Cleaning

Solvent scouring (or "dry cleaning") has some technical advantages compared to water scouring of raw wool. The removal of hydrophobic substance from fabric is easier, energy consumption is lower and no water is required.

Dry cleaning may be carried out continuously in full width (for woven and knitted fabrics) or discontinuously in rope form (generally for knitted fabrics).

Impurities are carried away by solvent which is purified and recycled in a closed circuit. Total solvent consumption ranges from 1 % to 4 % on the weight of fiber, depending on the technology used. Consumption does not necessarily equal emission because of the presence of filters which remove solvent from exhaust gases. In many cases, finishing treatments (e.g., softening) may also be carried out, in the same plants and using the same machinery. In this case, water and chemicals based on surfactants are added to solvents.

Solvent plants have a built-in solvent treatment and recovery system, which removes impurities and dirt through solvent distillation. The residual sludge
must be discarded. In case of high concentration of solvent, sludge must be disposed of as a hazardous waste.

After distillation, the solvent must be cooled, which requires large quantities of cooling water. Note that heated water is never contaminated by solvent and can be reused, for example, for water washing in mills which have both solvent and water washing facilities. The most widely solvent used is perchloroethylene. But methylene chloride may also be used. Risks caused by perchloroethylene to humans are not yet well understood. It has been proven to be carcinogenic to rats in high quantities. Possible emissions during operation result from losses via machine parts (which can be eliminated or reduced by hermetic sealing of machinery) and transport of solvent attached to the dried wool fabric (1000 ppm). Most modern machines have a built-in control system that makes it impossible to open the machine’s front door if the solvent concentration in the machine is greater than values established by national regulations.

Possible sources of solvent emissions may be located in residual sludge, air emissions and residual solvent on the fabric.

Large plants require both thermal and electric energy, while in small units the heat necessary for solvent distillation is provided by electricity.

The dry cleaning machines may be classified as open-circuit machines or closed-circuit machines, depending on the path of the air flow used for fabric drying and solvent removal from the fabric at the end of the washing process.

It should be noted that the solvent circuit is always a closed circuit. Solvent is continuously recycled and recovered, and used for the next washing process.

4.4.2.3 Loose Wool Carbonizing

Sometimes scoured wool contains impurities such as vegetable particles, which must be removed before textile processing. Vegetable substances are destroyed and removed during carbonizing with sulfuric acid. Wool fibers are of protein origin, and therefore are not destroyed by mineral acid. Combing and spinning remnants are very often carbonized before processing. Depending on the kind of raw goods, energy, water and chemical emissions may considerably vary.

The process consists of soaking the fibers in a bath containing sulfuric acid. Fibers are then dried and pressed, so that carbonized particles of vegetable matter are crushed and removed. Next, the pH is adjusted in a neutralization bath which contains alkaline substances (typically, sodium carbonate), and finally the fibers are dried again. The efficiency of loose fiber carbonizing ranges from 90 % to 95%.
### Table 4.10: Resource Consumption in Loose Wool Carbonization

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>12 – 93</td>
<td>m³/t</td>
</tr>
<tr>
<td>Electricity</td>
<td>170 – 380</td>
<td>kWh/t</td>
</tr>
<tr>
<td>Thermal Energy</td>
<td>15,700</td>
<td>MJ/t</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>~ 30</td>
<td>kg/t</td>
</tr>
</tbody>
</table>

### Table 4.11: Water Discharges from Loose Wool Carbonization

<table>
<thead>
<tr>
<th>Discharges</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>~ 100</td>
<td>mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>N.A.</td>
<td>mg/l</td>
</tr>
<tr>
<td>Sulfate</td>
<td>~ 3,000</td>
<td>mg/l</td>
</tr>
<tr>
<td>TS</td>
<td>~ 4,000</td>
<td>mg/l</td>
</tr>
<tr>
<td>pH</td>
<td>~ 4</td>
<td></td>
</tr>
</tbody>
</table>

4.4.3 Pre-treatment of Cotton and Flax

4.4.3.1 Singeing

Singeing is possible on yarns (in hank form; especially for sewing threads), but is normally carried out on fabrics such as cotton, cotton/polyester and cotton/polyamide substrates. Cotton fabrics show protruding fiber ends at the fabric surface; these disturb the surface appearance of the woven fabric and in the dyeing they produce an effect known as “frosting.” Singeing reduces the piling tendency in synthetic fabrics. It is the process of removing surface fibers by passing the fabric rapidly (50 m/min - 300 m/min) over a row of gas flames and then immediately placing it in a quench bath to extinguish the sparks and cool the fabric. The quench bath often contains a desizing solution and thus the final step is a combined singeing and desizing operation.

### Table 4.12: Resource Consumption in Singeing (Thermal Energy)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal energy</td>
<td>0.4 – 1.2</td>
<td>MJ/kg</td>
</tr>
</tbody>
</table>

Singeing has no effects on the effluent, as it requires only cooling water.

A relatively strong odor can be observed during the process (approximately 6000 OU/kg). The specific VOC content in the exhaust air is approximately 0.16 g organic C/kg textile. Dust content in exhaust air is measured to 0.26 g/kg textile.
An alternative to burning off is a wet “polishing” treatment carried out with cellulase enzymes (which degrade protruding fiber ends) and dispersing agents (which keep degradation products in solution, thus avoiding redeposition on the treated material).

4.4.3.2 Desizing

Warp size is a chemical mixture applied to fibers before the weaving operation in order to improve the strength and bending behavior of yarns. Twisted warp yarns already show a good resistance and do not usually need sizing, except for very fine yarns. Flax yarns are not sized but waxed, and therefore do not need to be desized. Waxes are eliminated in the scouring phase.

Size has to be removed from the fabric when the weaving operation is complete. Efficient desizing is an absolutely essential requirement for good fabric preparation. Desizing effluents account for 40 % - 60 % of the amount of COD in the waste water of cotton finishing mills.

COD load in desizing effluents depends on the sizing choice made by the weaver. A greater size add-on normally improves the weaving process, therefore yarns are sometimes overloaded with size. If the sizing process is not well controlled, sizing may be distributed in a non-homogeneous way on the yarn, perhaps overloading some parts. Overloaded yarn obviously causes more problems in the desizing phase. Non-integrated companies should seek agreement on the choice and the quantity of sizes used within the weaving mills, and weaving mills should optimize the weaving efficiency/ size add-on ratio.

<table>
<thead>
<tr>
<th>Table 4.13: Resource Consumption in Desizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inputs</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Thermal energy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.14: Water Discharges from Desizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharges</td>
</tr>
<tr>
<td>BOD</td>
</tr>
<tr>
<td>COD</td>
</tr>
<tr>
<td>Suspended solids (starch – not starch)</td>
</tr>
<tr>
<td>pH</td>
</tr>
</tbody>
</table>

Enzymatic Desizing

Enzyme treatments are used widely on cotton fabrics sized with starch; amylases are particularly suitable. Enzymes are useful because they react specifically to starches. For example, amylase decomposes starch but not cellulose. Malt extracts were once widely used, but now bacterial amylases are
preferred. When the size composition is not completely known, a mix of enzymes might be a useful desizing option (cellulase, lipase, amylases). The stability and activity of enzymes depends on many factors, including pH, temperature, the presence of activators (especially metal ions) and wetting agents.

The operation might be carried out in a batch process, but more commonly is done using semi-continuous or continuous systems. Under bulk conditions the fabric is padded in the enzyme preparation and batched, but in general the temperature of the enzyme liquor on the textile material is well below the optimum. As the enzymatic degradation of starch size is a time- and temperature-dependent reaction, in practice a period of heating or an adequate dwell time in the cold will be necessary. Swelling, degradation and dissolution of size degradation products are reactions that require up to 20 hours in order to produce a homogeneous aqueous solution of starch degradation products on the fabric that can be readily removed. Employing enzymes stable at high temperatures allows an easier and quicker desizing, with continuous pad steam.

After enzymatic degradation, some starch residues are water soluble, but some relatively long- or branched-chain residues require an alkaline treatment to become soluble. Removal of soluble starch degradation products by washing has to be thorough, as any residual degraded starch causes problems in dyeing. Depending on fabric type and structure, fabrics are washed in rope form or open width on continuous washing machines. Alternatively, washing on a winch or jig is possible, although this is slow by comparison with continuous processing.

**Oxidative Desizing**

Oxidative degradation of starch sizes, as an alternative to enzymes or acids, has been known for many years. Prior to kier bleaching with hydrogen peroxide, dilute hypochlorite liquors were used for desizing by pad-steep processing. More recently, hydrogen peroxide or persulfates have been generally associated with oxidative desizing.

Oxidative desizing is particularly useful when the composition of sizes is not completely known, or when starches with low biodegradability (especially tapioca starch) or oil-containing sizes are present. Oxidative desizing is suitable in these situations because it is not substrate-specific; however, if not well controlled, it may attack cellulose fibers. Oxidative desizing with sodium persulfate, auxiliaries and alkali is very useful with sizes composed of starch and PVA.

**Acid Desizing**

Acid treatments degrade starch-based sizes and offer the advantage of removing calcium and magnesium salts from cellulosic fabrics. The concentration of hydrochloric acid used may be as high as 2 % for short steeping times or as low as 0.2 % for overnight steeping. Care must be taken to avoid any risk of localized drying out, otherwise hydrolytic damage of cellulose may occur.
Removal of Water-Soluble Sizes

Water-soluble sizes are desized in a mildly alkaline solution containing a detergent or without any auxiliary (as with size reclamation using ultrafiltration technology). Water solubility of synthetic sizes is decreased by drying of the sized yarn and singeing. Adequate time must be allowed for immersion in the desizing liquor to ensure maximum uptake of the liquor and size swelling. A thorough hot water washing is required to remove the solubilized size.

In bulk runs, where the singed fabric passes through the desizing liquor at the same time as the singeing machine, a double dip/ double nip process with intermediate air passage is preferred. Semi-continuous processes which allow the size to swell by storing the impregnated fabric for some hours are very effective. Subsequent washing in this case is only performed to remove the size which has been previously detached.

4.4.3.3 Mercerizing

Note: Mercerizing is not carried out on flax products, which are treated with a lower concentration of caustic soda instead.

Caustic Soda Mercerizing

Caustic soda mercerizing treatment swells and reorients the cellulose structure, creating more sites for chemical and physical bonding in mature cotton fibers, thus improving dye uptake, tensile strength, dimensional stability and luster.

Mercerizing is carried out on the following:

- twisted yarns after singeing
- yarns destined for sewing or knitting (in batch for hanks or continuous for warp yarns)
- woven or knitted fabrics, either grey, singed and desized, bleached, or dyed.

Fabrics may be mercerized on (a) a chain mercerizer (for woven fabrics), which applies tension directly to warp and weft; or (b) on a chainless mercerizer (for woven and knitted fabrics), which applies only indirect tension across the weft. Treatment under tension is the most effective option, but chainless mercerizing is often preferred for its increased yield.

The concentration of caustic soda typically used is 270 g/l - 300 g/l (28 °Bé - 30 °Bé).

A hot mercerizing process has been introduced, which consists of saturation with caustic soda close to the boiling point, hot stretching and cooling, followed by washing and rinsing under tension. This procedure ensures the following:

- Better penetration of the liquor
- Increased efficiency of the treatment, both in terms of time and of performance
• Flash scouring effect, equivalent to caustic scouring prior to peroxide bleaching
• Good desizing action

Wetting agents are fundamental to improve penetration of the mercerizing liquor into the fabric, especially in processing at ambient temperature. Sulfonates are commonly used as wetting agents in mercerizing, mixed with non-ionic surfactants and phosphoric esters.

Use of mercerizing can achieve a reduction of 30% - 50% of dyestuff consumption, because of the increased exhaustion. On the other hand, the waste water discharge from the mercerizing process is characterized by a high pH.

<table>
<thead>
<tr>
<th>Table 4.15: Resource Consumption in Mercerizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inputs</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>23-95</td>
</tr>
<tr>
<td>l/kg</td>
</tr>
<tr>
<td>Electricity</td>
</tr>
<tr>
<td>N.A.</td>
</tr>
<tr>
<td>KWh/kg</td>
</tr>
<tr>
<td>Thermal energy (included drying)</td>
</tr>
<tr>
<td>5-11</td>
</tr>
<tr>
<td>MJ/kg</td>
</tr>
<tr>
<td>Chemicals</td>
</tr>
<tr>
<td>N.A.</td>
</tr>
<tr>
<td>g/kg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.16: Water Discharge from Mercerizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharges</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>BOD</td>
</tr>
<tr>
<td>10 - 14</td>
</tr>
<tr>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>COD</td>
</tr>
<tr>
<td>N.A.</td>
</tr>
<tr>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>Suspended solids</td>
</tr>
<tr>
<td>~ 1</td>
</tr>
<tr>
<td>g/kg textile</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>5.5-9.5</td>
</tr>
</tbody>
</table>

Ammonia Mercerizing

Anhydrous liquid ammonia can be used to obtain effects similar to those of caustic soda mercerizing and to improve crease recovery, although intrafibrillar swelling is not as effective and luster grade is inferior. Traces of ammonia have to be removed, preferably with dry heat treatment followed by steam.

4.4.3.4 Caustic Soda Treatment

Caustic soda treatments are sometimes carried out under the following conditions in order to induce fabric shrinking, thus strengthening it and improving mercerization performance:
• at lower alkali concentration (145 g/l - 190 g/l = 18 °Bé - 22 °Bé) than for mercerizing,
• at temperatures between 20 °C and 30 °C, and
• without tension.

This treatment is usually carried out on non-mercerized cotton and on flax (on which the mercerizing step is never carried out).

4.4.3.5 Scouring

Scouring uses alkali (sodium hydroxide, sodium carbonate; T: 90 °C - 102 °C) to saponify natural oils, and surfactants to emulsify and suspend non-saponifiable impurities in the scouring bath. With flax, scouring also serves to eliminate the waxes applied before the weaving process. Hull particles (in cotton) or straw particles (in flax) become softer and are subsequently demercerized through bleaching. This leads to a more absorbent fiber, with greatly enhanced wettability characteristics.

Scouring can be carried out on sized or desized woven fabrics, knitted fabrics and yarns. The specific scouring cycles vary depending on the type of fiber, yarn, and cloth construction. Cotton and flax can be scoured in many different ways. The degree of removal of impurities from the fabric depends upon time, temperature and concentration of alkali (caustic soda). The range of operating conditions for scouring is very wide, from long-low temperature to quick-high temperature treatments. These factors in turn relate directly to costs in terms of processing time, chemicals and energy. Scouring at severe conditions (high temperature, high pH) can lead to a loss of weight of up to 14 % - 18 %. The scouring phase also inevitably results in some chemical damage to the cotton fiber.

The two main sources of pollution in the process are grey fabrics contaminants (especially natural cotton by-products: pectins, waxes, metals and pesticides) and non-readily biodegradable surfactants.

Surfactants used for scouring typically are mixtures of:

• Non-ionic surfactants: alcohol ethoxylates, alkylphenol ethoxylates (see Section 3.3.1)
• Anionic surfactants: sulfonates, phosphates, carboxylates

Complexing agents are used to eliminate metallic impurities (iron, copper, etc.) which might damage the fabric during bleaching with hydrogen peroxide, (i.e. catalyzers), or lead to spots in dyeing (i.e. alkaline-earth ions). Water must be softened to ensure elimination of alkaline-earth metals.
### Table 4.17: Waste Water Discharges from Scouring

<table>
<thead>
<tr>
<th>Discharges</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>~ 23</td>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>COD</td>
<td>~ 94</td>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>2,200 – 17,400</td>
<td>mg/l</td>
</tr>
<tr>
<td>pH</td>
<td>10 – 13</td>
<td></td>
</tr>
</tbody>
</table>

#### 4.4.4 Pre-treatment of Silk

**4.4.4.1 Scouring**

To prepare a silk yarn for dyeing and silk fabrics for dyeing and printing, it is necessary to partially or completely remove sericine, natural oils, and organic impurities. According to the specific quantity of sericine removed through scouring, the processing can be defined as unscoured, souple, degumming. Unscoured processing is only carried out on fabrics.

Scouring removes sericine more uniformly when performed on the yarn itself, but the process is generally carried out on the fabric in order to exploit the protective action of sericine as a “natural size” against possible damage during weaving.

Hydrolytic degradation of the sericine protein macromolecule is achieved by simply using soaps, synthetic surfactants, and mixtures of soaps and synthetic surfactants in an enzymatic procedure, in water, at high temperature and under pressure.

Scouring can be carried out in a neutral, acid or alkaline solution, as required for the intended results.

**4.4.4.2 Unscoured Processing**

Unscoured processing removes all the different substances derived from previous operations from raw silk fabrics, at a minimum eliminating sericine (1%-2 %), so that the fabric keeps the characteristic stiff handle. The operation is carried out in a slightly alkaline soap bath at low temperature.

**4.4.4.3 Degumming**

This treatment is carried out both on yarns and on fabrics and ensures a complete elimination of sericine (present in raw silk at a ratio of 20 % to 25 %), as well as products added in previous operations, without modifying fibroin. The treatment can be carried out in a neutral, acid or (most commonly) alkaline solution. It is extremely important to control temperature.

**Degumming with Soap**

Yarns and fabrics are plunged into two baths (degumming baths). Each bath contains green soap at different concentrations. Yarn or fabric is then washed with ammonia and rinsed.
The process temperature varies between 95 °C and 98 °C; the degumming bath soap concentration varies between 10 g/l and 15 g/l. On average, the entire treatment lasts for 2 hours. It is possible to reuse exhausted baths after appropriate addition of soap.

Degumming with Synthetic Detergents

This degumming process uses synthetic non-ionic surfactants (e.g., ethoxylate fatty alcohol) to partially or totally replace soap.

It is possible to combine degumming with oxidizing or reducing bleaching and in some cases even with dyeing, thus conserving water and energy. Generally, alkali and detergent mixtures are used at temperatures around 95 °C - 98 °C. Such a treatment is suitable to continuous processing.

Degumming under Pressure at High Temperature

Degumming under pressure at high temperature is a specific treatment used to degum yarns. It requires an aqueous bath without surfactants and the temperature should vary between 110°C and 140°C. A post-treatment washing is required to eliminate substances used in previous processes.

4.4.4.4 Silk Weighting

The weighting operation is carried out mostly on yarns and allows yarn to recover the weight loss resulting from the elimination of sericine. The treatment consists of the deposition of tin salts or in grafting polymer chains to the functional groups of the fibroin protein chain. Weighting is defined as “equal” if the substrate final weight is the same as it was before degumming, “higher” if the weight is higher. Weighted silk is different in touch and in draping.

The most frequently applied procedure is mix weighting.

Mineral Weighting

The silk yarn undergoes a treatment using tin tetrachloride in baths at different concentrations (strong or weak baths) in an acid medium. In a strong bath, silk weight can be increased by about 10 % simply by absorbing the salt. The procedure is then followed by washing cycles to eliminate unfixed salt and to hydrolyze salt present on the fiber. Such operations can be repeated to further increase the silk weight. To ensure fixation of tin salts, weighting is finished first with a treatment in a sodium phosphate bibasic solution and then with a sodium silicate treatment.

Disadvantages of this procedure are (a) the long processing times, (b) the high water and energy consumption, and (c) the environmental impact associated with the high amount of tin in the waste water.

Weighting with Vinyl Monomers

Grafting vinyl monomers onto silk represents an alternative to the traditional mineral weighting. Such a method not only allows silk fabric to reach the desired weight increase, but also improves silk characteristics and performance. Copolymerization with vinyl monomers is carried out using radical activation methods (redox systems, UV, γ rays and so on). Silk dyeing behavior can be modified by weighting.
Methacrylamide (MAA) is one of the most frequently applied monomers at an industrial level.

Silk Weighting with Methacrylamide (MAA)

MAA weighting is a simple application. Radical activation is obtained through ammonia or potassium persulfate. Other radical activators, which consist of redox systems described in literature, are not currently applied at the industrial level.

Mix Weighting

Mix weighting with tin/MAA is done quite often at the industrial level in order to mediate the final characteristics of compounds submitted to mineral or MAA weighting.

4.4.5 Bleaching

Bleaching is necessary for all grey goods (cotton, wool, synthetics) when the natural color of the fabric might interfere with the results of coloration. Usually, though, when dark shade dyeing is foreseen, bleaching can be avoided. The principal oxidizing bleaching agents are hydrogen peroxide, sodium hypochlorite, and sodium chlorite. Chlorine-based oxidation processes pose the problem of AOX formation. Of particular concern is the developing of the suspected carcinogen trichloromethane (chloroform) during treatments with hypochlorite and, in increased quantity, during combined peroxide/hypochlorite bleaching.

The principal reducing bleaching agents are sulfur dioxide, sulfites, disulfites and dithionite.

Oxidizing bleaching agents are used on cellulose fibers; both reducing and oxidizing bleaching agents are used on protein fibers.

Because chlorine concentration in waste water discharge is subject to legislative limits, hydrogen peroxide is becoming the most common bleaching option. Flax and cotton are still bleached with sodium chlorite when a high grade of whiteness is required, or to bleach out a faulty coloration. Flax is usually bleached in fiber; in this case, mills treating flax fabrics need not carry out a severe bleaching step on them.

4.4.5.1 Hydrogen Peroxide Bleaching

Hydrogen peroxide is the most common bleaching agent for cotton. Bleaching with peroxide can be carried out on grey or scoured fibers.

Bleaching with hydrogen peroxide is done under alkaline conditions (pH 12 - 12.5) usually provided by caustic soda. Operating temperature can vary in a wide range, from ambient to high temperature. A good bleaching action occurs between 60 °C - 80 °C.

Unlike treatment with hypochlorite, bleaching with hydrogen peroxide together with caustic soda at high temperature degrades hull particles. Scouring in autoclave becomes unnecessary. If appropriate dispersing agents and detergents are used, scouring can be eliminated altogether. Stabilizing chemicals (sodium silicate, tripolyphosphate, sodium pyrophosphate, borate, polyacrylic polymers, and phosphonates) are also required, because peroxide is extremely unstable under alkaline and high temperature conditions.
Ferrous impurities must be eliminated because they catalyze the decomposition of peroxide with subsequent damage to cellulose and loss of the bath's bleaching properties. Acrylic resins are commonly used chelating agents, as are phosphonates. De-aerating agents such as tributyl phosphate and tributoxyethyl phosphate are usually added.

The air emissions resulting from bleaching are negligible (0.04 g organic C/kg textile), as they are from drying after bleaching (0.02 g organic C/kg textile).

<table>
<thead>
<tr>
<th>Table 4.18: Resource Consumption in Peroxide Bleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
</tr>
<tr>
<td>Treatment water</td>
</tr>
<tr>
<td>Cooling water</td>
</tr>
<tr>
<td>Electricity</td>
</tr>
<tr>
<td>Thermal energy</td>
</tr>
<tr>
<td>Auxiliaries</td>
</tr>
<tr>
<td>Chemicals (H\textsubscript{2}O\textsubscript{2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.19: Water Discharges from Chemical Bleaching of Wool and Pre-treated Man-made Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Emissions</strong></td>
</tr>
<tr>
<td>BOD</td>
</tr>
<tr>
<td>COD</td>
</tr>
<tr>
<td>Suspended solids</td>
</tr>
<tr>
<td>pH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.20: Water Discharges from Chemical Bleaching of Cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Emissions</strong></td>
</tr>
<tr>
<td>BOD</td>
</tr>
<tr>
<td>COD</td>
</tr>
<tr>
<td>Suspended solids</td>
</tr>
<tr>
<td>pH</td>
</tr>
</tbody>
</table>

### 4.4.5.2 Sodium Hypochlorite Bleaching

Hypochlorite may be supplied as a solution of sodium hypochlorite or in powder as calcium hypochlorite or sodium dichloroisocyanurate. In alkaline conditions, active oxygen develops and performs its bleaching action. Excessive formation of active oxygen must be avoided by adding soda ash to keep the pH around 9 - 11, and bleaching temperature should remain around 20 °C – 25 °C.
Bleaching with hypochlorite can be carried out in batch (overflow, jig, winch beck, jet) semi-continuous (pad-batch) and continuous (U-Box, J-Box, conveyor and immersion systems).

Washing and anti-chlorine treatment with reducing agents (especially dithionite, thiosulfate) at room temperature must follow to eliminate hypochlorite and chlorine amines generated by bleaching. Hydrogen peroxide can also be employed to obtain an increased degree of whiteness (combined chlorine-peroxide bleaching).

4.4.5.3 Sodium Chlorite Bleaching

Bleaching with chlorite produces optimum results on cellulose fibers and in particular it ensures a high degree of whiteness. It is particularly suitable for flax bleaching. When fabrics are sized with starch, fibers can be treated as greige even without desizing. Hull particles are eliminated, as they are with peroxide bleaching. Bleaching with sodium chlorite is carried out under acidic conditions (pH 3 - 5 to allow for maximum reaction speed), adding buffers such as salts of phosphoric, formic, or acetic acid at a temperature of 70 °C - 95 °C. Sodium nitrate is added as a corrosion inhibitor to protect stainless steel surfaces. Cold procedures have been developed that diminish toxicity and corrosion problems, using formaldehyde as an activator.

An anionic surfactant is necessary help with penetration and soil removal. The order in which the different auxiliaries are introduced has to be controlled to avoid direct contact between the concentrated sodium chlorite solution and acids.

Sodium chlorite must be handled and stored carefully because of toxicity and corrosion risks. Mixtures of sodium chlorite with combustible substances or reducing agents can create hazards, especially when subject to heat, friction or impact. Chlorine dioxide is released in contact with acids and sodium chlorite decomposition produces oxygen, which supports combustion. Sodium chlorite is very corrosive and any spillages need to be washed away with large amounts of water.

4.4.5.4 Combined Bleaching

Sometimes bleaching is carried out in two stages: an oxidizing agent is used, which is followed by another bleaching system to improve whiteness. The most common combination consists of a hypochlorite treatment followed by a hydrogen peroxide bath with the addition of optical whitening agents.

4.4.5.5 Optical Bleaching

In addition to the usual bleaches, mills use optical bleaches. Optical bleaches are not true bleaches, but fluorescent chemicals that give off a bluish light, thereby hiding the yellowish hue. The substances are applied using the same kinds of processes used for dyestuffs. These brightening agents are often stilbene compounds and act as an invisible direct dye. Note that optical bleaching can also be performed in the finishing step.
4.4.6 Fabric Washing

4.4.6.1 Water washing

Normally, hot water (40 °C– 60 °C) is used with specific detergents. Delicate fabrics are sometimes washed in solvent instead of water, and sometimes both in water and by dry cleaning.

Important factors in washing are:

- Water characteristics
- Choice of soaps and detergents
- Mechanical actions
- Temperature and pH
- Rinse

Washing uses a combination of wetting agent and detergent because it is important for all air to be expelled from the fabric so that the detergent can perform effectively. Normally a combination of anionic and non-ionic surfactants are used. The choice of surfactants is important since they must be effective in strong alkali. The detergents emulsify mineral oils and disperse undissolved pigments. The choice of surfactants also varies with the type of material fiber.

Large quantities of water are required for washing and rinsing. The washing process also consumes high amounts of thermal energy, first because washing is done at 40 °C - 60°C, and then because drying is necessary. The consumption of electricity is quite low. Table 4.21 shows consumption and emission levels during washing (for cotton scouring see Table 4.17). For further information on specific emissions of synthetic materials during pretreatment/washing, see Section 4.4.1.

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>6 – 20</td>
<td>l/kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.02 – 0.120</td>
<td>kWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>1.3 - 3.4</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>Chemicals</td>
<td>10 – 30</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

Table 4.21: Resource Consumption in Water Washing

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>~ 47</td>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>COD</td>
<td>~ 113</td>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>N.A.</td>
<td>g/kg textile</td>
</tr>
<tr>
<td>pH</td>
<td>N.A.</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.22: Water Discharges from Wool Washing
Table 4.23: Water Discharges from Synthetics Washing

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>~14</td>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>COD</td>
<td>~86</td>
<td>g O2/kg textile</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>5–60</td>
<td>g/kg textile</td>
</tr>
<tr>
<td>pH</td>
<td>8–10</td>
<td></td>
</tr>
</tbody>
</table>

4.4.7 **Dry Cleaning**

Industrial dry cleaning is sometimes necessary. Solvent scouring has some technical advantages compared to water scouring; the removal of hydrophobic substance from the fabric is easier, there is lower energy consumption and no water is required.

Dry cleaning may be carried out continuously in full width (for woven and knitted fabrics) or discontinuously in rope form (generally for knitted fabrics).

Impurities are carried away by the solvent, which is then purified and recycled in a closed circuit. Total solvent consumption ranges from 1% to 4% by weight of fiber, depending on the technology used. Consumption is not necessarily equal to emission, because of the presence of filters which remove solvent from exhaust gases. In many cases, finishing treatments (e.g., softening) may be carried out in the same plants and using the same machinery. In this case, water and chemicals based on surfactants are added to cleaning solvents.

Solvent plants have a built-in solvent treatment and recovery system, which removes impurities and dirt by solvent distillation. Residual sludge must be disposed of and, depending on the solvent concentration, must be disposed of as a hazardous waste.

Solvent must be cooled after distillation, requiring large amounts of cooling water. Note that the heated water is never contaminated by the solvent and can be reused, for example, for water washing in mills that have both solvent and water washing facilities. The most widely solvent used is perchloroethylene. Possible emissions during operation dry cleaning operations result from losses via machine parts (which can be eliminated or reduced by hermetic sealing of machinery) and transport of solvent attached to the dried wool fabric (10 ppm). Most modern machines have a built-in control system that makes it impossible to open the machine front door if the solvent concentration in the machine is greater than values established by national regulations. Other possible solvent emission sources are the residual sludge and the residual solvent on the fabric.

Large plants require both thermal and electric energy, while in small plants the heat necessary for solvent distillation is provided by electricity.

The dry cleaning machines may be subdivided into two groups – open-circuit machines and closed-circuit machines – depending on the path of the air flow used for fabric drying and solvent removal from the fabric at the end of the washing process:

The solvent circuit is always a closed circuit; the solvent is continuously recycled and recovered, and used for the next washing process.
4.4.7.1 Open-Circuit Machines

When the washing cycle is over, open-circuit machines take large quantities of air from the environment, warm it up with a steam heat exchanger and introduce it in the machine, thus evaporating solvent so that it is almost completely eliminated from clean fabrics. These machines then send the solvent-rich air to a centralized active-carbon filtering plant. (Filters require maintenance to maintain optimum cleaning performance.) Most modern filtering plants allow discharge into the atmosphere below 3 - 4 ppm of solvent, much below current regulation. The drying process is very fast because in each cycle, fresh air is used.

4.4.7.2 Closed-Circuit Machines

Closed circuit machines instead use the same volume of air to carry out the drying process in order to reduce the quantity of solvent released to the atmosphere. The process is consequently slower (it takes approximately a 30 % - 40 % longer time) and requires a sophisticated plant scheme. In this case, solvent-poor air is first heated by a heat exchanger and then sent inside the machine. Then, instead of being filtered and released to the atmosphere, solvent-rich air is internally treated. Such treatment consists of recovery of solvent by condensation in a chiller. When solvent has been removed from air and recovered, solvent-poor air is heated and continuously reused. A refrigerating plant is therefore necessary, increasing overall electricity consumption, which is partially compensated for by reduced solvent consumption. Recovered solvent is sent to a centralized plant, where it is distilled and purified.

Closed circuit machines do not require an active-carbon filter.

Even if water is not directly used in the process, large quantities of water are required for cooling. Such water is not contaminated by solvent and is stored in reservoirs. If there are aqueous washing machines in the same factory, warm water from the cooling plant may be used, allowing water and energy savings. The cooling water is otherwise discharged without any treatment.

<table>
<thead>
<tr>
<th>Table 4.24: Resource Consumption in Continuous Dry Cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Electricity</td>
</tr>
<tr>
<td>Thermal energy</td>
</tr>
<tr>
<td>Solvent</td>
</tr>
</tbody>
</table>
Table 4.25: Resource Consumption in Batch Dry Cleaning (10 kg load unit, closed-circuit)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>~ 30</td>
<td>l/kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>~ 0.3</td>
<td>kWh/kg</td>
</tr>
<tr>
<td>Solvent</td>
<td>~ 15</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

Table 4.26: Chemical Consumption in Dry Cleaning

<table>
<thead>
<tr>
<th>Dry Cleaning - Open Circuit</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Perchloroethylene</td>
<td>~ 35</td>
<td>g/kg</td>
</tr>
<tr>
<td>Dry Cleaning - Closed Circuit</td>
<td>Quantity</td>
<td>Unit</td>
</tr>
<tr>
<td>• Perchloroethylene</td>
<td>~ 15</td>
<td>g/kg</td>
</tr>
<tr>
<td>Softening Treatment – Open Circuit</td>
<td>Quantity</td>
<td>Unit</td>
</tr>
<tr>
<td>• Water</td>
<td>~ 0.07</td>
<td>l/kg</td>
</tr>
<tr>
<td>• Perchloroethylene</td>
<td>~ 35</td>
<td>g/kg</td>
</tr>
<tr>
<td>• Other chemicals</td>
<td>~ 22</td>
<td>g/kg</td>
</tr>
<tr>
<td>Softening Treatment – Closed Circuit</td>
<td>Quantity</td>
<td>Unit</td>
</tr>
<tr>
<td>• Water</td>
<td>~ 0.07</td>
<td>l/kg</td>
</tr>
<tr>
<td>• Perchloroethylene</td>
<td>~ 15</td>
<td>g/kg</td>
</tr>
<tr>
<td>• Chemicals</td>
<td>~ 22</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

4.5 Dyeing

Dyeing is a necessary process in the textile chain and significantly increases the economic value of the product. Fibers, yarns, fabrics, and even garments may be dyed. Two main techniques used for dyeing are exhaust dyeing and pad dyeing. In exhaust dyeing, the material is brought to equilibrium with a dye-containing solution over a period of minutes to hours. The exhaust dyeing is a discontinuous (batch) process.

Different machines are used in exhaust dyeing, depending on the substrates to be dyed and the end-use of the dyed textiles. Each machine is characterized by a typical liquor ratio (textile weight (kg)/bath volume (l)).

In pad dyeing, the dyestuff is mechanically applied to the substrate (the liquor pick-up ranges from 50% to 100%, depending on the substrate and dyeing process) and then fixed in a semi-continuous or continuous process (usually by steaming). Normally, dyeing takes place in facilities that specialize in such operations and process raw goods that belong to customers (commission finishers), but integrated plants may include a dye house to process their own materials.

As previously mentioned, the dyestuffs are partly discharged to the waste water depending on their degree of fixation. Nearly all of the organics and inorganics used as auxiliaries in the dyeing process
are discharged as waste water effluent. For some substances (e.g., carrier systems), air emissions
(working place atmosphere, off-gas emission during thermal treatment) have to be considered.

Normally the waste water emissions for continuous dyeing (especially for large lots) are lower than for
batch (exhaust) dyeing. Waste water discharges associated with continuous dyeing are caused by the
residues from the padding mangle and the rinsing of the dyed goods.

With exhaust dyeing, the waste water discharges can be estimated if one has the following
information:

- the dyeing recipe (with knowledge of the active substance concentrations -- COD, AOX, metal
  content, etc. in dyestuffs and auxiliaries)
- the degree of fixation of the dyestuffs
- possible exceptions (esp. carrier substances) such as substances that are partly fixed on the
  substrates (dyestuffs) or substances which react during dyeing (reducing agents etc.)

Dyestuff concentrations in the bath in exhaust dyeing range between 0.1 g/l and 1 g/l (max. 10 g/l); for
semi-continuous processes the dyestuff concentration in the pad liquor ranges between 1 g/l and 10
g/l (max. 100 g/l). For continuous dyeing, concentrations between 10 g/l and 100 g/l are normally
used.

Consumption of water, energy, dyestuffs, and auxiliaries varies within a considerable range depending
on the substrate being dyed (type of fiber (PES, CO, PA etc.), make-up (loose fiber, yarn, fabric), the
textile’s end use, different dyeing machines, the loading of the machine, the dyeing process used, size
of lots, customer quality requirements and economic aspects, etc. Moreover, dyestuff consumption
depends on the color shade (normally dark shades require more dyestuff than light shades).

Results of a survey on water consumption in finishing (including pre-treatment) of loose fibers, yarns,
knitted textiles and woven textiles are provided below. Data were collected from 75 % of the
companies in the German finishing industry (1996). As the survey results show, water consumption –
directly linked to the consumption of auxiliaries, chemicals and dyestuffs - can vary in a large range
and reaches a maximum for the mean value in printing mills.

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loose fibers/yarns</td>
<td>69 l/kg</td>
<td>10 – 185 l/kg</td>
</tr>
<tr>
<td>Knitted textiles</td>
<td>97 l/kg</td>
<td>20 – 133 l/kg</td>
</tr>
<tr>
<td>Woven textiles</td>
<td>103 l/kg</td>
<td>38 – 280 l/kg</td>
</tr>
<tr>
<td>Printing</td>
<td>179 l/kg</td>
<td>70 – 229 l/kg</td>
</tr>
<tr>
<td>Total mean value</td>
<td>111 l/kg</td>
<td></td>
</tr>
</tbody>
</table>

The following sections describe the dyeing of different substrates (cotton, wool, etc.). Loose fiber
dyeing, package dyeing, hank dyeing and piece dyeing (rope form and full width) are explained and
consumption and emission levels are reported.
4.5.1 Dyestuff Application

4.5.1.1 Wool

Acid dyes, Mordant dyes, 1:1 metal complex dyes, 1:2 metal complex dyes, reactive dyes and vat dyes or leuco esters of vat dyes may be used to dye wool; however about 70 % of wool is currently dyed using metal-containing dyes. Approximately 35 % of these dyestuffs are mordant dyes. Black and navy blue shades can only be achieved by using these kinds of dyes and the effectiveness (i.e., the rate of fixed dye) is very low.

Wool and Cotton Blends

Direct dyestuffs are applied that have affinity for both wool and cotton; alternatively, acid dyestuffs can be used for wool and direct dyestuffs used for cotton.

Wool and Polyamide Blends

Polyamide is chemically related to wool. Therefore, the same dyes used for wool are suitable for wool-polyamide blends.

Wool and Polyacrylonitrile Blends

Many types of dyes may be used on these blends of fibers, due to their similar structure. For example:

- Metal complex dyes 1:1 for wool and cationic dyes for acrylonitrile
- Metal complex dyes 1:2 for wool and cationic dyes for acrylonitrile
- Acid dyes for wool and cationic dyes for acrylonitrile

Wool and polyacrylonitrile dyeing is performed using one of two main technologies: the one-bath or the two-bath process. In all cases, the different dyes must be dissolved and added to the dye bath separately in order to avoid mutual precipitation.

- **The One-Bath Process**

  The recommended method of application using the single bath process is to make the dye liquor up with 3 % ammonium acetate, 1 % glacial acetic acid, 0.5 % of a fatty ethylene oxide condensate, and 1% of a cationic dye-retarding agent. The goods are treated for 10 to 15 minutes at 50 °C in the liquor with all the auxiliaries and the pH is adjusted to 5.5. The pre-dissolved anionic dye is then added. The temperature is increased to 80 °C for a period of 30 minutes, when most of the anionic dye will be exhausted and the pre-dissolved cationic dye may then be added. Next, the temperature is increased to 95 °C over a period of 15 minutes and then to the boiling point; this temperature is maintained for one hour. Finally, the dye bath is cooled slowly to 70 °C before the goods are taken out.

- **The Two-Bath Process**

  In the two-bath process, the polyacrylonitrile fiber is dyed first. The dye bath is made up with the dye and sufficient acetic acid is added. A cationic retardant agent is added to bring the pH to 4.5 – 5. The
temperature is increased to the boiling point. If the wool is heavily stained, it can be cleaned in a bath containing 3 g/l of sodium dithionite at 60 °C, followed by rinsing. A fresh liquor is then made up and the wool is dyed in the normal manner with the appropriate dyes. After cooling to below 70°C, the goods are taken out.

**Wool and Polyester Blends**

When dyeing blends of these fibers, it is most convenient to dye the fibers separately before blending. However, when the fibers must be dyed after blending, it is best to dye the polyester with disperse dyes in a first step and then dye the wool with specific wool dyes. Dyeing carriers are normally used for polyester.

### 4.5.1.2 Cotton

**Direct Dyes**

Direct dyes are usually applied by batch dyeing, but they can also be used in pad–jig, pad-roll and pad-steam processes for light shades, where a poorer fixation rate is less critical.

Exhaust dyeing is performed at boiling temperature for 45 - 60 minutes with leveling agents and sodium sulfate. Performing an after-treatment with cationic fixation agents will improve dyestuff fixation. Direct dyes do not require several washing cycles after dyeing.

**Reactive Dyes**

Reactive dyes are most often applied in pad-batch processes for woven fabrics and by batch dyeing for knit fabrics because continuous dyeing would result in excessive loss of dyestuff. The dyeing procedure varies with the reactive agent. Application is usually carried out at 40 °C for fluoropyrimidines, at 50 - 60°C for vinyl sulfone and at 80 °C for chlorotriazine at a high pH (9.5 – 11.5). Temperature and pH have to be carefully controlled to avoid hydrolysis and successive loss of dyestuff reactivity. Washing is done with anionic surfactants and soft water to avoid making the dyestuffs and surfactants insoluble.

After dyestuff application, fabrics are soaped at 100 °C and rinsed to remove unreacted dye. Washing requires considerable amounts of water. The relatively high amount of unfixed, hydrolyzed dye and the use of great amounts of salts are the main environmental impacts of reactive dyes.

**Vat Dyes**

Vat dyes are applied by exhaust or continuous methods. Oxidized vat dyes have no affinity for fibers and have to be reduced (mainly with alkali and sodium dithionite) before application. Once the dyestuff is on the fiber, it has to be oxidized again (mainly with peroxide). The most common vat dyeing process consists of padding the material in a solution of the reduced form of the dyestuff, drying to improve dye penetration, developing (in batch or continuous machines at 50°C to 60°C), oxidizing back to the water-insoluble form, rinsing, soaping at 100°C, and rinsing again. The main environmental impact of vat dyeing is the sulfur-containing waste water from the reducing agents (mainly sodium dithionite).
Sulfur Dyes

Sulfur dyes are usually applied in the reduced state. Reduction with sodium sulfide and dissolving in strong alkali leads to the water-soluble leuco form. Sulfur dyeing is similar to vat dyeing (continuous processes are normally used) except for the drying phase, which is not necessary in this case. A pad-batch process is not possible because of the instability of the reduced form. Developing occurs at higher temperatures (85°C to 90°C) than for vat dyeing, whereas oxidizing (mainly with peroxide, bromate, and iodate) takes place at 50°C. The main environmental impacts of sulfur dyeing are air emissions and waste water discharges of sulfur compounds (hydrogen sulfide, polysulfides, sulfur, and sulfur dioxide) and AOX if bromate or iodate is used as oxidizing agent.

Naphthol Dyes

Naphthol dyes can be applied in both continuous and batch processes. The process steps are: pasting the naphthol compound (alkali, alcohol or dispersing agent), applying the naphthol compound (+ sodium sulfate), applying a diazo compound (+ acetic acid). Soaping is done at 100 °C to eliminate any uncoupled dye.

When coupling occurs in the solution, the molecule loses affinity for the fiber and remains instead in the effluent. The use of naphthol dyes has declined because of application costs and the possible presence of arylamines on the fabric and in the waste water effluent. Air emissions may include the alcohol present in the dyestuff compound.

4.5.1.3 Polyacrylonitrile (PAN) Fibers

Polyacrylonitrile fibers can be dyed with disperse dyes, cationic dyes and acid dyes. The fibers are made dye-able by including a neutral, plasticizing comonomer (5 -10 %) and an acidic comonomer (1 %) that renders affinity for cationic dyes, or a basic comonomer (6%) that renders affinity for acid dyes. Several monomers can be used as copolymers to modify the affinity of various classes of dyes for polyacrylonitriles.

Fibers made of 100% acrylonitrile without suitable comonomers have a high glass transition temperature and therefore exhibit insufficient dye binding properties. Fibers of this type can only be dyed in light shades with disperse dyes or with acid dyes by using the copper-ion process.

Disperse Dyes

The dye is stirred in combination with 10 to 20 times its weight of water at 50°C to 60°C and allowed to stand for 10 minutes. Before adding the dyestuff, approximately 1 - 1.5 kg of a synthetic dispersing agent per 1000 liters should be dissolved in the liquor. When the dye bath is prepared, the goods are placed inside it while still cool and the temperature is slowly raised to 70°C and 85°C; dyeing is then continued at that temperature for approximately one hour.

Cationic Dyes

With cationic dyes, the bath pH is adjusted to 4 – 5 with about 1 g/l acetic acid and the same amount of sodium acetate. It is also advisable to add 1 g/l of a
non-ionic dispersing agent. The temperature is increased rapidly to 75°C and then the liquor is allowed to boil for one hour.

**Acid Dyes**

The acid dye bath is made up with 2 % (by weight of the goods) of sulfuric acid and suitable leveling agents. The goods are added at 40°C and the dye bath runs for 10 minutes. The dissolved dye is then added and the liquor temperature is raised to the boiling point over a period of 45 minutes. These parameters are maintained for one hour. After dyeing, the liquor is cooled to 70°C with the goods in motion before the dye bath is run off.

### 4.5.1.4 Polyamides

Polyamide 6 and PA 6.6 are easily dyed with various types of dyes, since their chains contain several hydrophilic groups. The most commonly used dyes are disperse dyes, acid dyes, reactive dyes and 1:2 metal-complex dyes.

Polyamides can also be modified to accept basic dyes by introducing strong acidic groups such as sulfonic acids (especially 5-sulfoisophtalic acid with 1,6-diaminohexane).

Polyamide dyeing is performed using the exhaust process, and by continuous dyeing, gel dyeing and mass dyeing. In mass dyeing, the pigments must be stable under melting process conditions. Inorganic pigments are used (especially titanium dioxide, carbon black, cadmium sulfide, phthalocyanine green, phthalocyanine blue and cadmium sulfoselenide).

**Acid Dyes**

Acid dyes are used for moderate depths of shades on polyamides. A leveling agent is added to the liquor, and the pH is adjusted to between 3 and 5 with a buffer, such as a mixture of mono- or disodium phosphates or mono-ammonium phosphate alone. Then the goods are placed in the bath and the temperature is increased to 40°C - 50°C, where it is maintained for 10 minutes. The dye is then added and the temperature raised to the boiling point within a period of 20 minutes; this temperature is then maintained for 45 - 60 minutes. For deep shades, the exhaust process is completed by adding acetic or formic acid. The wet fastness of acid dyes can be improved by after treatment with tannin or synthetic products (high molecular condensation products of aromatic sulfonic acid with formaldehyde or condensation products of phenol, cresol, catechol and naphthol with formaldehyde).

**Disperse Dyes**

A dispersing agent (0.2 - 2 g/l) is added to the liquor, and the pH is adjusted to 5 with acetic acid. The process begins with the material at 40°C and the dye is added after 5 minutes. After another 5 minutes, the system heats up for 30 minutes, and finally dyeing is carried out for 60 minutes at near to boiling temperature.

**1:2 Metal Complex Dyes**

Metal-complex dyes are recommended for dark and somber shades. Dyestuff and 0.5 – 1 g/l of auxiliary agent (amphoteric and non-ionic leveling agent) are added to the liquor. It is then made weakly acidic by adding 0.5 - 2 g/l of
ammonium sulfate and 0.5 - 1 g/l of acetic acid. The process begins at 30°C - 40°C, is then heated up for about 30 - 60 minutes, and the fibers are finally dyed at boiling temperature for 30 - 60 minutes.

**Reactive Dyes**

Reactive dyes are typically used for brilliant colors. The reactive dyes used for wool are also suitable for polyamides. The process starts at 20°C - 45°C with a weakly acidic (pH 4.5 – 5) dye bath, followed by heating and dyeing for 30 - 90 minutes near boiling temperature. After-treatment is performed with 0.5 g/l of a non-ionic surfactant and 1 g/l of sodium bicarbonate or ammonia at 95°C for 20 minutes.

4.5.1.5 Polyamide and Polyacrylonitrile Blends

These blends of fibers are generally used to produce socks and panty hose. Polyamides are dyed with acid dyes, whereas polyacrylonitrile fibers are dyed with cationic dyes.

4.5.1.6 Polyester

Polyester is normally dyed with disperse dyestuffs. Because the diffusion of disperse dyes into the polyester is a very slow process, the normal exhaust dyeing process would take too long. Instead, exhaust dyeing is carried out in two ways:

- Carrier dyeing (mainly for wool/PES blends) at 100°C
- High temperature (HT) dyeing under pressure at temperatures up to 130°C

The dyeing process is followed by rinsing steps and a reductive after-treatment for dark shades.

Polyester is usually dyed in a continuous way (thermosol process). The dyestuff is padded to the textile, together with a thickening agent (alginate). A drying step (100°C - 140°C) and the thermosol process (200°C - 225°C; curing time: 12 - 25 s) follows. The dispersing agents and thickener are washed out. Reductive after-treatment is normally performed, as well.

4.5.2 Loose Fiber Dyeing

Loose fiber dyeing machines generally consist of large vats with a vertical axis, into which loose fibers are introduced after being pressed in a circular form. Dyeing machines may work under pressure or at atmospheric pressure, depending on the dyeing temperature. The dye bath always flows from inside to outside, since color homogeneity is not of primary importance in loose fiber dyeing. (All fibers will be mixed together during the following processes, such as carding, blending or combing.)

The liquor ratio in loose fiber dyeing can vary from 1:4 to 1:12 (depending on the type of machine, loading of machine, type of fiber, etc.). The following tables give some examples of dyeing recipes (Data collection: Prato textile district, Italy).
The values given here are typical for light and medium shades (for dark shades, dyestuff consumption can be in the range of 100 g/kg textile!). The consumption data can vary widely, depending on the process parameters. Note that dyeing auxiliaries and dyestuffs are formulations (water solutions/dispersions) and the active component can vary greatly.

### Table 4.28: Resource Consumption in Loose Fiber Dyeing (Energy) (audits in Prato, Italy textile district)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>0.1 - 0.4</td>
<td>KWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>4 – 14</td>
<td>MJ/kg</td>
</tr>
</tbody>
</table>

### Table 4.29: Inputs to Loose Fiber Wool Dyeing (acid, chrome or metal complex dyestuffs)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 8</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>8 – 16</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>16 – 24</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuffs</td>
<td>0.5 – 25</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>0 – 10</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

### Table 4.30: Inputs to Loose Fiber PAN Dyeing with Cationic Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 4</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinsing</td>
<td>4 – 16</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>8 – 20</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuffs</td>
<td>0.5 – 20</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>0 – 10</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

### Table 4.31: Loose Fiber Polyester Dyeing with Disperse Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 6</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>~ 12</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>~ 18</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuffs</td>
<td>0.5 – 25</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>0 – 10</td>
<td>g/kg</td>
</tr>
</tbody>
</table>
Table 4.32: Inputs to Loose Fiber Cotton Dyeing with Direct Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 8</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>8 – 32</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>16 – 40</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuffs</td>
<td>1 – 25</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>0 – 10</td>
<td>g/kg</td>
</tr>
<tr>
<td>NaCl</td>
<td>0 – 250</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

Table 4.33: Inputs to Loose Fiber Cotton Dyeing with Reactive Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 8</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>8 – 32</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>16 – 40</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuffs</td>
<td>1 – 70</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>0 – 10</td>
<td>g/kg</td>
</tr>
<tr>
<td>NaCl</td>
<td>0 – 250</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

Table 4.34: Inputs to Loose Fiber Polyamide Dyeing with Direct, Acid Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 6</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>6 – 12</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>12 – 18</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuffs</td>
<td>0.5 – 25</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>0 – 10</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

4.5.3 Package Dyeing

Yarn dyeing usually takes place with the yarn wound on cones or cylinders, rather than in hank forms, because of cost competitiveness. Cones are stacked on a metal frame, which is then placed in the dyeing machine. The cones and cylinders have holes drilled in them, and the dye bath is pumped through these drill holes from inside to outside and vice versa, in order to guarantee a homogeneous dyeing. Dyeing machines consist of a cylindrical autoclave, which may be laid in a horizontal or vertical position. With a vertical lay out, different frames may be adopted so that eventually different materials can be dyed (loose fibers, tops or beams). On the other hand, a horizontal lay out allows
for fully automatic loading systems, which increase productivity and reduce human work.

The typical liquor ratio for package dyeing is between 1:8 and 1:20.

An example of energy consumption for a typical autoclave for yarn dyeing and consumption of water, dyestuffs and auxiliaries for package dyeing of different substrates is reported in the tables below. (Data collection: Prato textile district, Italy)

### Table 4.35: Resource Consumption in Autoclave for Yarn Dyeing (Energy)

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>0.8 - 1.1</td>
<td>KWh/kg</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>13 – 16</td>
<td>MJ/kg</td>
</tr>
</tbody>
</table>

### Table 4.36: Inputs to Wool and Polyamide Blends Yarn Dyeing

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 15</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>~ 30</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>~ 45</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuff</td>
<td>1 – 40</td>
<td>g/kg</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>20 – 25</td>
<td>g/kg</td>
</tr>
<tr>
<td>Surfactants</td>
<td>~ 20</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

### Table 4.37: Inputs to PAN Yarn Dyeing

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 15</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>~ 30</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>~ 45</td>
<td>l/kg</td>
</tr>
<tr>
<td>Dyestuff</td>
<td>1 – 20</td>
<td>g/kg</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>20 – 25</td>
<td>g/kg</td>
</tr>
<tr>
<td>Surfactants</td>
<td>~ 20</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>~ 30</td>
<td>g/kg</td>
</tr>
</tbody>
</table>
### Table 4.38: Inputs to Cotton and Linen Yarn Dyeing with Direct Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 15</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>~ 45</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>~ 60</td>
<td>l/kg</td>
</tr>
<tr>
<td>Direct dyestuff</td>
<td>5 – 15</td>
<td>g/kg</td>
</tr>
<tr>
<td>NaCl</td>
<td>50 – 200</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>~ 45</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

### Table 4.39: Inputs to Cotton and Linen Yarn Dyeing with Reactive Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for dyeing</td>
<td>~ 15</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for washing</td>
<td>~ 15</td>
<td>l/kg</td>
</tr>
<tr>
<td>Water for rinse</td>
<td>~ 45</td>
<td>l/kg</td>
</tr>
<tr>
<td>Total water</td>
<td>~ 75</td>
<td>l/kg</td>
</tr>
<tr>
<td>Reactive dyestuff</td>
<td>20 – 90</td>
<td>g/kg</td>
</tr>
<tr>
<td>NaCl</td>
<td>600 – 1,350</td>
<td>g/kg</td>
</tr>
<tr>
<td>NaCO3</td>
<td>~ 450</td>
<td>g/kg</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>~ 38</td>
<td>g/kg</td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>~ 10</td>
<td>g/kg</td>
</tr>
<tr>
<td>Surfactants</td>
<td>~ 30</td>
<td>g/kg</td>
</tr>
</tbody>
</table>

### Table 4.40: Inputs to Cotton and Linen Yarn Dyeing with Sulfur Dyestuffs

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total water</td>
<td>~ 100</td>
<td>l/kg</td>
</tr>
<tr>
<td>Sulfur dyestuff</td>
<td>~ 80</td>
<td>g/kg</td>
</tr>
<tr>
<td>Dextrin</td>
<td>~ 120</td>
<td>g/kg</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>~ 110</td>
<td>g/kg</td>
</tr>
<tr>
<td>Surfactants</td>
<td>~ 30</td>
<td>g/kg</td>
</tr>
<tr>
<td>NaCl</td>
<td>~ 300</td>
<td>g/kg</td>
</tr>
<tr>
<td>H2O2</td>
<td>~ 20</td>
<td>g/kg</td>
</tr>
</tbody>
</table>
4.5.4 Hank Dyeing

Yarn dyeing in hanks form has been very popular in the past, but recently this technology has largely been replaced by the use of cones because of lower costs. Dyeing in hanks is currently used, however, for high quality and delicate yarns and where high voluminosity, regularity, and good mechanical characteristics are required (especially for the hand knitting sector and carpets).

4.5.5 Piece Dyeing

4.5.5.1 Rope Form Dyeing

**Batch Processes**

- **Flow (Winch Dyeing)**

  The flow dyeing machine is normally used for lightweight fabrics in rope form and tubular knits. With fabrics that are not in tubular form, selvedges must be sewn before dyeing to avoid dyeing heterogeneity. In flow machines, the fabric is kept in motion by a reel and the bath stands still. The fabric is soaked into a dye bath, is circulated by a reel at the speed of 0.3 - 0.6 m/s and then soaked again. A heat exchanger heats the bath and keeps it at the dyeing temperature. Reductive and low affinity dyestuffs are not generally used because of the high bath ratio (1:20 - 1:50). High affinity dyestuffs cannot be used either, due to the risk of fabric coloring heterogeneity.

  One of the main advantages of this method is that it results in a good dye homogeneity in warp and weft directions because there is no tension on the fabric. The development of synthetics (especially polyester) has led to the production of pressurized dyeing machines, in order to (a) dye at high temperature, (b) avoid the use of carriers, and (c) reduce dyeing time. High temperature machines are very similar to normal machines and may reach 130°C - 140°C.

- **Jet**

  Jet machines have been designed to eliminate some of the problems that used to affect flow machines. In particular, the reel is eliminated and the fabric is kept in motion (200 - 300 m/min) by a strong jet of the bath itself, which is pumped through a nozzle. The fast recirculation and therefore high turbulence of the bath favors dyestuff fixation on the fabric. This machine has the advantages of low water consumption and short dyeing time, but it causes high mechanical stress on the fabric so it cannot be used for some delicate fabrics.

- **Overflow**

  In many cases, the fast recirculation and high turbulence of the bath in a jet dyeing machine does not suit delicate knitted and woven items. With the overflow technology, there is no dye bath injection on the fabric, which, in rope form, is carried through the dyeing pipe by the stream of the bath. The fabric is soaked in the dye bath without any tension and is finally transported into the higher part of the machine by a reel, where a
new cycle begins. Such machines have been designed for knitted and woven items made of natural and synthetic fibers. Overflow HT dyeing machines are very similar to normal overflow machines, except that they also allow high pressure and consequently higher temperature.

- **Air Jet**

Air jet dyeing machines are very similar to jet machines; instead of moving fabric with a water jet, however, they use an air jet. An air compressor is substituted for the water pump. Air flows through a nozzle and makes the fabric circulate in the machine. The main advantages of the air jet technology are reduced water, energy and chemical consumption.

- **Continuous Dyeing in Rope Form**

This process uses a padding device for fabric in rope form, a reaction room, and a washing appliance. The padding device consists of a long basin containing the dye bath and a couple of rollers posed at the inlet and at the outlet. The fabric is pressed by the two rotating rollers at the inlet in order to obtain a homogeneous dye absorption and eliminate air; the other two rollers at the outlet only squeeze the fabric. The rope then enters the reaction room (generally called the j-box) where the dyestuff is fixed on the fiber. The j-box is filled to one-third full with the treatment bath. Washing and rinsing then follow.

The main problem with this process is the risk of longitudinal creases on the dyed fabric; for this reason the process is generally only used for white end products.

### 4.5.5.2 Full Width Piece Dyeing

**Batch Processes**

- **Beam Dyeing Machine**

A beam dyeing machine is composed of a horizontal cylinder which contains the fabric wound on a beam. There are both non-pressurized and pressurized beam dyeing machines, thus allowing dyeing at high temperatures. The beam has holes drilled in it and the dye bath is pumped inside the beam and flows outside through the drill holes. In this case, the fabric stands still and only the dye bath recirculates.

This dyeing process is particularly efficient for knitted and woven products made of texturized polyester. The fabric is wound on the beam in full width; there is, therefore, no risk of creasing. A disadvantage is the risk of dyeing heterogeneity if the dyestuff has not optimally penetrated the fabric.

- **Jigger**

This machine involves a trapezoidal tub containing the dye bath and two rolls onto which the fabric is alternatively wound. With this machine, the fabric is in motion while the bath stands still. The fabric, initially wound on the first roll, flows through the bath and then is wound on the second roll; the rotation is then reversed and the cycle continues. The fabric is led in
its path by a few small rolls. The range of fabric speed is 30 - 150 m/min. This machine is not used exclusively for dyeing processes, but also for various wet treatments on fabrics in full width. Its main disadvantage is the risk of longitudinal fabric dyeing heterogeneity due to variations in feed speed, fabric tension, temperature, and dyestuff concentration. In modern jiggers, however, constant speed and fabric tension are maintained during the whole process.

HT jigger machines are available; they allow high temperature dyeing (140°C).

Semi-Continuous and Continuous Processes

• Padding Machine

A padding device is used for continuous and semi-continuous dyeing. In this machine (known as a foulard machine), the fabric flows through the dye bath led by a few small rolls and then is squeezed by two pressing rolls. Dyestuff thus deposited on the fabric is not sufficiently fixed on the fiber, therefore various subsequent operations are necessary (see sections below). Temperature is the main factor influencing dye fixation, so usually steamers (wet heating) or ovens (dry heating) are used after padding. Only when dyeing cellulose fibers with reactive dyestuffs can fixation be obtained at ambient temperature. The fixation phase can take place on dry or wet fabric.

How much dyestuff is deposited on the fabric is a function of the fabric’s absorption and of the pressing strength of the squeezing rolls. Homogeneous coloring will be obtained only if the nip pressure and the dyestuff concentration in the bath are kept uniform throughout the whole process. The pressing strength of the squeezing rolls is commonly applied by means of a hydraulic system. Like jiggers, foulards are not used exclusively for dyeing.

• Pad-Jig (semi-continuous)

This dyeing technique typically uses direct or reactive dyes. In this process, the fabric passes through a padding machine, where it is drenched with dye bath at a temperature of about 60°C – 80°C. Then it passes through a jigger, where the dyestuff is fixed. At this point, the fabric is washed and oxidized. This process is used for heavyweight fabric dyeing. Sometimes the fabric can be dried in a hot-flue drier after padding and before entering the jigger machine.

The application of dyestuff by padding allows for homogeneous dyeing and can save time when compared to a traditional jigger dyeing process. In many cases, about 5 -10 % of the dye bath from the padding machine is added to the fixation bath in the jigger in order to prevent dyestuff discharge from the fabric. Salt can be added to the fixation bath for the same purpose.

• Pad-Batch (semi-continuous)

Direct and reactive dyestuffs are normally used for pad-batch dyeing processes. The fabric passes through a padding machine where it is (a)
drenched with the dye bath and with other chemicals (reducing agents),
(b) rolled without drying, and (c) subjected to slow rotation (2 - 4 rpm, so
that the dye bath will not concentrate at the boom of the roll) until
complete fixation is achieved (8 - 24 hours, depending on the
concentration of dyestuff applied). The fabric is then washed and rinsed.

This process is used on cellulose fibers and other highly hydrophilic
fibers, but is not suitable to obtain high intensity coloring. The process is
characterized by low water and energy consumption (about 50 - 80 %
less than conventional systems), low auxiliaries consumption, simple
dyestuff application, and good coloring repeatability.

- Pad-Roll (semi-continuous)

This process is quite similar to pad-batch. The fabric passes first through
the padding machine, next through an infrared oven where it reaches
fixing temperature (80°C – 90°C), then is rolled and subjected to slow
rotation inside a special heated compartment until complete fixation (1 - 8
hours) is achieved. The fabric is then washed and oxidized.

- Pad -Steam (continuous)

Reactive dyestuffs are typically used in the pad-steam dyeing process,
but direct, vat and sulfur dyes can also be used. The fabric passes
through a padding machine where it is drenched with the dye bath, then
through a steamer where the dyestuff is fixed on the fiber. The fabric is
finally washed and rinsed. The temperature inside the steamer is about
100°C.

- Pad-Dry (continuous)

In this process, the fabric passes through a padding machine where it is
drenched with the dye bath, then through a hot flue dryer for fixation
(150°C for 45 seconds - 60 seconds).

An intermediate drying (100°C - 150°C for 1 - 3 minutes) can be
performed before the fixation phase. This process can be quite
inexpensive if it is performed in high efficiency plants.

- Pad-Salt (continuous)

This process is analogous to the previous one, except that the fixation
phase occurs in a hot saline bath.

- Thermosol (continuous)

This process is used for polyester (and its blends) dyeing. Disperse
dyestuffs are used. The dyeing effect is obtained by heating polyester at a
temperature of 200°C for about 1 minute, so that the fiber becomes
plastic and acts as a solvent for the dyestuff.

In the thermosol process, the fabric passes through a padding machine
containing the dye bath and other chemicals (in particular, thickening
agents to avoid dyestuff migrating from the fabric before thermal fixation),
through an infrared oven for pre-drying, then through a hot flue dryer for
complete drying. Next, the fabric passes through a stenter for thermal
fixation; this phase uses a hot air flow of about 200 °C. Finally, the fabric is washed and rinsed.

- Pad-Williams Unit (continuous)
  This process is used to dye cotton with direct or reactive dyestuffs. After padding, the fabric passes through various special basins with rollers (Williams unit). The dyestuff is fixed during this phase; low bath ratios can be reached.

4.6 Printing

The most common printing technologies are:

- Direct printing
- Discharge printing
- Resist printing
- Transfer printing

Most classes of dyes are adaptable to one or more types of printing; vat, reactive and disperse colors generally produce good fastness properties. Pigments are also used in printing.

Silk is usually printed with acid dyes, cotton with vat and reactive, man-made fibers with disperse and cationic, and wool is printed with acid or mordant dyes after being treated with chlorine to make it more receptive to color. Pigment printing can be used for all materials.

4.6.1 Paste Application Methods

Various printing paste application methods are used:

- Roller
- Flat screen
- Rotary screen
- Transfer
- Ink jet

4.6.1.1 Roller Printing Process

In roller printing, dyestuff is applied in paste form from a brush roller to an engraved copper cylinder which, transported by a rotating smooth roller, prints the fabric. A sharp blade scrapes the excess dye from the surface of the engraved roller. As the fabric passes between the engraved roller and the smooth cylinder, the dye from the shallow areas is pressed onto it. Another fabric called a “printing blanket” follows behind and along with the fabric being printed; the printing blanket absorbs the excess printing paste and prevents it from striking through and staining the smooth roller. The printed textile is immediately passed into a drying chamber and then into a steam chamber, where the moisture and heat set the dye. When printing with multiple colors, one engraved roll must be used for each color. Because of the high quality
achievable, roller printing is the most appealing method for printing designer and fashion apparel fabrics.

4.6.1.2 Flat Screen Printing Process

In flat screen printing, a screen onto which the printing paste has been applied is pressed onto a section of fabric. A design is reproduced on the screen, and a coating of lacquer or other impermeable substances is applied to all parts of the screen that are not part of the design. A squeegee then moves across the screen, forcing the print paste through the permeable parts of the surface of screen and thereby reproducing the design and printing the fabric. This process is repeated for each color to be used in the design. This process is rather expensive, but very versatile and has a high production rate when fully automated machines are used.

4.6.1.3 Rotary Screen Printing Process

This type of machine employs a rotary screen made of metal foil. The fabric to be printed is fed into the printer section of the machine under uniform tension and passes under the rotating screen through which the printing paste is automatically pumped from a tank. A squeegee in each rotary screen forces the paste through the screen onto the fabric as it moves along at rates up to 90 m/min. The fabric then passes into a drying oven and is finally washed. This process combines the advantages of roller and flat screen printing techniques. Production output is considerably higher than on flat screen machines.

4.6.1.4 Transfer Printing Process

This process consists of transferring a decoration from a paper support on the fabric by mean of dry or wet heating. Two main processes have been developed: dry heat transfer and wet heat transfer. Production costs are reduced in heat transfer printing because after treatments (such as steaming) are eliminated. Fabrics printed with this process have a good hand and a high definition of pattern. Rich and deep shades may be reproduced. Heat transfer printing can be applied to both woven and knitted items (including circular knitted goods around a circumference without slitting the material). Color fastness depends upon the fiber and the dyestuffs used; an appropriate choice is important for the best performance.

4.6.1.5 Ink-Jet Printing

Ink-jet technology was developed for document printing. The color is propelled in small drops towards the substrate and directed to the desired areas. The process control can be easily computerized. In textile applications, this technology is now used mainly to print polyester substrates (especially small lots and sample lots).
4.6.2 Printing Technologies

4.6.2.1 Direct Printing

Direct printing is the most common approach used to apply a color pattern. Direct printing is used on white fabrics or previously dyed fabrics (generally in light colors to make the print stand out), in which case it is called overprinting.

The dyes are dissolved in a limited amount of water, to which a thickening agent has been added to give the necessary viscosity to the print paste. Gums are typically used because they are easy to wash out and do not absorb the color themselves (which would subsequently be washed out during washing phase); they also allow better color penetration.

The printed textile is fixed by steam, dry heat, or chemical reaction and then washed. One-phase and two-phase printing cycles are used. In the one-phase process, the printing paste is prepared in one step with all the components. In the two-phase process, the fixation agent (for vat dyes, alkali and reducing agents; for reactive dyes, alkali and electrolyte) is padded after the printing step. Two-phase reactive printing can be done without addition of urea.

4.6.2.2 Pigment Printing

Approximately 50% of textile printing is done using pigment printing technology. The pigments used have no affinity for the fiber; therefore, a binder and fixating agent must be added to the printing paste. The advantage of pigment printing is that it can be done without the subsequent washing step necessary for all other printing technologies. A typical printing paste recipe for pigment printing contains water, emulsifier, thickening agent, pigment dispersant, softening agent, binder, and fixation agents. Printing paste emulsions based on mineral oils emit a considerable amount of VOC during drying and fixation and are no longer used in Europe. Nevertheless the printing pastes with synthetic binders can still contain approximately 10% mineral oils.

4.6.2.3 Discharge Printing

The discharge printing method is declining in use. In this process, the fabric is dyed as a piece and then printed with a chemical that destroys the color in designed areas. Sometimes the base color is removed and another one is printed in its place. The usual method is to print the design with a paste containing a reducing (or oxidizing) agent; steaming, and then washing to remove the reaction by-products. The most common oxidizing agents used are sodium chlorite and potassium dichromate; the most common reducing agent is sodium dithionite.

4.6.2.4 Resist Printing

Bleached goods are printed with a resist paste (a resinous substance that cannot be penetrated when the fabric is soaked in a dye); the dye affects only the parts that are not covered by the resin paste. After the fabric has passed through the dyeing process, the resist paste is removed, leaving a white pattern on a colored ground. The composition of the resist paste depends on the kind of
dye that will be subsequently used. In the discharge method, the fabric is first dyed and then the color is extracted by an imprinted chemical; in the resist method, a paste is first imprinted and then the fabric is dyed. The durability of the fabric is not affected by the resist method.

### 4.6.3 Environmental Aspects of Printing

Major printing paste components include color concentrates (dyestuffs or pigments), thickening agents, and in pigment printing, a binder.

The main pollutants associated with the printing process are volatile organic compound (VOC) emissions from the printing paste solvents. These may be aqueous, organic (mineral spirits) or both. The solvent concentration in printing pastes may vary from 0 to 60 weight percent. Urea, used as hydrotropic agent, is one of the most polluting substances, contributing to nitrogen concentration in waste water discharges and to ammonia in air emissions as it decomposes during drying and printing (biuret reaction).

Although some solvent evaporates in the early stages of the printing process, the majority of air emissions are from the printed fabric drying process, which drives off volatiles. For some specific printing paste/fabric combinations, color fixing occurs in a curing process, which may be entirely separate or merely a separate segment of the drying process.

After the printing process, the fabric is steamed; the combined action of high temperature and condensation of the steam on the piece expands the fabric, allowing the paste to penetrate into the fiber. The following table reports thermal energy (steam) consumption for a 150 g/m² fabric printed on 75% of its surface.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Temperature [°C]</th>
<th>Thermal energy [MJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>100 – 102</td>
<td>~ 1.5</td>
</tr>
<tr>
<td>Polyamide</td>
<td>101 – 103</td>
<td>~ 0.7</td>
</tr>
<tr>
<td>Polycrylonitrile</td>
<td>101 – 103</td>
<td>~ 0.7</td>
</tr>
<tr>
<td>Acetate</td>
<td>101 – 105</td>
<td>~ 0.7</td>
</tr>
</tbody>
</table>

Major pollution problems also relate to (a) the off-gas discharge from the steaming chamber, which contains ammonia and (b) washing water streams containing urea. During the drying process, fixing agents of the printing paste may generate formaldehyde.

Except for pigment and transfer printing, washing is necessary to remove unfixed color on the fabric.

Main pollutants in pigment printing are mineral oils (white spirit) from thickeners and methanol and formaldehyde from melamine resins/fixing agents. These may be emitted in levels up to 10 g organic C/kg textile (approximately 500 mg organic C/m³).
4.6.3.1 Typical Consumption and Emission Levels by Printing Processes

The following sections show typical consumption and emission levels for printing processes (vat discharge printing, two-phase vat printing, printing with disperse dyestuffs and pigment printing). The data were collected in German finishing mills.

Vat Discharge Printing (ground dyeing: reactive pad batch)

In a first process before vat printing, the ground dyeing must be prepared. The waste water discharge from this dyeing step is loaded with a specific COD of approximately 27 g/kg textile. The following substances are observed in the rinsing waste water: NaOH, SiO₂, NaCl, sulfate, phosphate, surfactants and dyestuffs. Water consumption can be 70 l/kg textile. The dyed textiles are treated with nitrobenzene sulfonic acid (contour fixing agent), dried, printed, dried, damped, washed (reoxidation) and finally dried.

Table 4.42 gives an overview of chemical/auxiliary consumption during the vat discharge printing. Table 4.43 summarizes the specific COD and AOX load in the total process (ground dyeing + printing inclusive pre-treatment) waste water discharge.

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Chemical/auxiliary:</th>
<th>Specific consumption [g/kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pad batch dyeing</td>
<td>NaOH (50 %)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Water-glass</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Auxiliaries</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Dyestuffs</td>
<td>148</td>
</tr>
<tr>
<td>Printing</td>
<td>Nitrobenzene sulfonic acid</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Printing paste (100 % covering)</td>
<td>570</td>
</tr>
<tr>
<td>Washing (reoxidation)</td>
<td>H₂O₂ (50 %)</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Auxiliary</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Acetic acid (60 %)</td>
<td>20</td>
</tr>
</tbody>
</table>
It is apparent from these data that the majority of the COD load during vat discharge printing is caused by the pre-treatment process and the washing chemicals; the AOX load is caused by the printing paste. The effluent load from washing the printing blankets and cleaning the printing system must be added to the COD values mentioned above.

The exhaust air from the drying and damping steps is loaded with VOC; approximately 0.3 g organic C/kg textile (drying) and 0.8 g organic C/kg textile (damping) are observed.

Two-Phase Vat Printing

Two-phase vat printing is done in the following process steps: application of the printing paste, padding of the developer, fixation, washing (reoxidation), and drying.

Table 4.44 provides the levels of chemicals/auxiliaries consumed during the two-phase vat printing process.

<table>
<thead>
<tr>
<th>Chemical/auxiliary: Chemical/auxiliary:</th>
<th>Consumption [g/kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing paste (100 % covering)</td>
<td>570</td>
</tr>
<tr>
<td>Developer</td>
<td>260</td>
</tr>
<tr>
<td>Washing (Reoxidation)</td>
<td>28</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$ (50 %)</td>
<td>28</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>25</td>
</tr>
<tr>
<td>Auxiliary</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 4.45 summarizes the specific COD and AOX load in the total process (pre-treatment inclusive) waste water discharge.
Table 4.45: Specific COD and AOX Load in Two-Phase Vat Printing (including pre-treatment)

<table>
<thead>
<tr>
<th>Process</th>
<th>Specific COD [g/kg textile]</th>
<th>Specific AOX [mg/kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-treatment</td>
<td>132</td>
<td>0.00</td>
</tr>
<tr>
<td>Developer</td>
<td>39</td>
<td>0.00</td>
</tr>
<tr>
<td>Printing paste</td>
<td>10</td>
<td>7.10</td>
</tr>
<tr>
<td>Chemicals for washing</td>
<td>117</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>298</strong></td>
<td><strong>7.12</strong></td>
</tr>
</tbody>
</table>

The majority of the COD load is caused by pre-treatment and washing liquor. The printing paste contains AOX. The effluent load from washing the printing blankets and cleaning the printing system must be added to the COD-values mentioned above.

Table 4.46 gives an overview of the exhaust air emission values during two-phase vat printing (including pre-treatment and finishing processes).

Table 4.46: Exhaust Air Emissions in Two-Phase Vat Printing (German plant)

<table>
<thead>
<tr>
<th>Process</th>
<th>VOC [g/kg textile]</th>
<th>Dust [g/kg textile]</th>
<th>Odor [OU/kg textile]</th>
<th>Aldehyde [g/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singeing</td>
<td>0.16</td>
<td>0.26</td>
<td>5,922</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Scouring</td>
<td>0.12</td>
<td>-</td>
<td>2,271</td>
<td></td>
</tr>
<tr>
<td>Bleaching</td>
<td>0.04</td>
<td>-</td>
<td>896</td>
<td></td>
</tr>
<tr>
<td>Drying (stenter)</td>
<td>0.02</td>
<td>-</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Two-phase printing</td>
<td>0.55</td>
<td>-</td>
<td>5,666</td>
<td></td>
</tr>
<tr>
<td>Fixation</td>
<td>1.28</td>
<td>-</td>
<td>17,113</td>
<td></td>
</tr>
<tr>
<td>Drying, finishing</td>
<td>0.6</td>
<td>-</td>
<td>2,044</td>
<td></td>
</tr>
<tr>
<td>Condensation</td>
<td>0.91</td>
<td>-</td>
<td>2,788</td>
<td></td>
</tr>
<tr>
<td><strong>Total process</strong></td>
<td><strong>3.68</strong></td>
<td><strong>0.26</strong></td>
<td><strong>37,000</strong></td>
<td><strong>&lt;0.01</strong></td>
</tr>
</tbody>
</table>

Printing with Disperse Dyestuffs

Printing on PES substrates can be done with disperse dyestuffs. The process steps are: printing, drying, fixation (HT-steam), washing (partially reductive after treatment).

Table 4.47 summarizes chemical/auxiliary consumption for this process.
Table 4.47: Chemical/Auxiliary Consumption in Printing with Disperse Dyestuffs (German Plant)

<table>
<thead>
<tr>
<th>Chemical/auxiliary:</th>
<th>Consumption [g/kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing paste</td>
<td>570</td>
</tr>
<tr>
<td>(100 % covering)</td>
<td></td>
</tr>
<tr>
<td>Washing:</td>
<td></td>
</tr>
<tr>
<td>Auxiliary</td>
<td>23</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 4.48 shows the specific COD and AOX loads observed in the washing waste water discharge.

Table 4.48: Specific COD and AOX Loads, Printing with Disperse Dyestuffs (German Plant)

<table>
<thead>
<tr>
<th></th>
<th>Specific COD [g/kg textile]</th>
<th>Specific AOX [mg/kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing paste</td>
<td>42</td>
<td>2.8</td>
</tr>
<tr>
<td>Chemicals for washing</td>
<td>38</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>80</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The majority of the exhaust air emission is observed during the drying process, as shown in Table 4.49 below.

Table 4.49: VOCs in Exhaust Air from Printing with Disperse Dyestuffs (German Plant)

<table>
<thead>
<tr>
<th>Process</th>
<th>VOC [g/kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>1.34</td>
</tr>
<tr>
<td>HT-steam fixation</td>
<td>0.01</td>
</tr>
<tr>
<td>Total</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Pigment Printing

Pigment printing is a process with no washing step (after treatment). Water pollution only results from the pre-treatment steps of washing the printing blankets and cleaning the printing system. Table 4.50 summarizes air pollution associated with pigment printing of cotton.
Table 4.50: Pigment Printing of Cotton (German Plant)

<table>
<thead>
<tr>
<th>Process</th>
<th>Organic C [g organic C/kg textile]</th>
<th>Formaldehyde [g /kg textile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>3 – 5</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Curing</td>
<td>1 - 2</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td>4 - 7</td>
<td>0.1 - 0.2</td>
</tr>
</tbody>
</table>

### 4.7 Finishing

Fabric goods must pass through various finishing processes to be suitable for their intended end use. “Finishing” encompasses a number of treatments that improve or modify fabrics, enhancing properties such as aesthetics, “hand,” performance, durability, and resistance to biologic agents, fire or heat, electric charge accumulation, etc. Finishing alternatives are extremely varied, ranging from mechanical to chemical treatments. In some cases, the same results can be achieved through both mechanical and chemical treatments.

Some finishing treatments are specific for one kind of fabric (e.g., easy care finish for cotton, antistatic finish for synthetics, moth proofing and superwash finish for wool).

A typical recipe for chemical finishing of cotton and cotton blends is a combination of:

- easy-care agents,
- softener, and
- functional additives (e.g. water repellent, flame retardant).

Finishing treatments can be carried out in batch or continuous methods. Batch finishing procedures present the same problem for finishing as they do for dyeing: incomplete exhaustion of chemicals. After the finishing agents are applied, drying (at a temperature of approximately 120°C) and curing (by condensation at temperatures from 150°C to 180°C) are necessary.

#### 4.7.1 Chemical Treatment

##### 4.7.1.1 Overview of Methods

**Easy-Care Treatment**

Easy-care finishing results in cellulose fabrics that (a) are easy to wash, (b) resist creasing during wash and wear and (c) require no ironing or a minimum of ironing. These requirements now exist because cellulose fabric characteristics must compete with polyamide and polyester, which both have a higher in-built stability.

**Water-Repellent Treatments (Hydrophobic Treatment)**

Water-repellent treatment consists of eliminating or reducing the space among the threads, by which water (and air) may penetrate the fabric. It is generally done on cellulose fabrics.
Water-repellent treatment of a garment must assure its resistance to water but not to air and humidity. This may be achieved in two ways:

- Precipitation of hydrophobic substances on the fiber, such as paraffin emulsions and aluminum salts
- Chemical transformation of the fiber surface, that is, adding a hydrophobic group to the fiber molecule (substances used are silicones and fluorocarbons).

Softening Treatment

Especially for cotton or cellulose fibers, softening is a primary finishing treatment. Softening treatment consists of applying specific chemicals that make the fibers soft and comfortable; it is often done in the last rinsing bath after the dyeing process or in connection with a drying process. With continuous and semi-continuous dyeing processes, the fabric is soaked into a bath containing the softening agents, and then excess chemicals are squeezed by two cylinders and recovered. Impregnated fabric is then dried in a tentering machine, whereby softening agents are fixed.

Flame-Retardant Treatment

Flame-retardant finishing has become increasingly important and in several countries, it has become compulsory for some items. Many natural and synthetic fibers (except those designed for flame-retardant purposes) are flammable. Flame-retardant agents should protect fabric from burning, without modifying the hand, color, and look of the fabric. Many substances may be used to obtain flame-retardant properties.

A different approach to obtain fire-retardant properties of textiles is to create flame-retardant fibers by adding certain chemicals to existing fiber spinning solutions. This approach has become more acceptable to the textile industry because it represents a more stable situation and to consumers because the health hazard is removed.

The third approach to flame retarding is the development of special flame-retardant fibers that are produced in specific generic classes. These fibers generally are more expensive than the modified flame-retardant fibers. They also have technical limitations with aesthetic qualities, finishing, and dyeing.

Antistatic Treatment

When two surfaces are rubbed, they may get charged with electrostatic energy. For textiles, this may be uncomfortable. Moreover, charged fabrics attract dust and dirt. Thus, in many cases antistatic treatment is necessary. The process consists of treating the fabric with hygroscopic substances (antistatic agents) to increase the electrical conductivity so that it is impossible to accumulate electrostatic charge. It is important that antistatic agents keep their properties for a long time and are not removed by washing.

Antistatic treatment is very important for synthetic fibers because they accumulate electrostatic energy very easily, compared to natural fibers. Some antistatic agents also have anti-pilling effects.
Treatment with Hand Builders

Handle modifiers, or “builders” are added to the finishing recipe to add body or stiffness to fabrics and to modify their handle from soft to firm. Builders include natural polymers (starches, modified starches, alginates), crosslinking agents (trimethylol melamine, urea, formaldehyde), and synthetic polymers (PVA, polyacrylates). Generally, builders are film-forming agents that can react with the fabric or not. Unless used in conjunction with polymeric or crosslinking reactants, the stiffening effect is not durable.

Soil-Release Treatment

Finishes can be applied to impart stain and soil/oil repellence to apparel fabrics (usually work wear), military and automotive fabrics, carpets, and primary upholstery. Such finishes increase washing or dry-clean efficiency in case of stains derived from food, motor oil, alcoholic and non-alcoholic beverages, ink and mud.

The finishes are applied by pad-dry processes and are generally effective through many cleanings; some are durable for the life of the garment.

Bactericidal and Fungicidal Finish

Biocides are used in textile processing to prevent biological growth, and as a finish to (a) impart biocidal or fungicidal properties to apparel fabrics or fabrics for hospitals and floor coverings, and (b) act as odor suppressants for socks/hosiery.

Shrink-Resistant Treatment

Fibers spun into yarn are under constant tension during the weaving process. Their physical condition is changed, but not permanently fixed; the fibers tend to revert to their natural state, causing shrinkage. The yarns are made to assume a final condition by shrinking the fabric in a preparatory finishing process that minimizes subsequent shrinkage such as immersion in cold water, followed by hot water, steaming, or a chemical treatment. Even when textile fabrics are pre-shrunk, they are liable to further shrinkage when washed. The amount of additional shrinkage that may occur after washing must be clearly stated on the label.

Shrinkage is a very important matter in case of wool and wool-rich fabrics, because wool may felt, thus reducing dimensions of the fabric. In order to avoid this, anti-felting treatments aim to make wool fabrics shrink-resistant during usage and washing, and may include treatment with the following chemicals:

- Chlorine gas followed by washing with sodium bisulfite (NaHSO₃)
- Hydrochloric acid (HCl) and sodium hypochlorite (NaClO) in bath
- Dichloroisocyanuric acid
- Enzymes
- Resins

Wool Superwash Treatment

Superwash finishing treatment aims to increase wool’s anti-felting properties and consists of applying resins to the wool tops or to the wool fabric. Several
products and methods are used, but the most popular is the chlorine-Hercosett process. Hercosett resin cannot be applied directly onto wool because under normal conditions it does not distribute itself uniformly on the surface of the fibers. In order to avoid such a problem, wool is treated with chlorine, which increases the superficial tension of wool, so that Hercosett resin can easily distribute itself on the surface, thus obtaining a thin and homogeneous film.

**Mothproofing Treatment**

Mothproofing of wool and wool-blend textiles is largely restricted to textile floor coverings. In the case of apparel textiles, mothproofing agents may be applied to protect articles that will be stored for extended periods of time between uses - military uniforms, for example. Three active compounds used are: permethrin, sulcofuron and a hexahydropyrimidine derivative (together with permethrin). Adequate fastness to washing and dry cleaning is achieved by applying the treatment in the dyeing process.

4.7.1.2 Emission Levels During Chemical Finishing Treatments

Environmental and health issues of concern during chemical finishing treatments are, in order of priority:

- Air pollution emissions
- Waste water discharges
- Diffuse emissions to workplace air

**Waste Water Discharges**

Discharges to waste water are created by residual formulations and liquor baths, as well as cleaning of the application equipment. Because textile auxiliaries are expensive, businesses typically keep the loss based on the total consumed liquor amount in the range of 1 %–5 %. In a few instances (especially with small commission finishers) higher losses up to 50 % may be observed. This depends on the size of the foulard chassis and the lot sizes to be finished.

It can generally be assumed that the environmental impact from chemical finishing is nearly negligible compared to the impact from pre-treatment, dyeing and printing processes. Most of the COD output has low biodegradability, but is largely non-toxic (this is important for consumer safety). The main exceptions are formulas based on biocides.

**Air Emissions (including to Workplace Atmosphere)**

The bulk of air emissions are created by more or less volatile components, by-products or impurities of the used auxiliaries. They may be summarized as follows:

*Substances with less dangerous properties:*

(Classified as classes II, III, IV, V by the different technical guidelines in the EU member states)

- Aliphatic hydrocarbons (C1 –C40)
- Aromatic hydrocarbons
- Ketones
- Alcohols (low molecular)
- Esters (low molecular)
- Siloxanes
- Carbonic acids (low molecular)
- Fatty acids
- Fatty alcohols
- Fatty esters
- Fatty amides
- Fatty amines
- Amino alcohols
- Dioles, polyoles
- Glycol ethers (acetates)
- Ethers (aliphatic, aromatic)
- And a lot more (altogether about 1000)

**Substances with More Dangerous Properties:**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid-(2-ethoxyethyl)-ester</td>
<td>Softeners/fluorocarbon-resins</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>Polyvinyl acetate, acetic acid</td>
</tr>
<tr>
<td>Acrolein (2-propenoic aldehyde)</td>
<td>Decomposition of glycerol</td>
</tr>
<tr>
<td>Acrylates (methyl, ethyl, butyl)</td>
<td>Polymers</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>Polymers, thickeners</td>
</tr>
<tr>
<td>Aliphatic amines</td>
<td>Polymers, polyurethanes</td>
</tr>
<tr>
<td>2-Aminoethanol</td>
<td>Wetting agents, softeners</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>Dyeing carrier</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Dyeing carrier</td>
</tr>
<tr>
<td>N,N’-Bis(2-aminoethyl)-1,2-ethanediameine</td>
<td>Softeners</td>
</tr>
<tr>
<td>Butyne-1,4-diol-2</td>
<td>Fluorocarbon resins</td>
</tr>
<tr>
<td>Caprolactam</td>
<td>Polyamide 6 powder/textiles</td>
</tr>
<tr>
<td>Chloromethane (methyl chloride)</td>
<td>Quaternary ammonium compounds</td>
</tr>
<tr>
<td>Chlorinated aromatic hydrocarbons</td>
<td>Dyeing carriers</td>
</tr>
<tr>
<td>Chloroethanol</td>
<td>Decomposition of flame retardants (chlorinated P-ester)</td>
</tr>
<tr>
<td>Chloroparaffins</td>
<td>Flame retardants</td>
</tr>
<tr>
<td>Dichloroethene</td>
<td>Polyvinylidene chloride</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>Solvent cleaning</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>Softeners</td>
</tr>
<tr>
<td>Di(ethylhexyl)phthalate</td>
<td>Dyeing auxiliaries/polymer-</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Use</td>
</tr>
<tr>
<td>---------------</td>
<td>-----</td>
</tr>
<tr>
<td>Diglycidyl ether</td>
<td>Epoxide resins</td>
</tr>
<tr>
<td>2,4-Diisocyanatetoluene</td>
<td>Fluorocarbon resin extender</td>
</tr>
<tr>
<td>2,6-Diisocyanatetoluene</td>
<td>Fluorocarbon resin extender</td>
</tr>
<tr>
<td>N,N-dimethylacetamide</td>
<td>Fiber solvent (polyamide 6.6, metaramide)</td>
</tr>
<tr>
<td>1,1-Dimethylethylamine</td>
<td>Rare</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>Tensides (ethoxylate)</td>
</tr>
<tr>
<td>Diphenylmethane-2,4 diisocyanate</td>
<td>Extender, polyurethanes</td>
</tr>
<tr>
<td>Diphenylmethane-4,4’diisocyanate</td>
<td>Extender, polyurethanes</td>
</tr>
<tr>
<td>Dipropylenetetramine</td>
<td>Softeners</td>
</tr>
<tr>
<td>2,3-Epoxy-1-propanol</td>
<td>Some antistatics</td>
</tr>
<tr>
<td>Ethoxyethanol</td>
<td>Softeners/fluorocarbon-resins</td>
</tr>
<tr>
<td>Ethanedialdehyde (glyoxal)</td>
<td>Crosslinkers</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>Softeners</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Softeners</td>
</tr>
<tr>
<td>Fluoro organics, low molecular</td>
<td>Fluorocarbon resins</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Crosslinkers, conservation agent, stenter off-gas</td>
</tr>
<tr>
<td>Hexamethylenediamine</td>
<td>Polycondensation products</td>
</tr>
<tr>
<td>Hexamethylenediisocyanate</td>
<td>Fluorocarbon resins, polyurethane</td>
</tr>
<tr>
<td>2-Hexanone</td>
<td>Fluorocarbon resins, polyurethane</td>
</tr>
<tr>
<td>Isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate,3</td>
<td>Rare</td>
</tr>
<tr>
<td>Methoxy-1-propanol, 2-</td>
<td>Rare</td>
</tr>
<tr>
<td>Methoxypropyl acetate</td>
<td>Rare</td>
</tr>
<tr>
<td>Monochloroacetic acid, Na-salt</td>
<td>Rare</td>
</tr>
<tr>
<td>Monochloroacetic acid, 1-methylethylester</td>
<td>Rare</td>
</tr>
<tr>
<td>Monochloroacetic acid, ethyl ester</td>
<td>Rare</td>
</tr>
<tr>
<td>Monochloroacetic acid, methyl ester</td>
<td>Rare</td>
</tr>
<tr>
<td>N-alkylmorpholine</td>
<td>Non-wovens coating</td>
</tr>
<tr>
<td>Sodium trichloroacetate</td>
<td>Rare</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>Bleaching auxiliary</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>Dry cleaning</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Dyeing auxiliary</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>Rare</td>
</tr>
<tr>
<td>Tricresyl phosphate (ooo, oom, oop, dispersions</td>
<td>Flame retardants</td>
</tr>
</tbody>
</table>
om, omp, opp)

Triethylamine  •  Special crosslinkers
Trimethylphosphate  •  Flame retardants
Tin derivatives, organic, inorganic  •  Fluorocarbon resins, hydrophobing agents, biocides
Vinyl acetate  •  Polyvinyl acetate

**Substances with Carcinogenic Properties:**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>Crack products in off gas (very low)</td>
</tr>
<tr>
<td>Dioxins (Br, Cl, F)</td>
<td>Crack products in off-gas (very low)</td>
</tr>
<tr>
<td>Bischloromethylether</td>
<td>Strongest synthetic carcinogen, spontaneous formation when working with formaldehyde and hydrogen chloride (very low)</td>
</tr>
<tr>
<td>Arsenic trioxide/ antimony trioxide</td>
<td>Flame retardants</td>
</tr>
<tr>
<td>Dimethyl sulfate</td>
<td>Quaternary ammonium compounds</td>
</tr>
<tr>
<td>Ethyleneimine</td>
<td>Flame retardants</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>Polymer dispersions</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>Polymer dispersions</td>
</tr>
<tr>
<td>2-vinyl cyclohexene</td>
<td>Polymer dispersions</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>Polycondensation products</td>
</tr>
<tr>
<td>1,2 - epoxypropane (propylene oxide)</td>
<td>Tensides (propoxylate)</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>Tensides (ethoxylate)</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>Polymer dispersions (PVC)</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>Reactive polymers, flame retardants</td>
</tr>
<tr>
<td>Butanone oxime</td>
<td>Fluorocarbon resins, polyurethanes</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>Pesticide</td>
</tr>
<tr>
<td>Propylenemine</td>
<td>Flame retardant and polyurethane crosslinker</td>
</tr>
<tr>
<td>N-vinylpyrrolidone</td>
<td>Polyvinylpyrrolidone dispersions</td>
</tr>
</tbody>
</table>

A typical emission mixture of dangerous substances in a stenter off-gas may be represented as:

- Formaldehyde
- Caprolactam
- d-limonene, terpene-hydrocarbons
- Phenol
• Ethanolamine
• Vinyl acetate
• Formic acid
• Acetaldehyde
• Ethyl acrylate
• Butyl acrylate
• Triethylamine
• 1,4-Dioxane
• Chloroacetamide
• Thiourea
• Diisooctylphthalate
• N-vinylpyrrolidone
• Methyl acrylate
• Glyoxal
• Acrylic acid
• Epoxyethylbenzene
• Methoxypropylacetate-1,2

Reasons for Emissions:
The likelihood that these substances will be emitted depends upon (a) their specific physical/chemical properties (such as vapor pressure and hydrophilic/hydrophobic balance) and (b) the process parameters:

• Curing time
• Curing temperature
• Ventilation rate
• Off-gas matrix
• Textile material (natural/hydrophilic, synthetic/hydrophobic)
• Catalyst in recipe
• pH value in recipe/textile

In more than 90 % of cases, the emission result is a purely additive procedure. In other words, if you know the emission behavior of the single components of a formulation, you may add them up according to their proportion of the recipe and factoring in the wet pick up.

Range of Emissions
(Data referred to below are based on emission measurements in the European [mainly German] textile industry.)

Emissions may be in the range of

• 5 – 500 mg organic C/m³ with 50 – 4,000 g organic C/hour or 0.1 – 10 g organic C/kg textile

The emission concentration mostly depends upon the available off-gas volume.
Typical emissions are in the range of

- 20 – 100 mg organic C/m³ with 20 – 800 g organic C/hour or 0.4 – 2.0 g/kg textile

More dangerous emissions like formaldehyde are in the range of 1 – 20 mg/m³, with 10 – 200 g/h, or 0.1 – 0.4 g/kg textile. In rare cases, emissions may reach up to 80 mg/m³, with 800 g/h, or 1.6 g/kg textile.

Carcinogenic substances should not be generally an emission problem. Typical values are less than 1 mg/m³ with 10 g/h, or 0.02 g/kg textile. Chemicals suppliers typically guarantee a residual monomer content of less than 10 mg/kg in the auxiliaries.

The total output for typical finishing plants ranges between a few hundred kg/h to 100 metric tonnes per year (including hydrocarbons in form of preparation emissions).

The typical range for the different substances is shown in Table 4.51, which compares the plant emissions and the "natural" traffic emissions based on the road segments just along the borders of the plant (as the segments are doubled, the traffic emissions double, and so on).

<table>
<thead>
<tr>
<th>Quality of Emissions</th>
<th>Plant traffic Emissions in kg/year (traffic on site, traffic due to delivery, suppliers, employees)</th>
<th>General traffic emissions in kg/year (area considered: ~ 4 km²)</th>
<th>Plant process emissions in kg/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic-C Class II and higher</td>
<td>500 – 1,000 mostly hydrocarbons</td>
<td>6,000 – 16,000 mostly hydrocarbons</td>
<td>2,000 – 90,000 mostly aliphatic and substituted hydrocarbons</td>
</tr>
<tr>
<td>Organic Substances Class I</td>
<td>40 – 150 mostly aldehydes</td>
<td>500 – 2,500 mostly aldehydes</td>
<td>200 – 5,000 mostly formaldehyde and caprolactam</td>
</tr>
<tr>
<td>Carcinogenic Substances</td>
<td>15 – 30 mostly benzene</td>
<td>300 – 800 mostly benzene</td>
<td>1 – 20 mostly monomers</td>
</tr>
<tr>
<td>Inorganic Substances mostly NOx</td>
<td>1,000 – 4,000</td>
<td>15,000 – 40,000</td>
<td>1,000 – 10,000</td>
</tr>
</tbody>
</table>

With respect to organic carbon emissions and emissions of Class I substances, the plant process emissions are clearly dominant. However, in the case of smaller companies, the traffic emissions are dominant with respect to these two emission categories. Regarding carcinogenic substances, the plant emissions may be considered negligible. As expected, inorganic plant emissions are clearly lower than traffic emissions.
Emission Reduction Measures

All the above-mentioned emissions may be reduced by different off-gas cleaning technologies. The following are commonly used:

- Aqueous scrubber
- Electro filter
- Condensation
- Combinations of these
- Thermal incineration

Reduction rates range between 10 and 90 %. It is estimated that globally, approximately 1 % of all stenters have been equipped with such equipment to date.

Machine-Based Emissions

Another important fact with respect to the emission situation is that the direct heated (methane, propane/butane) stenters themselves may produce relevant emissions. These are the result of incomplete burning of the primary sources such as gas. This leads to additional emissions such as:

5 – 1000 mg C/m³ with up to 10 kg organic C/hour
2 – 30 mg/m³ with up to 300 g/hour

- for methane

2 – 50 mg organic C/m³ with up to 500 g organic C/hour
10 – 500 g/m³ with up to 5 kg/h
5 – 10 g/m³ with up to 0.1 kg/h

- for formaldehyde (in single cases up to 60 mg/m³)

- for propane butane

- for carbon monoxide

- for nitrogen oxides

This is important to know when controlling the off-gas by analysis.

Under these circumstances, for example, it doesn’t make any sense to work with finishing recipes based on formaldehyde-free resins if the burners of the stenter are poorly adjusted and produce high formaldehyde in the ventilation air.

Odor-Intensive Emissions

In most cases odor is the reason to begin the textile off-gas discussion. Odor occurring in the neighborhood of a textile finishing plant may have different causes. These include:

- the quantity and quality of the smell intensive substances
- the distribution of these substances
- the meteorological situation of the area

Typical sources are:

- Caprolactam
- Polyamide powder coating
- Mineral oil
- Ester oil
- Polyamide 6 thermofixation
- Synthetics, thermofixation preparations
Ammonia, monomers
Special alcohols like iso-octanol or widespread n-butanol
Aromatic hydrocarbons like trimethylbenzene
Solvent printing
Terpene hydrocarbons
Washing

- Coating, printing
- Carrier dyeing, washing
- Melamine resins
- Reactive flame retardant
- Sulfur dyeing, reduction processes
- Singeing
- Decomposition of glycerol, etc.

4.8 Coating/Laminating

The following is only a brief overview of textile coating and laminating processes.

Coated and laminated textiles usually consist of a textile substrate, which is typically a woven, knitted or non-woven textile fabric, which has been combined with a thin, flexible film of natural or synthetic polymeric substances.

A coated fabric usually consists of a textile substrate onto which the polymer is applied directly as viscous liquid. The thickness of the film is controlled by applying it via a blade or similar aperture.

A laminated fabric usually consists of one or more textile substrates combined with a pre-prepared polymer film or membrane by use of adhesives or heat and pressure.

The basic technique for coating/laminating fabrics requires the following:

- The fabric to be coated/laminated is supplied full width on a roll
- The fabric is fed under careful tension control to a coating or laminating heat zone
- After application, the coated fabric is passed through an oven to cure the composite and remove volatile solvents before cooling and rolling up.

In the textile industry, flame lamination of foams is a widely used technique. A pre-prepared thin, thermoplastic foam sheet is exposed to a wide-slot flame burner situated before the laminating rolls. No drying or curing oven is required in this process.

The major environmental impacts associated with coating and laminating are VOCs from solvents, softeners, etc. (See also Section 3.10.3 on environmental impacts of coating agents.)

5 Role of Pesticides

This section will describe the steps in which pesticides may be used in textiles, the types of pesticides, and the impacts their use may have on the environment, worker health and safety, and consumer safety.
5.1 Cotton Production

During its growth cycle, cotton has to be protected against insects, nematodes, diseases, and weeds. Pest management is of crucial interest for cotton farmers. Although the chemicals used may have a certain environmental impact, responsible pest management has some considerable positive ecological effects, as well. Crop losses are minimized and as a consequence resource consumption is minimized:

- water consumption (7000-29000 l/kg cotton fiber)
- consumption of energy (13,5 kWh/kg cotton fiber)
- fertilizers (0-560 g/kg cotton fiber)
- agrarian area

Without pest management, crop losses would be too high to supply the world-wide cotton markets today. World cotton production was estimated at 18.9 million tons in 2000, which is approximately 41% of the total world-wide demand for fibers [Townsend, 2001].

Production of organic cotton (cotton growth without synthetic inorganic and organic fertilizers, pesticides, growth regulators and defoliants) is estimated to be less than 10,000 tons (< 0.1 % of the total world-wide production) [Chaudry, 2000].

5.2 Insect Control

Organochlorines, organophosphates, pyrethrds and carbamates are the major insecticide groups used to control insects [Chaudry, 1996]. The insecticides are applied by back-mounted hand operator sprayers, motorized sprayers, tractor-mounted sprayers, and airplane.

Pesticides that are banned in industrial countries are still being used in developing countries. (In 1998, DDT still represented 75 % of the pesticides used in India) [VITO, 1998]. However, biological based products (such as Bacillus thuringiensis) are being increasingly applied.

Organophosphates and pyrethrds are the only insecticide groups used in almost all countries. Pyrethrds account for approximately 38 % of the market.

Based on Laursen (1997) and Frahne (2000), the following list includes those insecticides most commonly used in the 1990s:

- Aldicarb (carbamate)
- Cypermethrin (pyrethroid)
- Deltamethrin (pyrethroid)
- Diflubenzuron (organochlorine)
- Endosulfan (organochlorine)
- Esfenvalerate (pyrethroid)
- Ethyl parathion (organophosphate)
- Fenpropathrin (pyrethroid)
- Fenvalerate (pyrethroid)
- Monocrotophos (organophosphate)
- Methomyl (carbamate)
- Methyl parathion (organophosphate)
• Thiodicarb (carbamate)
• Qinalphos (organophosphate)
• Endosulfan (organochlorine)

Amitraz, Endrin, Curacron, Chloropyriphis, Dimethoate, and DDT are also applied.

The kind and quantity of insecticides sprayed in cotton growth strongly depends on the country (region) and the season. Heavy pest infestation can lead to the use of 30 sprays per season. The specific consumption of insecticides in different countries is shown in Figure 6-1:

![Bar chart showing insecticide consumption per hectare in different countries]

**Figure 5.1: Quantity of Insecticide Consumption per Hectare in Different Countries [Chaudry, 1996]**

### 5.3 Nematode Control

Nematodes can be controlled by injecting gases or liquids into the soil. The following halogenated substances are applied [Laursen, 1997]:

• Methyl bromide
• Dichloropropane
• Methyl isothiocyanate
• Trichloronitromethane
• Dibromoethane

Organophosphates and carbamates can be applied in granular form to the soil.
5.4 Disease Control

Most cotton diseases are controlled by treating seeds. Fungicidal products like carboxin, panogen and carbendazim are used. 0.2 – 0.25 kg product per ton of seed are applied (one kg seed yields approximately 30 kg cotton) [Laursen, 1997].

5.5 Weed Control

The type of herbicides used vary according to the types of weeds. Most herbicides are based upon toluidine, urea and arsenic chemistry [Laursen, 1997] and include:

- Trifluralin
- Fluometuron
- Diuron
- Pendimethalin
- Metholachlor
- Fluazifob-butyl
- Methyl arsonates
- Cyanazine

5.6 Chemicals to Aid Cotton Harvesting

5.6.1 Defoliants

Chemical defoliation is a prerequisite for machine picking. In some cases, defoliants are used to enhance crop maturity and also to improve uniformity. In the United States, almost all cotton is defoliated in the West but only 20 % is defoliated in the Southeast.

The following defoliants (desiccants) are applied [Laursen, 1997 and DPR, 1999]:

- 2,4-dichlorophenoxyacetic acid (2,4-D)
- Arsenic acid (75 % concentration)
- Cacodylic acid
- Dimethipin
- Endothall
- Paraquat (1-1’-dimethyl-4,4’bipyridinium bis methyl sulfate)
- Sodium chlorate
- Thidiazuron
- Thidiazuron+diuron
- Tribufos

5.6.2 Plant Growth Regulators

Plant growth regulators allow greater harvest efficiency through once-over mechanical harvesting.

In use are [Laursen, 1997]:

Page 122 of 158
• PIX (1,1-dimethyl piperidinium chloride)
• ETHEPHON (2-chloroethyl-phosphonic acid)
• DROPP (Thiadiazuron derivative)
• HARVADE 25 F (dimethipin (2,3-dihydro-5,6-dimethyl-1,4-dithiin-1,1,4,4-tetraoxide)

5.7 Consumption of Pesticides

Chaudry estimates an average insecticide consumption of approximately 2 kg/ha (see Figure 6.1). According to Dollacker, approximately 450 g/ha phosphoric acid esters and/or 60 g/ha pyrethroids (active ingredients) are used per spray [Dollacker, 1996].

According to a personal communication (Clariant, 2001), the specific pesticide consumption has strongly decreased in the last few years and it can now be estimated that 0.5 kg – 1kg/ha pesticides (active ingredients) are applied. The minimum today is 25 g active substance /ha.

Assuming an average cotton yield of 1000 kg/ha and a pesticide consumption of 1 kg/ha, then 1 g pesticide/kg cotton (0.1 %) is applied.

5.8 Transport Conservation Agents

Data on the types and quantity of transport conservation agents applied to cotton are rare.

Jute wrapping materials used for cotton bales may contain 0.01 % of pentachlorophenol (PCP). [Laursen 1997]

Chlorinated phenols, arsenic, metallic salts (arsenic, zinc, copper or mercury), DDE, and DDT may be employed as transport conservation agents [Laursen, 1997]; and pyrethroids and phosphoric acid esters may be used, as well [Enquete, 1994]. According to another source, PCP-laurates are also used [Flemish BAT, 1998].

5.9 Residual Pollutants in Raw Cotton

5.9.1 Investigations of the Bremer Baumwollbörse (Bremer Cotton Stock Exchange)

In the last few years the Bremer Baumwollbörse analyzed raw cotton from different countries. Investigations focused on defoliants, heavy metals, PCP, formaldehyde and pesticides. The results are summarized below [Bremen, 2000].

5.9.1.1 Defoliants

Cotton was tested from Argentina, Chad, Israel, Mali, Mexico, Turkmenistan, US, and Uzbekistan for the following substances, with the corresponding limits of detection:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit Value (for food, in Germany)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5-T</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>Dichlorprop</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>Chemical</td>
<td>Limit (ppm)</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>0.10</td>
</tr>
<tr>
<td>2,4-D</td>
<td>0.10</td>
</tr>
<tr>
<td>MCPA</td>
<td>0.10</td>
</tr>
<tr>
<td>MCPB</td>
<td>0.10</td>
</tr>
<tr>
<td>Fenoprop</td>
<td>0.10</td>
</tr>
<tr>
<td>DEF</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Detectable amounts of DEF were found in Israel (0.008 ppm), Turkmenistan (0.006 ppm) and US (0.010 ppm). Otherwise, these chemicals were not detected.

5.9.1.2 Heavy Metals

In 1992 and 1998, cotton from Argentina, Chad, Cote d’Ivoire, Greece, Israel, Syria, Turkey, Turkmenistan, US, and Uzbekistan was tested for the following heavy metals: arsenic, cadmium, chromium III, chromium VI, cobalt, copper, lead, mercury, and nickel. No residues were found.

5.9.1.3 Pentachlorophenol (PCP)

Cotton from Argentina, Chad, Cote d’Ivoire, Egypt, Greece, Israel, Mali, Paraguay, Peru, Senegal, Turkey, Turkmenistan, US, Uzbekistan, and Zimbabwe was tested for PCP in 1992, 1993, 1994 and 1998 and no residues were found.

5.9.1.4 Formaldehyde

In 1992, 1993, 1994, and 1998, cotton from Argentina, Chad, Egypt, Israel, Mexico, Peru, Sudan, US, and Uzbekistan was tested for formaldehyde. Detectable levels of formaldehyde were found in samples from Argentina (0.0048 ppm), Chad (0.0012 ppm), Sudan (1.0 ppm) and Uzbekistan (0.0004 ppm).
5.9.1.5 Pesticides

Raw cotton is tested for the following pesticides according to Ökotex:

<table>
<thead>
<tr>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5-T (organochlorine compound)</td>
</tr>
<tr>
<td>2,4 D (organochlorine compound)</td>
</tr>
<tr>
<td>Aldrin (organochlorine compound)</td>
</tr>
<tr>
<td>Carbaryl (naphthylmethylcarbamate)</td>
</tr>
<tr>
<td>DDD (organochlorine compound)</td>
</tr>
<tr>
<td>DDE (organochlorine compound)</td>
</tr>
<tr>
<td>Dieldrin (organochlorine compound)</td>
</tr>
<tr>
<td>Alpha-Endosulfan (organochlorine compound)</td>
</tr>
<tr>
<td>Beta-Endosulfan (organochlorine compound)</td>
</tr>
<tr>
<td>Endrin (organochlorine compound)</td>
</tr>
<tr>
<td>Hepatachlor (organochlorine compound)</td>
</tr>
<tr>
<td>Heptachlorepoxide (organochlorine compound)</td>
</tr>
<tr>
<td>Hexachlorbenzol (organochlorine compound)</td>
</tr>
<tr>
<td>Alpha-Hexachlorocyclohexan (organochlorine compound)</td>
</tr>
<tr>
<td>Beta-Hexachlorocyclohexan (organochlorine compound)</td>
</tr>
<tr>
<td>8-Alpha-Hexachlorocyclohexan (organochlorine compound)</td>
</tr>
<tr>
<td>Lindane (organochlorine compound)</td>
</tr>
<tr>
<td>Methoxychlor (organochlorine compound)</td>
</tr>
<tr>
<td>Mirex (organochlorine compound)</td>
</tr>
<tr>
<td>Toxaphen (Camphechlor) (organochlorine compound)</td>
</tr>
<tr>
<td>Trifluralin (fluorinated compound)</td>
</tr>
</tbody>
</table>

Test results are presented below, by test year.

2000:
Trace amounts of DDTs (0.048 ppm) and lindane (0.028) were found in cotton from Mali, and 0.034 ppm DDTs were found in cotton from Argentina. In cotton samples from Benin, Cameroon, Egypt, Israel, Sudan, Syria, Togo, US, Uzbekistan, and Zimbabwe, no residual pesticides were found.

1998:
Trace amounts of DDTs were found in cotton from Turkmenistan (0.0013 ppm), and the US (0.0640 and 0.3500 ppm). No residual pesticides were found in cotton samples from Burkina Faso, Chad, Israel, Mali, Mexico, Sudan, Uzbekistan and Zimbabwe.

1996:
Hexachlorocyclohexane (HCH) (0.005 ppm) and lindane (0.016) were found in cotton from Turkmenistan. Trace lindane amounts were found in cotton from Uzbekistan (0.005 ppm) and Zimbabwe (0.005 ppm). Samples from Cote d'Ivoire, Chad, Mali, Paraguay, Senegal, Turkey, US, and Zimbabwe showed no pesticide residues.
5.9.2  Additional Data and Conclusions Regarding Residues in Raw Cotton

All the above-referenced results for residues of pesticides, defoliants, PCP, heavy metals, etc. are far below standards according to German food law and/or Ökotex 100 limit values. However, the Bremer Baumwollbörse analysis focused on chlorinated pesticide types; only one carbamate compound is on the list and organophosphates and pyrethroids were not considered.

Raw cotton is commonly pretreated before dyeing/printing/finishing is carried out. The aqueous pre-treatment processes (except for enzymatic desizing) are carried out in relatively strong alkaline solutions, mostly at elevated temperatures. A study on lindane and PCP-removal in pre-treatment steps undertaken by Küster [1996] affirms that these pesticides are not stable in alkaline solutions. This study found that in pre-treatment:

- Lindane can be removed up to 100%
- Approximately 7% of PCP residues remain on the fibers; therefore we can estimate the effectiveness in removing chlorinated pesticides to be at least 90% in pre-treatment.

The most important pesticides (phosphoric acid esters, carbamates and pyrethroids) are not stable in alkaline solutions. Residues of these pesticide types on cotton and cotton blend textiles are negligible, from a consumer safety perspective. Wool is normally treated in acid to neutral baths; for woolen fabrics, the situation has to be considered separately.

5.10 Biocides in Sizing Agents

According to sizing agent producers (personal communications with Emsland-Stärke, BASF, Südstärke, Avebe) sizing agents in powder form are delivered without preserving agents (biocides). In tropical regions with a high air humidity, however, biocidal ingredients in sizing agents (added by the size producer or the weaving mill) can be found. Information on the kind and quantity of the biocides is difficult to find. Laursen reported that 1% by weight of preservatives can be added to sizing agents [Laursen, 1997].

Sizing agents delivered in liquid form (polyacrylates, polyesters) contain biocides in amounts of 15 - 20 ppm (active substance) [BASF, personal communication].

We can estimate pesticide content on loomstate fabrics based on

- 1 % biocide content(10 g/kg)
- 15 % size add-on on the warp yarns
- ratio warp yarn/weft yarn: 40/60

This would lead to a pesticide content of 0.06 % (0.6 g/kg) or 600 ppm before other pre-treatment steps occur. In desizing, scouring and bleaching, biocides present due to biocide additives in sizing agents are removed up to nearly 100%.

5.11 Biocides in Other Textile Auxiliaries

Biocides are used in textile auxiliaries that contain natural components sensitive to biocidal degradation. A main source for biocides are thickeners, based on alginates that are mostly used in printing pastes.
The biocide content in the auxiliaries depends on the biocides applied. For example, if chlorinated cresol-derivatives are used, approximately 0.5% (and in some cases up to 1%) active substance is added. If isothiazolinone-based biocides are used, 15-50 ppm active substances are commonly used.

5.12 Conclusion

The studies of pesticide residues in raw cotton, along with the fact that many of the commonly used pesticide types are unstable in alkaline pre-treatment solutions, lead to the conclusion that pesticides applied in cotton production pose a negligible consumer safety risk.

It is important to note that the above-mentioned investigations on pesticide content of raw cotton looked at only a selection (and not always the proper selection) of pesticides. More information on pyrethroid and carbamate pesticide residues would be useful. Analysis of pesticide residues in cotton should be aligned with the pesticides commonly used in cotton production.

Less information is available on transport conservation and preservation additives to sizing agents in tropical regions. As calculated above, residues in loomstate textiles caused by size preservatives are only expected in textiles delivered from tropical regions. They can be roughly estimated at 600 ppm and pre-treatment and subsequent aqueous processes should result in a reduction of nearly 100% in these residues.

6 Natural Leather

6.1 Raw Material

The raw material for making leather is animal hide, which is a by-product of meat production. Immediately after butchering, bacteria begin to decompose the animal hide. As this natural process damages the surface of the hide, it must be prevented. In Central Europe, this decomposition process is slowed by chilling, which, compared to traditional salting, is much more environmentally friendly.

6.2 Beamhouse / Tannery

6.2.1 Lime/Liming

Hides are placed in the liming drum for the first step, in which they are soak in water to clean them of any natural hide dirt and to restore the hides to a natural water content of approximately 65%. After this, lime and sodium sulfide are added to the same drum. This allows the tanner to wash natural oils and proteins (that are not important to leather production) out of the hide and raises the pH of this solution to chemically remove hair from the hide. Aliphatic thioles are used as auxiliaries in the hair stripping process. Soaking and liming are carried out in one process, which typically lasts from 24 to 36 hours. The limed and dehaired hide is now called "pelt."

6.2.2 Fleshing

In this step, excess flesh and fatty tissue from under the pelt are mechanically removed and the pelt is trimmed. During this process, the sections of the root of the tail, the navel, the kneecaps, and other unwanted parts of the hide are removed. The organic
remains that are obtained are a valuable natural raw material for the glue and gelatin industries or for methane gas plants.

6.2.3 Splitting

A band knife is used to split the pelt horizontally into a grain split and a flesh split. The grain or leather split is later processed into upper leather. The flesh split is supplied to the gelatin industry.

6.2.4 Tanning

Tanning is the process by which the hide is preserved and made durable. Until it is tanned, the hide is perishable. This process is made up of the following five steps and takes about 20 hours to complete. These steps are performed one after another in the tanning drum:

- **Deliming**: In this step, the lime added in the liming drum is released. At the tannery, this step uses carbon dioxide, which is considered to be environmentally friendly. Hydrogen peroxide can be used before CO2 insertion in order to reduce hydrogen sulfide formation (preferably under redox control).

- **Bating**: Collagen and other proteins are removed by the use of enzymes. This causes the fibers to become more flexible and the leather to become softer.

- **Pickling**: In this step, acid and salt are added to lower the pH of the hide and prepare it for the tanning agent. When the hide has reached a pH of about 3 throughout its full width, it is ready for the tanning agent.

- **Tanning and Basification**: Hides can be tanned using a large number of different substances; however chromium is most commonly used. When the pH is low, the chromium molecules can easily penetrate the hide and incorporate into the skin fibers. During basification, the pH-value is now slightly elevated, which makes the chromium particles in the hide grow larger and connect with the skin collagen in at least two places. This connection between tanning agent and hide material is called tanning. The chromium tanning dyes the hide into a bluish color; therefore, after tanning it is called "wet blue."

6.2.4.1 Unintended Oxidation of Chromium III to Chromium VI in Leather and Leather Products

Chromium (VI) is not intended or used in the production process and must be regarded as cross contamination by avoidable oxidation of trivalent Chromium to hexavalent chromium, which is a harmful substance. Oxidation of Cr (III) into Cr (VI) normally occurs in presence of strong oxidation agent in acid environment but it can also take place in presence of mild oxidation agents at high pH. In leather processing neutralization is a stage where such conditions are created; therefore, leather and leather products sometimes contain Cr (VI) although only chromium compounds in the form of Cr (III) were used in the tanning process.

Also the hydrogen peroxide left over from the first step of tanning will contribute to unintended oxidation of Cr (III) to Cr (VI).
Unintended oxidation might also be the result of some undesired reactions in leather itself. The influence of wetting back agents like ammonia, sodium bicarbonate, cationic auxiliary or a reducing auxiliary does not directly increase the Cr (VI) content, however ageing processes caused by treatment with ammonia or sodium bicarbonate can contaminate leather after some time. The use of a reducing auxiliary prior to dyeing instead of ammonia or other stronger alkaline wetting back agents is recommended.

Storing chrome tanned leathers in moist and warm situations for extended periods should be avoided; this recommendation should be provided to downstream users, as well.

Fat liquoring has a heavy influence on formation of chromate in leather. The greatest effect is shown by the classical sulfated and sulfited fish oils and products with simple or multiple unsaturated fatty acids (free or esterified). Natural or synthetic fat liquoring agents without the above-mentioned substances do not lead to chromate formation. Chlorinated hydrocarbons of chain length C16-30 (chlorinated paraffins) may also be applied.

6.2.4.2 Tanning with Substances Other than Chromium

Other minerals can be used to produce tanned leathers, although the overall characteristics of the leathers produced will not be comparable with the ones obtained in chromium-tanned leathers.

**Aluminum.** Use of aluminum as a substitute is still debated because of indications that it might have considerable adverse effects on human health and environment. Other tanning agents are vegetable tanning agents, syntans, and aldehydes.

**Vegetable Tanning Agents.** Vegetable tanning agents are poly-phenolic compounds and may be classified as either of the following:

- Hydrolyzable pyrogallol (Myrabolan, Oak, Sumac, Chestnut, etc.)
- Condensed tannins based on catechol (Mimosa, Quebracho)

**Syntans, Resins, and Polyacrylates.** Syntans, resins, and polyacrylates are agents used alternatively or in addition to chrome and vegetable tannins. **Syntans** are sulfonated condensation products of hydroxyl-substituted aromatic compounds (phenol, cresol or naphthalene) with formaldehyde and often with amides. Attention must be paid to the monomer content of syntans. Residual amounts of formaldehyde and phenol are detected in many products.

Sulfonated polyphenols are used not only as tanning agents, but also as dispersing agents, surfactants, wetting agents, auxiliaries for suspensions, and stabilizing agents. These broad applications by many users lead to small but continuous releases from seemingly diffuse sources.

**Resins** are derived from aliphatic compounds such as polyurethanes, dicyandiamide and melamine. Resins contain (low) concentrations of free formaldehyde and inorganic fillers.

Glutaraldehyde is the most commonly used aldehyde, but formaldehyde is still used. Aldehydes have to be carefully evaluated with respect to workplace safety. As a carcinogen, formaldehyde requires special control measures.
Glutaraldehyde has bactericidal effects and is therefore also used as a disinfectant. Glutaraldehyde has limited biodegradability, high toxicity and probably influences biological treatment negatively. Glutaraldehyde is undoubtedly a stronger mutagenic substance than formaldehyde, although less volatile.

### 6.2.5 Tanning Auxiliaries

Natural, mineral, or synthetic fatty substances, polymers, polycondensates, polyaddition products, metallic-acid complexing compounds, silicon derivatives and perfluorinated organic compounds are used to correct the hydrophilic properties of the leather (from earlier addition of surfactants) or to achieve water-proof properties.

Other pelt-impregnating agents intended to improve wearing qualities include oil-repellent agents and agents to reduce the permeability to gas; these are solvent-containing or solvent-free preparations of perfluorinated organic compounds.

Flame retardants are often phosphorus-based, but can also be based on antimony trioxide and/or other metallic oxides, as well as on boron and nitrogen compounds.

Abrasion reduction agents are very similar to the water-repellent agents. Anti-electrostatic agents are mostly anionic or cationic surface-active agents. Polycondensates and polymers are also used.

### 6.2.6 Cutting/Sammying

The wet blues, which are soaking wet, are placed on the sammying machine and two felt rollers press out some of the water under high pressure. Afterwards, the complete hide is cut into two sides, for ease of handling in further processing. Each side is marked to make it easier to trace.

### 6.2.7 Dye-House Sorting

On the moist wet blue, damages in the hide such as scratches, scars, or parasitic damage are easy to identify. During sorting, the hides are separated and sorted into different classes of quality (based on these hide damages).

### 6.2.8 Shaving

Soft nappa for children’s shoes requires a different thickness than the thick leather for alpine hiking boots. Shaving adjusts the hide for the preferred leather thickness; the layer that is not needed is mechanically shaved from the wet blue’s back side. The shavings are further processed into bonded leather.

### 6.2.9 Retannage

Only during retannage does the leather get its special and customer-specific character. Retannage is carried out according to a special formula in a dyeing drum. It consists of several different production steps:

**Neutralization:** In this step, the wet blue’s pH is adjusted to a particular value for the adding of dyeing, tanning, and greasing chemicals.
**Retannage:** To give the leather the character the customer wants along with other certain technical characteristics, additional tanning agents are added to the wet blue during retannage. These influence softness, feel, tearing values, elasticity, and other features of the leather. The leather industry widely uses anionic dyestuffs, which are divided into the following families: acid dyes, direct dyes, mordant dyes, pre-metallized dyes and solubilized sulfur dyes. Azo- and anthraquinone dyes are applied as either dispersion or solutions.

**Dyeing:** Dyestuffs are added to obtain the desired color on the surface of the leather. The dyestuff must penetrate the complete hide to ensure that the cutting edges also have the right color during further processing.

Wetting agents, leveling agents, bleaching agents, shade intensifiers, after treatments and fixing agents can be applied during the dyeing operation. All these products have different effects on the dyestuff and on the leather. Surfactants may be added to dyestuff. Chemically these auxiliary substances can be classified as:

- dispersing agents: e.g., sulfated acid esters and amide, fatty acid condensates,
- alkyl aryl sulfonates or ethoxylation products
- wetting agents (auxiliaries) can be divided into categories of anionics (e.g. alkyl-sulfates, alkane sulfonates, alkyl aryl sulfonates, etc.), non-ionics (e.g. phosphoric acid esters, etc.), and cationics (e.g. alkyl aryl amine polyglycol ethers, amine derivatives, betaines, polyamine condensates, etc.).
- Solvents may be used to promote the dissolution of dyestuffs in water. Solvents which can be used in this way are: alcohols, esters, polyols, thio-esters and mixtures thereof.
- Sequestering agents to be added to the water can be divided into the following groups: nitrilotriacetate (NTA), ethylenediamine-tetra-acetate (EDTA), polyphosphate (Calgon), carboxylic acids.
- pH regulators are: organic acids, acids, buffering salts, or mixtures of these chemicals.
- Anti-foaming agents are low-foaming standardization of wetting agents, mixtures of alcohols of higher valence and neutral phosphoric acid esters.
- After-treatment and fixing agents are surface-active substances, particularly cationic polyquaternary ammonium compounds, cationic formaldehyde poly-condensates and other nitrogen derivatives as well as inorganic complexing agents, metallic salts and preparations thereof.

**Greasing:** The skin grease that was removed during liming is replaced by one chosen by the tanner. The grease chosen determines how the end product looks in terms of color, shade, luster, and feel. Only hydrophobic greases are used at the tannery. These greases make the leather water repellant and reduce the leather’s ability to absorb water. During this process, the skin fibers are wrapped by the fat liquor in a way that retains the leather’s natural breathability. The result of this hydrophobing step is that water cannot get into the shoe through the leather, but moisture or foot sweat can escape to the outside.
Sammying
Now, the sides are again piled on pallets and placed into the sammying machine. Absorbed water is partially mechanically removed from the leather.

6.3 Drying

6.3.1 Setting-out
On the setting-out machine, the sides are flattened and stretched out on the grain side by a setting-out cylinder with blunt blades. This step makes the leather surface smoother and more even.

6.3.2 Vacuum Dryer
During vacuum drying, the sides are placed with the grain side down on a plate with a temperature of 40°C. The leather is further dehumidified under the vacuum; the leather becomes slightly drier and the fibers are fixed in this step.

6.3.3 Hang Dry
The last drying step is carried out by hang drying, so any remaining moisture in the leathers evaporates. Chemical reactions in the hide now have enough time to take place, and the moisture within the hide has time to spread evenly.

By removing moisture, the chemicals added earlier connect better with the skin fibers. This raises the fastness and later gives the leather a more comfortable feel. The natural structure of the hide needs time to adjust to the different processes that have been carried out.

6.3.4 Damping
After the leathers have been dried, they are dampened once again, since the water is needed as "fiber lubrication" for the next production step. Because the leathers have been given water-repellant characteristics, dampening the leather is not easy. The leathers need to sweat under a cling wrap; this allows steam to diffuse into the gaps within the leather.

6.4 Pre-Finishing

6.4.1 Staking
After drying, the skin fibers have bonded to each other and the leathers have hardened a bit. During staking, the leathers are softened by using heavily vibrating metal bolts. In this way, the fibers are loosened up towards each other and become more flexible. The leathers become smoother and display a better surface.

All the different parts of the hide are given very precise treatment during staking. Because of their different fiber structure, the belly and shoulder regions need less staking compared to the backbone line. With the help of state-of-the-art machinery, an effort is made to make every side evenly hard or soft in each place. The softness of the leather is defined during staking.
6.4.2 Dynasec

The leathers are treated with heat and pressure on the Dynasec machine to give them a smoother surface. During this step, the leather surface is ironed at a temperature of about 90° C and carefully stretched, which gives the leather a smoother feel and appearance. The smoother the whole piece of leather, the easier it can be processed in the finishing step.

6.4.3 Toggling Dryer

Soft and stretchy leathers are stretched and pulled on a metal frame to make them larger and smoother; then they are dried in the stretched position.

6.4.4 Trimming

Fringes and other unwanted parts of the hide are removed in the trimming step. In its present stage, the leather is called "crust leather." Crust leather is the name for the re-tanned and dried leather. Technically, "crust" is a product ready to use. All further working steps of the finishing stage only change the surface and visual characteristics of the leather.

6.5 Finishing

6.5.1 Similarities between Textile Finishing and Leather Finishing

Many of the processes and chemicals used in both these industries are more or less the same from a general chemical perspective. There is not much difference between a melamine resin and a fluorochemical used in the textile industry versus the leather industry. There is not much difference between using a polyurethane in DMF to coat a polyester fabric for a sportswear jacket and using it to make artificial footwear leather. Therefore, not much emphasis is placed on possible residual chemicals in the natural and artificial leather sections; the reader instead should seek the chemical or process terms of interest and refer to the related chapters in the textile section.

6.5.2 Finishing Chemicals

There is no fixed production flow in finishing. The leather surface is treated with different products or mechanical procedures according to the leather type and the customer’s requirements. The basic components of leather finishes are binders, coloring agents (pigments and dyes), auxiliaries and lacquers.

Binders. Resin emulsions are the most commonly used binders in tanneries. This includes acrylics, butadienes, polyurethanes, and vinyl acetates. Resins are water-based emulsions.

Coloring Agents. Coloring agents include dyes and pigments. Dyes may be used in finishing formulations for particular application. Dyes used in finishing are supplied in liquid form, and are generally pre-metallized dyes. Various organic solvents and/or water surface-active substances may be added to disperse the pigments. Dye preparations can furthermore contain waxes, plant mucilages, cellulose products or polymers as protective colloids, natural or synthetic oils as softening agents. For special properties, other agents may be added such as: bottoming, grain tightening, and
penetrating agents; anti-sticking agents; thickening and stabilizing agents; plasticizers (phthalates); and dulling and fixing agents.

**Cross-Linking Agents.** Cross-linking agents are used to join the various polymers in the finish formulation, and reduce the water solubility of the compounds. The following cross-linking agents may be used:

- Poly-isocyanates are applied for polyurethane finishes
- Carbodiimides for polyurethane base- and top-coats
- Aziridines are highly toxic and for this reason they have been replaced by poly-aziridines, which are less toxic and can be used for base-coats and top-coats
- Epoxies can only be used for top-coats
- Formaldehyde for casein and protein finishes
- Ethyleneimine-based cross-linking agents for top-finishes. Ethyleneimine is toxic and carcinogenic
- Metal oxides for butadiene finishes for splits

**Lacquers.** Lacquers and lacquer emulsions form the top or fix coat of a finish and are made by dissolving nitrocellulose in solvents (e.g., ethyl acetate, methoxypropanol, methyl isobutylketone). These solutions can be emulsified with water and surfactant to give lacquer emulsions. Polyurethane lacquers are also used.

**Carriers.** Carriers are used to produce suspensions/dispersions of binders used in finish formulations. Water and organic solvents are considered carriers. The organic solvents used can be divided into two categories: (1) solvents which actually dissolve the binders (e.g., ethyl acetate) and (2) diluents which enable the ready-made solution to be diluted to spraying viscosity or the desired concentration (e.g., methoxypropanol, isopropyl alcohol, etc.).

**Biocides.** Biocides can be applied in various tannery processes to protect the substrate against either bacterial or fungal attack. Generally, biocides are included in most liquid chemical formulations such as dyes, fat liquors and casein finishes. Furthermore, raw hides and skins may contain biocides applied to the animal to protect it from disease during its life. Clearly, all biocides are potentially toxic since they are designed to kill certain life forms.

Biocides are a subgroup of pesticides, and are divided into two main categories: bactericides and fungicides. Bactericides are used mainly at the beginning of the leather making process, when hides and skins are more vulnerable to bacterial degradation -- e.g., curing and soaking. Fungicides are used from the pickling stage to the drying stage because the pH conditions in these processes are ideal for mold growth.

### 6.5.3 Finishing Technologies

#### 6.5.3.1 Buffing

For ease of further processing by downstream users, the leather is sandpapered on the backside. Unwanted longer skin fibers are removed, which, when glued, could adversely affect the quality of the finished product. Buffing on the front side produces "nubuck." Due to its roughened surface, nubuck is
especially robust and hardwearing. Scratches on nubuck are less eye-catching than on plain leather, which is why it is well suited for outdoor use.

6.5.3.2 Dry-splitting

In order to level out the variations in thickness which have occurred during the production process, the leathers are split dry in the crust. This step allows an accuracy of 0.1 mm in leather thickness.

6.5.3.3 Milling

In the milling drum, the leathers are tumbled dry (meaning without water), and thereby made soft. Milling results in an especially soft leather with a very comfortable, velvety feel and a very natural surface structure. Probably the best-known milled leather type is “nappa.”

6.5.3.4 Spray Machine

Different products such as grounding agents, binding agents, dyestuffs, lacquers, or touch modifiers are sprayed on the leather surface. Here, for example, small corrections in color and adjustments to the desired end tone are carried out.

6.5.3.5 Roll Coater

Compared to the spraying machine, the roll coater is able to apply larger amounts of finishing products on the leather surface. With a heated cylinder, the roll coater can apply waxes, greases, and oils.

6.5.3.6 Embossing

The natural leather surface is smooth and has little pores. Sometimes a special design or a grain pattern on the leather’s surface is desired. Embossing only produces a different visual surface structure for the eye -- technically, the skin remains unchanged.

6.5.3.7 Ironing

Ironing increases the smoothness and gloss of leathers; it also influences the feel to the hand. Elegant leathers are usually ironed; sporty leathers are normally not.

6.5.3.8 Measuring

Leather is sold by the square meter. Each single leather side is electronically measured at the end of the production process. The measurement is stamped on the back side of each side.

7 Artificial Leather

The process for producing artificial leather is similar to natural leather by chemically processing porous, synthetic sheet material of known type comprising a porous polyurethane matrix containing
polyester or polyethylene fibers and a pressed polyurethane resin cover film patterned to imitate real leather.

7.1 Raw Materials

Polyurethane polymers are formed by reacting at least two isocyanate functional groups with at least two alcohol groups in the presence of a catalyst (tertiary amines, such as dimethylcyclohexylamine, and organometallic salts, such as dibutyltin dilaurate). The first essential component of a polyurethane polymer is the isocyanate. Molecules that contain two isocyanate groups are called diisocyanates. These are also referred to as monomers or monomer units, since they themselves are used to produce polymeric isocyanates that contain three or more isocyanate functional groups. Isocyanates can be classed as aromatic, such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI); or aliphatic, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI).

The second essential component of a polyurethane polymer is the polyol. Molecules that contain two hydroxyl groups are called diols, those with three hydroxyl groups are called triols, etc. In practice, polyols are distinguished from short-chain or low-molecular-weight glycol chain extenders and crosslinkers such as ethylene glycol (EG), 1,4-butanediol (BDO), diethylene glycol (DEG), glycerine, and trimethylol propane (TMP). Polyols are polymers in their own right. They are formed by free radical addition of propylene oxide (PO), ethylene oxide (EO) onto a hydroxyl or amine-containing initiator, or by polyesterification of a di-acid (such as adipic acid) with glycols such as ethylene glycol or dipropylene glycol (DPG). Polyols extended with PO or EO are polyether polyols. Polyols formed by polyesterification are polyester polyols.

7.2 Manufacturing of Polyurethane Resin

Reinforced polyurethane resin can be made by a resin injection process requiring high temperature and high pressure. Polyurethane resins are two-component systems consisting of a polyol blend and a polysisocyanate, typically based on a modified polymeric MDI (diphenylmethane diisocyanate). Therefore, a two-component metering unit is required to dispense mixed resin into a closed injection box or injection die. The metering unit includes metering pumps or cylinders, resin tanks, a mixhead and transfer hoses, mixing elements and a solvent flush system. A dual-action, air-driven cylinder pump is used to meter both the isocyanate and polyol from their day tanks to the mixhead, where the resin is combined. Thorough mixing of the chemical components occurs downstream of the mixhead in static mixing tubes. The unreacted polyurethane resin then flows into an injection box, where the composite reinforcement is wet-out and then subsequently pulled into the pultrusion die. A variety of additives and/or fillers may be included (typically in the polyol component), provided the component mix ratios are adjusted to maintain proper stoichiometry.

The mixhead, mix tubes and injection box must be flushed at the end of a pultrusion run in order to prevent resin from curing in place. The flush solvent is typically introduced into the mixhead through a three-way ball valve. Resin is initially purged out of the mixhead and mix tubes with air, followed by thorough flushing with solvent. Typically, a pressure pot works well as a solvent container.

7.3 Processing Synthetic Sheet Material

Artificial leather is generally produced by coating resin on the surface of a sheet for artificial leather consisting of two components, i.e., non-woven fabric made of ultra-fine fibers and polyurethane resin according to its uses or directly dyeing the surface. PVC is used instead of PU.
Polyester, polyamide and polyethylene fibers are embedded with the intention to get sheet material having a thickness of about 0.3 to 2 mm. Typically, staple non-woven fabric layer forms or woven or knitted fabric layer forms are used before polyurethane wet impregnating treatment is carried out on the composite sheet.

The impregnating solution is made by adding a detergent, pigments, functional particles and the like to such a DMF, ethyl acetate or toluene solution of polyurethane elastomer and diluting the resulting solution. The composite sheet is dipped in the impregnating solution, coagulated in an aqueous solution, washed in hot water at 50 to 80°C to completely remove temporary filled water-soluble polymer, and then dried. The content of the polyurethane after drying is preferably 20 to 50% by weight of the composite sheet.

Continuously, the fibers are converted into a bundle of fine fibers constituting the non-woven fabric layer and the woven or knitted fabric layer with a solvent or aqueous solution of sodium hydroxide, which is capable of dissolving the “sea-island” component. The sea island component exists in both fibers of the non-woven fabric layer and fibers of the woven or knitted fabric layer. If the types of the sea island components are different, fiber fining treatment has to be performed on each of them, which makes the treatment complicated.

If the sea island component is a copolymerized polyester, it is decomposed by a continuous or discontinuous arrangement method with a 5 to 15% aqueous solution of sodium hydroxide. If the sea island component is polyethylene or polystyrene, it is removed by treating with toluene, perchloroethylene or trichloroethylene. At last, the copolymerized polyester of the sea island component should be completely decomposed and removed by treating with a 10% aqueous solution of sodium hydroxide at 100°C for 5 to 10 minutes.

At this time, the composite sheet for artificial leather is finally treated according to its intended use. Generally, the composite sheet is made into an artificial leather of suede type by a dyeing treatment, or is made into an artificial leather of mirror-like type by forming a polyurethane coating layer on the surface. Where the used fiber consists of nylon-6, it is typically dyed with a metal complex dye or milling type acid dye. Polyester is dyed with a disperse dye in a high pressure, rapid dyeing machine. Lastly, a softening and functional agent treatment is carried out on the dyed product, resulting in a composite, suede-like artificial leather with excellent surface effect, superior form-stability and softness. The next steps are similar to the tanning of natural leather.

7.4 Treatments in Rotary Tanning-Type Drums

The sheet material is further treated with an aqueous solution containing at least one metal salt (selected from the group consisting of the sulfates of calcium, chromium, iron, aluminum, magnesium and titanium and the chlorides of chromium, iron, aluminum, magnesium and titanium) until it is saturated.

Then the sheet is treated with an aldehyde (selected from the group consisting of glutaric aldehyde, pyruvic aldehyde, crotonic aldehyde and 2-ethyl-butyraldehyde).

Subsequently, the pH of the solution is increased to a maximum of 7.5 by adding a strong base until the corresponding hydroxide is precipitated directly inside the pores of the sheet material.

This synthetic sheet material is greased in an emulsion of 20% to 40% by weight of a fatty material (selected from the group consisting of mineral oil, sulfated sperm oil and fatty acid esters having from 17 to 22 carbon atoms). Then the sheet can be dyed with a known metal-complex coloring agent for polyurethane, washed, and treated in an aqueous solution of 24% to 60% by weight of a flame retardant substance (selected from the group consisting of ammonium phosphates, pentaerythritol, guanidine or a mixture thereof) which will permeate the entire section of the sheet.
Subsequently, the material is softened by adding a softening solution consisting of water and 8% to 20% by weight of a substance with a linear hydrocarbon chain of about 12 to 18 carbon atoms coupled with a radical selected from the group consisting of \(-\text{SO}_3\ X\), wherein X is an alkali metal, and \(-\text{(OCH}_2\text{CH}_2)\_y\ \text{OH}\), wherein y is an integer between 1 and 18.

The synthetic sheet material is finally dried in hot air and rolled up.

8 Adhesives

An adhesive is a substance that sticks to the surface of an object such that two surfaces are bonded, as in the bonding of soles to the bodies of shoes (mainly based on polyurethane). Adhesives bind together all sorts of intermediates and parts from the textile and leather industries to build up more complex products for the market. Adhesives do not significantly contribute to the overall weight of a complex article, but they do contribute to air emission and workplace issues in a factory and to further residual chemical substances on these articles.

Adhesives cure when the small resin molecules (mers = basic building block of the polymer) join together to form extremely large molecules known as polymers. Adhesives may be classified as natural or synthetic adhesives and by their functionality, such as:

- Drying adhesives
- Contact adhesives
- Hot adhesives (thermoplastic adhesives)
- Reactive adhesives
- UV and light-curing adhesives
- Pressure-sensitive adhesives

Alternatively, they may be classified by their chemistry, such as:

- Styrene Butadiene Rubber Based Adhesives
- Polyolefin Adhesives
- Starch & Dextrin Based Adhesives
- Cyanoacrylic Adhesives
- Acrylic Emulsion Adhesives
- Polyvinyl Acetal Adhesives
- Neoprene Adhesives
- Polyurethane Adhesives
- Protein Based Adhesives
- Polyvinyl Chloride Based Adhesives
- Silicate Adhesives
- Polyamide Adhesives
- Nitrile Adhesives
- Polyester Adhesives
- Bitumen Based Adhesives
- Other Elastomeric Adhesives
- Phenolic Adhesives
- Epoxy Adhesives
- Acrylic Adhesives
- Acrylic PSA Adhesives
- Urea Formaldehyde Adhesives
- Polyvinyl Acetate Adhesives
- Thermoplastic Rubber Based Adhesives
- Natural Rubber Based Adhesives
- Furan Adhesive
- Reclaimed Rubber Based Adhesives
- Silicone Rubber Adhesives
- Polyvinyl Alcohol Adhesives
- Butyl Rubber & PIB Adhesives
- Ethylene Acrylic Acid (EAA) Adhesives
- Miscellaneous Adhesive
- Other Synthetic Resin Adhesives and Sealants
Other Natural and Inorganic Products

Many of the chemical substances used to make adhesives may be a concern because of their potential environmental, workplace safety and consumer safety impacts. The most important of these are the monomers and solvents. In comparison to the larger article on which the adhesive is applied, the monomers associated with adhesives have a negligible impact. However, the solvents may play a significant role as residuals. Many adhesive systems use solvents to keep the adhesive components in a liquid state and use solvent volatility to strengthen the cure process. The following solvents are listed according to their frequency of use in adhesive systems:

- Toluene (including benzene as an impurity)
- Acetone
- Ethyl acetate
- Benzene
- Butanone
- Methyl acetate
- Dichloromethane
- Cyclohexane
- Ethanol
- Methanol
- 4-Methylpentan-2-on
- 1,1,1-Trichlorethane
- Tetrahydrofuran
- Xylene
- N,N-Dimethylformamide (DMF)
- Heptane
- Butyl acetate
- Isopropanol

For shoe production, the main adhesive type is polyurethane, so release of methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) must be considered. From these substances, further components such as aliphatic amines, stabilizers, catalysts, etc. may be released or transferred to the final product.
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