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EMISSION SCENARIO DOCUMENT ON TEXTILE FINISHING INDUSTRY

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EMISSION SCENARIO DOCUMENT ON TEXTILE FINISHING INDUSTRY

Environment Directorate

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ABOUT THE OECD

The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Pacific, as well as the European Commission, meet to co-ordinate and harmonize policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised Committees and subsidiary groups composed of Member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's Workshops and other meetings. Committees and subsidiary groups are served by the OECD Secretariat, located in Paris, France, which is organised into Directorates and Divisions.

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The Environmental Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organization Programme for the Sound Management of Chemicals (IOMC) was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and the OECD (the Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. UNITAR joined the IOMC in 1997 to become the seventh Participating Organization. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used in textile finishing industry to assist in the estimation of releases of chemicals to the environment.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other that the leads (Germany and France). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The submitted information will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

Coverage

This ESD covers the Industry Category 13 – textile processing industry. It describes the processes of the life cycle stages "industrial and professional use" for all types of chemicals, including biocides, used in textile processing and the emission estimations to local surface water and air. The emission estimation for the life stages "production" and "formulation" are described in the Technical Guidance Document of Risk Assessment Part II Appendix I, in the A&B-Tables for IC-13 [EU, 2003]. The emission estimation of textile articles during the life cycle stage "service life" is included.

The industry categories, use categories and biocidal product types relevant to this document are as follows.

How this document was developed

This document is based on the ESD for Industry Category (IC-13) "Textile Finishing Industry" published in the "Technical Guidance Document (TGD) on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment for existing substances", Part IV Chapter 7 [EU, 1996]. In the years 2000/01 Umweltbundesamt (UBA) of Germany and the Institut National de l'Environnement Industriel et des Risques (INERIS) of France jointly amended this document and incorporated biocides in the context of the European EUBEES project entitled "Gathering, review and development of environmental emission scenarios for biocides". This amended document was published in the updated EU Technical Guidance Document on Risk Assessment with the provision that it may be revised after the on-going OECD consultation [EU, 2003 Part IV].

Germany (Umweltbundesamt) as the lead country submitted this draft to OECD for the review process that was initiated in February 2002. Comments were received from the following organizations, institutions and persons: Canadian industry; UK (Environment Agency); UK (Health and Safety Executives); German industry (TEWEGA and Gesamtverband der deutschen Textilveredelungsindustrie (TVI)); US EPA; US industry, Brent Smith (USA) and Henry Boyter, Jr. (Institute of Textile Technology Charlottesville, USA); Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers (ETAD) [OECD 2002].

In July 2002 Umweltbundesamt assigned Thomas Schäfer, EnviroTex GmbH, Augsburg/Germany (http://www.envirotex.de), to incorporate the OECD comments and to revise the draft document. Schäfer was the co-author of the BREF-documents [BREF, 2002; UBA-BREF 2003]. The revision focused on

- Incorporation of the comments to the February 2002 version (Compilation of Comments on the Draft Emission Scenario Documents. Task Force on Environmental Exposure Assessment. 9th Meeting, Oslo, 20-21 June 2002 [OECD 2002]
- harmonization of the BREF-documents for textile finishing industry [UBA-BREF, 2003] with the OECD ESD on textile finishing
- correction and completion of the description of processes in textile finishing
- improvement of the homogeneity of the document (esp. concerning biocides)
- introduction of all auxiliaries used in textile finishing as well as substances applied in up-stream processes in the emission calculation
- consideration of padding and exhaust processes as well as releases due to residual liquors in the emission calculations
- additional information on a method calculating air emissions
- additional information concerning the substances used in textile finishing
- implementation of the relevant items concerning surfactants from the UK Draft Emission Scenario Document on Industrial Surfactants [BRE, 2002]
- consideration of information given on a workshop on 29 October 2002 in cooperation with German associations (association of textile finishing industry (TVI) and association of textile auxiliary suppliers (TEWEGA)).

In February 2003, Health Canada submitted to OECD a document entitled "Determination of aqueous releases of chemicals from wet processing textile mills" that describes release scenarios for the Canadian textile wet processing industry based on site-specific data gathered from eight mills [Canada, 2003].

TABLE OF CONTENTS

| | ABOUT THE OECD | 4 |
|---|---|------|
| | Explanatory notes | 6 |
| | Purpose and background | |
| | How to use this document | |
| | Coverage | |
| | How this document was developed | 6 |
| 1 | INTRODUCTION | . 11 |
| 2 | THE EUROPEAN TEXTILE INDUSTRY | . 12 |
| 3 | NATURAL AND MAN-MADE FIBRES | . 14 |
| 4 | MAIN PROCESSES IN TEXTILE INDUSTRY | . 15 |
| | 4.1 Yarn and fabric formation | . 16 |
| | 4.1.1 Raw wool scouring | . 16 |
| | 4.1.2 Production of man-made fibres | . 16 |
| | 4.1.3 Yarn formation | . 17 |
| | 4.1.4 Fabric formation | . 17 |
| | 4.2 Finishing | . 20 |
| | 4.2.1 Pre-treatment | . 20 |
| | 4.2.1.1 Mechanical processes in pre-treatment | . 21 |
| | 4.2.1.2 Thermal processes in pre-treatment | . 21 |
| | 4.2.1.2.1 Heat setting | 21 |
| | 4.2.1.2.2 Singeing | 21 |
| | 4.2.1.3 Wet processes in pre-treatment | |
| | 4.2.1.3.1 Desizing | 22 |
| | 4.2.1.3.2 Scouring (kier boiling) | 22 |
| | 4.2.1.3.3 Bleaching | 22 |
| | 4.2.1.3.4 Mercerising | 23 |
| | 4.2.1.3.5 Causticizing (alkali treatment) | 23 |
| | 4.2.1.3.6 Carbonizing | 23 |
| | 4.2.1.3.7 Crabbing | 24 |
| | 4.2.1.3.8 Washing/Scouring (Synthetic fibres): | 24 |
| | 4.2.2 Dyeing | |
| | 4.2.2.1 Optical brightening | |
| | 4.2.3 Printing | |
| | 4.2.4 Finishing | |
| | 4.2.5 Coating and laminating | . 26 |
| 5 | WATER CONSUMPTION | . 27 |
| 6 | WASTE WATER TREATMENT | . 29 |
| 7 | TEXTILE AUXILIARIES. BASIC CHEMICALS. DYESTUFFS | . 29 |

| 7.1 Textile auxiliaries and basic chemicals | |
|---|----|
| 7.1.1 Surfactants | |
| 7.1.2 Biocides | |
| 7.2 Dyestuffs and optical brighteners | |
| 7.3 Consumption of textile auxiliaries, basic chemicals and dyestuffs | |
| 7.4 Chemical composition of waste water ingredients | 3/ |
| 8 RELEASE ESTIMATION | 38 |
| 8.1 Distribution of releases | 38 |
| 8.2 Releases during finishing | 38 |
| 8.2.1 Releases to waste water | 38 |
| 8.2.1.1 Pre-treatment | 38 |
| 8.2.1.1.1 Biocides in pre-treatment | 39 |
| 8.2.1.2 Dyeing and finishing | 39 |
| 8.2.2 Releases to air | 40 |
| 8.3 Releases during other life-cycle stages | 41 |
| 9 BRANCH SPECIFIC PARAMETERS | 42 |
| 9.1 Daily production volume (Q _{textile}) of a generic point source | 42 |
| 9.2 Number of working days | |
| 9.3 Application amount (Q _{product}) | |
| 9.3.1 Auxiliaries applied in upstream processes | |
| 9.3.2 Basic chemicals used in finishing | |
| 9.3.3 Textile auxiliaries | |
| 9.3.4 Dyestuffs | |
| 9.3.5 Printing. | |
| 9.3.6 Coating | |
| 9.3.7 Summary | |
| 9.4 Rate of release to waste water and degree of fixation | |
| 9.4.1 Auxiliaries applied in upstream processes | |
| 9.4.2 Basic chemicals | |
| 9.4.3 Auxiliaries in pre-treatment | |
| 9.4.4 Exhaust processes | |
| 9.4.4.1 Textile auxiliaries | 45 |
| 9.4.5 Padding techniques, printing and coating | 45 |
| 9.4.5.1 Padding of functional finishing agents (softening agents, repellents etc.). | |
| 9.4.5.2 Padding of dyestuffs (continuous and semi-continuous dyeing) | |
| 9.4.5.3 Printing | 46 |
| 9.4.5.4 Coating | 46 |
| 9.4.5.5 Dyestuffs | 46 |
| 9.4.6 Summary | 47 |
| 10 EMISSION CALCULATION | 49 |
| 10.1 Calculation of emissions to water | 49 |
| 10.1.1 Pre-treatment | 49 |
| 10.1.1.1 Example of calculation | 50 |
| 10.1.2 Exhaust processes | 50 |
| 10.1.2.1 Example of calculation | 51 |
| 10.1.3 Padding processes, printing, coating | 51 |
| 10.1.3.1 Example of calculation | 52 |
| 10.2 Calculation of emissions to air | 52 |

ENV/JM/MONO(2004)12

| | 10.2.1.1 | Example of calculation | 55 |
|-----|----------|--|----|
| 10. | | nissions from articles during their service life | |
| | 10.3.1 | Example of calculation | 55 |
| 11 | REFERE | ENCES | 57 |
| 12 | GLOSSA | ARY | 62 |
| ANN | EX I | | 64 |
| ANN | EX II | | 70 |
| ANN | EX III | | 74 |

1 INTRODUCTION

- 1. The purpose of this emission scenarion document (ESD) is to provide a realistic worst case emission scenario for the basic chemicals, textile auxiliaries and dyes used along the textile chain and released into the environment in textile processing and the "service life" life-cycle stage. It is not purpose of this document to describe further details of the textile industry. Well-founded information on the European input/output situation and on Best Available Techniques in the Textile Industry can be actually obtained from two sources [UBA BREF, 2002 and EU BREF, 2002; http://eippcb.jrc.es]. The abovementioned documents are cited partially literally in this document, in order to achieve consistency between these two important international activities on industrial processes and environmental protection. The document reflects the current situation in the textile industry. A periodical revision of the document is foreseen.
- 2. This emission scenario document is further based on two precursor ESDs prepared and published in the context of EU risk assessment for new and existing chemicals [EU, 2003] as well as biocides [Tissier, 2001; http://ecb.jrc.it].

2 THE EUROPEAN TEXTILE INDUSTRY

- 3. Textile finishing is a very diversified sector due to the processed raw materials, manufacturing techniques and finalised products. Trends in fashion cause a continuous change in colouring and functional finishing.
- 4. The textile industry is one of the longest and most complicated industrial chains in manufacturing industry. It is a fragmented and heterogeneous sector dominated by small and medium enterprises (SMEs), with a demand mainly driven by three main end-uses: clothing, home furnishing and industrial use. A recent research report provides an indepth survey on the different processing steps and compiles use information on function, processes and application of about 2500 chemicals substances in products used in textile finishing [Lacasse and Baumann, 2003].
- 5. Italy is by far the leading European producer, followed by Germany, the UK, France and Spain (in that order). These five countries together account for over 80 % of Community textile and clothing industry (see Table 1).
- 6. In 2000 the European textile and clothing industry represented 3.4% of the EU manufacturing industry's turnover, 3.8% of the added value and 6.9% of the industrial employment.
- 7. In 2000 the EU textile and clothing industry achieved a turnover of 198 billion euros, involving 114000 companies, who employed 2.2 million people.
- 8. The textile industry is composed of a wide number of sub-sectors, covering the entire production cycle from the production of raw material (man-made fibres) to semi-processed (yarn, woven, and knitted fabrics with their finishing processes) and final products (carpets, home textiles, clothing and industrial textiles).

Table 1: Country breakdown of the EU-15 textile and clothing industry (adopted from [EU-BREF, 2002]

| | Textile % in 2000 | Clothing % in 2000 | Textile and Clothing % in 2000 |
|----------------|----------------------|-----------------------|--------------------------------|
| Germany | 14.4 | 13.1 | 13.8 |
| France | 13.1 | 13.0 | 12.9 |
| Italy | 29.7 | 30.8 | 30.1 |
| Netherlands | 2.0 | 0.8 | 1.5 |
| Belgium | 5.6 | 2.2 | 4.2 |
| United Kingdom | 12.5 | 14.3 | 13.4 |
| Ireland | 0.7 | 0.5 | 0.6 |
| Denmark | 1.0 | 1.1 | 1.1 |
| Spain | 8.4 | 11.4 | 9.6 |
| Greece | 2.1 | 2.5 | 2.3 |
| Portugal | 6.1 | 7.9 | 6.9 |
| Austria | 2.8 | 1.2 | 2.1 |
| Finland | 0.8 | 1.0 | 0.9 |
| Sweden | 0.8 | 0.2 | 0.6 |
| Luxembourg | 0 | 0 | 0 |
| EU-15 | 100 | 100 | 100 |

9. Regarding the share of man-made fibres and natural fibres in 2001 on a worldwide level the following figures are available [Chemiefaser, 2002]:

- cotton: 38 % - wool: 3 %

- man-made fibres: 59 %

10. Worldwide fibre production share for man-made fibres by fibre type in 2000 was [fibersource, 2002]:

polyester: 56 %
polyolefine: 18 %
polyamide: 12 %
acrylic: 8 %
cellulose 6 %

11. The fibres end up in processed goods in Europe, the main categories in percentage being [EU-BREF, 2002]:

| - | clothing textiles | 45 |
|---|--------------------|----|
| _ | household textiles | 20 |
| - | interior textiles | 10 |
| - | technical textiles | 18 |
| _ | others | 7 |
| | TD + 1 100.0/ | |

Total 100 %

3 NATURAL AND MAN-MADE FIBRES

12. Textiles are manufactured from natural and man-made fibres (see Figures 1 and 2). Natural fibres are available from animals and plants. The most important fibre types are cotton and sheep's wool.

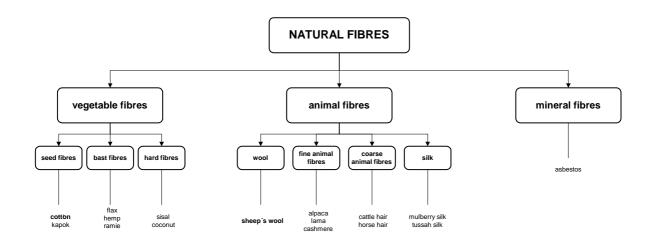


Figure 1: Natural fibres

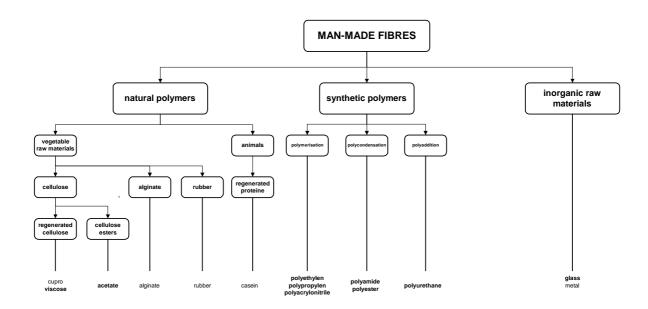


Figure 2: Man-made fibres

13. Polyester, polyamide, polyacrylonitrile, polypropylene, regenerated cellulose (viscose), and acetate are the most important man-made fibre types in textile industry. Blends of different types of fibres (e.g. cotton-polyester) are frequently used.

4 MAIN PROCESSES IN TEXTILE INDUSTRY

14. The production of textiles affords a great variety of processing steps. Figure 3 gives a simplified view on the input-output situation along the textile chain.

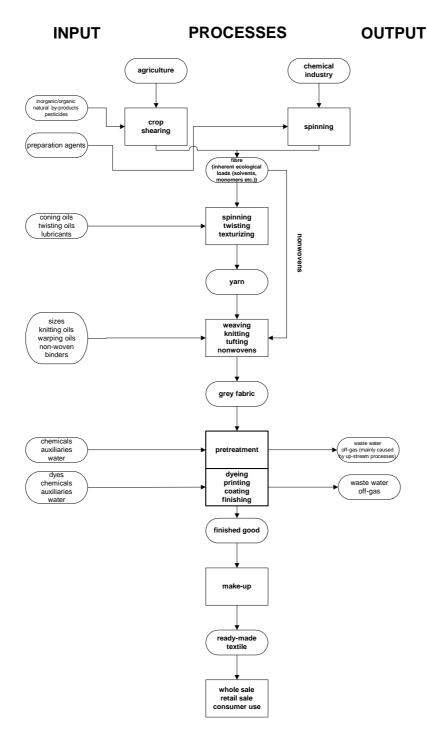


Figure 3: Typical textile processing flow chart [UBA-BREF, 2003]

- 15. The life cycle of a textile starts from natural fibres or the production of man-made fibres, the next step is the production of yarns from the natural or synthetic fibres. Fabrics are produced of the yarns/fibres by different technologies (weaving, knitting, non-woven technologies, braiding, tufting). Finishing processes (pre-treatment, dyeing, printing, and finishing) follows. Some textiles are coated or laminated. These process steps are not always in the same order. Dyeing, for example, can be carried out on loose fibres, on yarns, on fabrics, and on ready-made textiles. The make-up (cutting, sewing, assembling) is the last step before selling in retail trade or whole trade and consumer use.
- 16. After use textiles can be recycled (reuse in fibre processing, non-woven processing etc.).

4.1 Yarn and fabric formation

4.1.1 Raw wool scouring

17. Raw wool must be cleaned by wet processes before the fibre can be dry processed. Neither cotton, nor synthetic fibres require this initial wet cleaning, named wool scouring, before yarn processing (e.g. since raw sheep wool contains from 25 to 75% suint, the production of one kilo of scoured wool fibres produces 1,5 kg of waste impurities) [UNEP/IEO, 1994]. Usually, wool scouring involves passing the raw wool through four scouring bowls in succession, with the wool getting progressively cleaner in one direction and the solution getting dirtier in the opposite direction. Effluent is discharged from the first bowl, containing the wool impurities and used chemicals. The scouring liquid contains a mild alkali such as sodium carbonate and operates at temperatures of around 35 - 40°C; non-ionic surfactants are added.

4.1.2 Production of man-made fibres

- 18. As a first step in man-made fibre processing filaments from the raw materials mentioned in Chapter 3 are produced by
 - melt-spinning
 - dry-spinning
 - and wet-spinning.
- 19. In melt spinning, used for thermoplastic polymers (polyamide, polyester, polypropylene etc.), the polymer granulates are melted, pressed through spinning nozzles and winded after cooling. In dry spinning (polyacrylonitrile, elastane) and wet spinning (viscose, cupro) the polymers are dissolved in an appropriate solvent. In dry-spinning evaporation of the solvent by means of hot air after the filaments have passed the spinning nozzles is used. Wet spinning is carried out by immersing the filaments into a coagulation bath. Solvent-residues charging wastewater and off-gas are typical for man-made fibres which are produced by wet- or dry-spinning techniques.
- 20. After the spinning process the filaments are drawn to increase the orientation of the macromolecules and thereby the tensile strength of the yarns.
- 21. Man-made fibres can be used
 - as filaments or multifilament varns
 - or after converting (breaking, cutting) as staple fibres (further processing is carried out like natural fibres/spun yarns).

- 22. If man-made fibres are used as filament types, texturizing processes can be carried out. By means of mechanical and thermal stress (esp. twisting of the flat yarns at higher temperatures) the orientation of the macromolecules changes, on macroscopic level a crimp effect and a higher volume is achieved.
- 23. Preparation agents mostly on mineral oil or ester oil basis are applied on the filaments during the manufacturing and further processing to adjust the friction characteristic and to impart antistatic and other properties in order to enable downstream processing (see Figure 4). These preparation agents can cause the main part of ecological loads in pre-treatment processes in textile finishing mills.

4.1.3 Yarn formation

- 24. Spun yarn formation is done in spinning mills. Before spinning preparatory processes take place. The tasks of the processes are opening of the fibre bales, mixing of the fibres, cleaning, arrangement, parallizing, drafting, and twining of the fibres to a yarn.
- 25. Ring spinning is the most important technology (80 % of worldwide yarn production). The openend technique is the mostly used non-conventional spinning technology.
- 26. Some yarn qualities are twisted (two or more yarns are twined up).
- 27. From the ecological point of view it is to be taken into account that during spinning and twisting lubricants and twisting oils may be applied, which are responsible for ecological loads in waste water and off-gas in finishing (esp. in pre-treatment processes).

4.1.4 Fabric formation

- 28. The two major methods used are weaving and knitting. Weaving is the most common process and consists of interlacing yarns. Knitting is also frequently used. Knitted textiles are fabrics, which are made of yarns or yarn systems by stitch formation. Flat knitting, circular knitting, and warp knitting technologies exist. Besides the use in apparels (esp. jumpers, underwear, hoses) and home textiles (esp. net curtains), knitted textiles are also used for industrial textiles. Knitting oils used in the process are of ecological interest in downstream processing steps (esp. pre-treatment in textile finishing mills).
- 29. Most of the spun yarns and the main part of filament yarns have to be sized before weaving. Sizing is carried out in the weaving mill to protect the warp yarn during the weaving process from damage or break. The size forms a protective film on the warp yarn, protruding fibre ends causing loom stops are minimized. The yarns unreeled from warp beams are impregnated in the sizing box with the hot sizing liquor, surplus of size is removed by squeezing rollers, the yarns are subsequently dried and assembled to the loom beam. The size add-on on warp yarns, which approx. accounts for 60 % of the total weight of a woven textile, is in a range of 2-20 %. In finishing the sizes (and also warping oils) have to be removed from the fabric leading to the main charge in the wastewater drainage of finishing mills.
- 30. Fabrics made of fibres without an intermediate yarn processing are called non-wovens. A great variety of processes are used. In non-woven fabrication (thermal and chemical bonding) off-gas load caused by fibre inherent monomers (esp. caprolactam), monomers ex bonding polymers, and other fugitive substances in bonding agents are of ecological interest. In further processing steps, ecological loads due to non-woven raw material are negligible.

ENV/JM/MONO(2004)12

31. Carpets are mostly manufactured by means of tufting processes. One of the fundamental differences between tufting and weaving is that the pile and the carpet back are not formed at the same time. Tufting technique presumes an already constructed grounding layer or ground fabric also known as "primary backing" [US-EPA, 1997; VITO, 1999]. Pile threads (in loop form) are introduced with needles into the backing. The piles are fixed with the back coating. Loop pile materials and cut pile materials are produced.

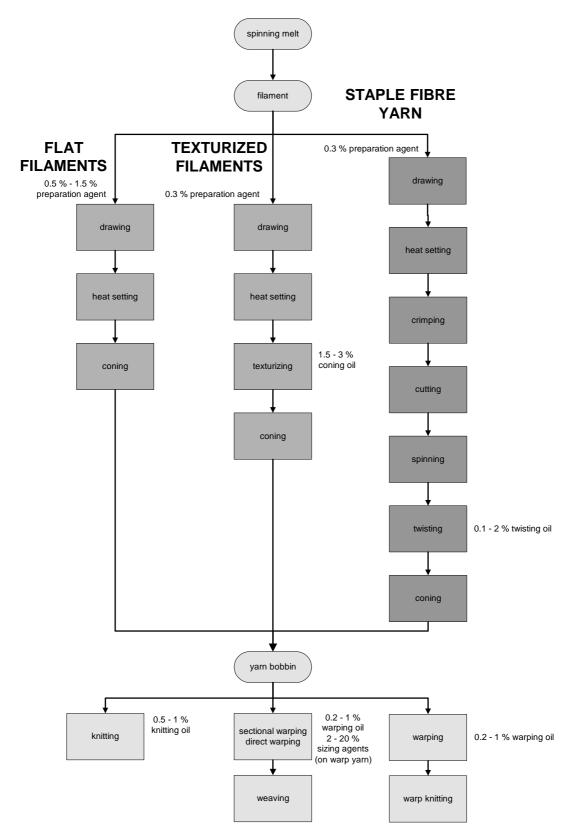


Figure 4: Main application points and characteristic add-on levels for preparation agents and sizing agents [UBA-BREF, 2003]

4.2 Finishing

- 32. Finishing enhances the appearance, durability and serviceability of fabrics. Finishing summarizes all mechanical (physical) and chemical/biochemical measures to improve the properties of the textile. A specific appearance (esp. colour), durability, and functionality etc. is given to textiles in finishing. For example, consumers demand on high fashion colours for apparel textiles or demands on waterproof and/or flame resistant finishing for industrial textiles are fulfilled in textile finishing. Finishing processes can be carried out at all the steps in the textile chain: On loose fibres, slivers, yarns, fabrics, and on the ready-made textiles. However, fabric finishing dominates.
- 33. For simplification, finishing can be divided in the following main steps (Figure 5):
 - fabric pre-treatment (e.g. desizing, washing, scouring, bleaching, etc.);
 - colouring (dyeing and/or printing)
 - functional finishing.

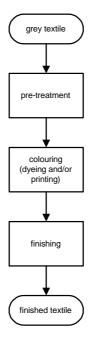


Figure 5: Main processes in textile finishing

- 34. Depending on the demanded end-use properties of the textile all or only some of the above-mentioned processes are carried out.
- 35. Coating and laminating not mentioned in Figure 5 can take place before or instead of the last finishing step.

4.2.1 Pre-treatment

36. Most fabrics need to be pre-treated before dyeing, printing, or finishing. In pre-treatment steps natural impurities on the textile raw material (greige, grey goods) e.g. by-products on cotton as waxes, proteins etc., vegetable impurities on wool, biocides but also by-products from upstream production steps (preparation agents; sizing agents etc.) and fibre specific by-products from man-made fibres (monomers, fibre solvents) are removed.

- 37. These by-products together with the auxiliaries and chemicals used in pre-treatment can cause a considerable ecological load in the wastewater as well as in the off-gas.
- 38. Pre-treatment is a key factor for all downstream finishing steps. Besides the cleaning effect pre-treatment has also an effect on the fibre properties:
 - Absorption of dyes and textile auxiliaries increases
 - Tensions in textiles are minimized; the dimensional stability is improved
 - Wettability of the material is improved
 - Mercerisation gives a change in crystallinity of the cellulose; the lustre is improved
 - Bleaching increases the whiteness of the substrates (important for undyed fabrics as well as for fabrics dyed in light shades or with a high brilliance)
- 39. Mechanical, wet, and thermal pre-treatment steps are used. The choice and sequence of processing steps is substrate specific (cotton, wool, man-made fibres, woven or knitted fabric, etc.), and depend also on the end-use resp. downstream processing steps of the textile and the installed equipment. Normally, wet processes are carried out with water. Esp. in pre-treatment of wool resp. wool blends and blends with elastane fibres dry-cleaning processes (perchloroethylene as solvent) is in use.

4.2.1.1 *Mechanical processes in pre-treatment*

40. In comparison to wet and thermal pre-treatment processes mechanical pre-treatment is accompanied with negligible environmental charges and not discussed in further detail.

4.2.1.2 Thermal processes in pre-treatment

4.2.1.2.1 Heat setting

41. Heat setting (also called thermo fixation) is carried out on fabrics made of man-made fibres or blends of them with natural fibres to relax tensions in the textile resp. fibres due to upstream fibre/yarn/fabric processing and to improve the dimensional stability of the textiles. Heat setting is carried out continuously in a stenter at temperatures between 170 - 220 °C. Heat setting can be done on grey fabrics as a pre-treatment step, as an intermediate step after dyeing or as a last finishing step (often in combination with application of finishing auxiliaries). Due to volatile substances (esp. preparation agents) on the raw material heat setting can cause a considerable off-gas load.

4.2.1.2.2 Singeing

42. Singeing is essential when a smooth surface is of interest (esp. as pre-treatment step before printing processes). The textile passes directly over a flame, metal plate, or indirectly between heated ceramic devices. Protruding fibres are burned off. Mainly woven and knitted textiles made of cotton and cotton blends are treated on singeing machines. Synthetic materials are singed to reduce pilling effects. Sewing yarns are singed to improve their running characteristics. Dust and volatile organic carbons (VOC) of ecological interest.

4.2.1.3 Wet processes in pre-treatment

4.2.1.3.1 Desizing

- 43. Desizing is a typical process step in pre-treatment of woven fabrics made of cotton and cotton blends but also necessary for all grey synthetic material containing sizes. The sizing agents on the warp yarns, applied in weaving mills for better weaving efficiency, have to be removed before further processing in textile finishing.
- 44. Desizing is done as a first step in cotton pre-treatment or as a second step after singeing. Water-insoluble sizing agents have to be degraded during desizing; water-soluble sizes can be simply washed out.
- 45. The following methods are commonly used (depending on the size type):
 - enzymatic desizing; starch
 - oxidative desizing (e.g. by means of persulfate); all size types
 - washing (with/without detergents); water soluble sizing agents.

4.2.1.3.2 Scouring (kier boiling)

46. To extract natural impurities (waxes, pectines, proteins, metal salts) cotton fabrics and their blends are treated in a discontinuous or continuous way with hot alkali. The scouring process can be carried out as separate pre-treatment step or in combination with bleaching or desizing.

4.2.1.3.3 Bleaching

- 47. Bleaching is carried out on natural fibres and man-made fibres. The whiteness of the material increases and the printing and dyeing processes are improved after bleaching.
- 48. During bleaching natural coloured by-products on the fibres are removed resp. destroyed. Bleaching is carried out for undyed natural material to achieve extra-white effects as well as for material to be coloured with high brilliance or in light shades. Normally, textiles made of man-made fibres are delivered with a high degree of whiteness. However, to achieve extra-white effects (e.g. for curtains) bleaching is commonly used.
- 49. Bleaching can be carried out on loose fibres, slivers, yarns, and (mostly) on fabrics in a continuous way or batch wise. The bleaching technologies resp. the bleaching agents vary with the textile substrate (Table 2).

Table 2: Bleaching agents

| Textile material/ | Peroxide | Sodium | Reductive |
|---------------------|----------|----------|-----------|
| Bleaching process | | Chlorite | |
| Cellulose fibres | + | + | |
| Cellulose/Polyester | + | | |
| Protein fibres | + | | + |
| Polyester | | + | |
| Polyamide | | | + |
| Polyamide/Wool | + * | | + |
| Polyacrylonitrile | | + | |
| Cellulose esters | | + | |
| Viscose | | + | - |
| Elastane | + | | + |

^{*:} protecting agent for polyamide necessary

50. It has to be taken into account that bleaching with sodium hypochlorite is not state of the art in Europe due to high loads of AOX and free chlorine generated.

4.2.1.3.4 Mercerising

51. Process for increasing the tensile strength, lustre, sheen, dye affinity, and abrasion resistance of cotton goods by impregnating the fabric with sodium hydroxide solution under tension stress. Mercerising follows singeing and may either precede or follow bleaching [US-EPA, 1997; EU, 2003; UBA-BREF, 2003].

4.2.1.3.5 Causticizing (alkali treatment)

52. Similar effects to mercerising can be achieved by the causticizing process. Causticizing in comparison to mercerising is done without tension stress on the textile at temperatures between $10~^{\circ}$ C and $15~^{\circ}$ C. The process induces shrinking of the textiles.

4.2.1.3.6 Carbonizing

- 53. Carbonizing is a pre-treatment step for wool (loose fibres and fabrics) with the aim to destroy and remove vegetable impurities with strong acid. The following process steps are involved:
 - contact with carbonizing liquor (sulfuric acid up to 7%)
 - centrifugation or squeezing
 - drying
 - burning (up to 140 °C)
 - mechanical treatment
 - neutralisation.

4.2.1.3.7 Crabbing

- 54. Tensions are removed at wool fibres by means of a hot water treatment (analogical to thermo fixing for synthetics).
- 4.2.1.3.8 Washing/Scouring (Synthetic fibres):
- 55. To remove preparation agents as spin finishes, coning-, warping- and twisting oils etc., as well as other impurities, synthetic materials are washed with water and detergents. The efficiency depends on dwell time, water throughput and the appropriate conditions concerning temperature and detergents.

4.2.2 Dyeing

- 56. Process of colouring textiles as a whole is called dyeing. In contrast printing means that only specific areas are coloured; patterns are created. The process of fixing a dye on the fabric may be realised by various chemical/physical mechanisms, namely covalent, electrostatic and hydrogen bonds and adsorption.
- 57. Two principal methods of dyestuff application exist:

Exhaustion mode:

Dyestuff preparation is dissolved in water. The dyestuff exhausts from the bath diffuses into the fibre and is subsequently fixed on to the textile fibre (exhaust dyeing is always carried out in a discontinuous way).

Foulard (padding) technique:

The textile is dipped in a concentrated dyestuff bath and passes the nip of a squeezing unit to avoid surplus of dyestuff on the textile. Fixation of the impregnated dyestuffs is carried out in subsequent steps.

- 58. Three types of dyeing processes, affecting the wastewater volume and wastewater load, can be evaluated:
 - batch (discontinuous) dyeing
 - semi-continuous dyeing
 - continuous dyeing.

Discontinuous dyeing:

Discontinuous dyeing (also called batch dyeing or exhaust dyeing) involves applying of a dyestuff in solution or suspension at a specific liquor ratio, which determines the depth of the colour obtained. At the end of the dyeing operation the spent dye-bath liquor is drained off. The post-dyeing stage consists of washing with water to remove unfixed amounts of dyestuff from the textile substrate. In some cases soaping and special aftertreatment steps are necessary. Common methods of batch or exhaust dyeing include beam, beck, jet and jig processes (US-EPA, 1997).

Continuous dyeing:

In continuous dyeing the dyestuffs are applied in a padding mangle to the material with direct subsequent dye fixation by means of chemicals, heat, or steam followed by washing steps. Pad-steam processes (padding and fixation by steaming) and thermosol processes (padding of disperse dyes with subsequent heating) are commonly used.

Semi-continuous dyeing:

In semi-continuous dyeing (pad-jig, pad-batch, pad-roll) the fabric is impregnated in a padding machine with the dye-liquor and afterwards treated batch wise in a jigger or stored with slow rotation for several hours (pad-batch: at room temperature; pad-roll: at elevated temperature in a heating chamber) for fixation of the dyes on the fibre. After fixation, the material is washed and rinsed in full width on continuous washing machines.

4.2.2.1 Optical brightening

59. Normally, fibres contain yellow colouring pigments. In order to get bright white or bluish shades optical brighteners, e.g. fluorescent whitening agents (FWAs) are applied. Fluorescent whitening agents are mainly applied by means of exhaustion or padding techniques, the later being the most important one due to economic advantages. The fixation mechanism of optical brighteners can be compared with dyestuffs.

4.2.3 Printing

- 60. Instead of colouring the whole fabric as in dyeing, the colour is applied only to specific areas mainly by screen-printing systems (flat screens or rotary screens) to achieve the designed pattern.
- 61. In principle three methods are available:

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printing with diffusing dyestuffs (printing - drying - fixation - washing)
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- printing with pigments (printing - drying - fixation)

- transfer printing (transfer paper - print on textile – paper waste disposal)

- 62. For preparing printing pastes the dyes are dissolved in a limited amount of water to which a thickening agent to give the necessary viscosity to the printing paste and other additives are added. The printing process is followed by a drying and steaming or curing process (pigment printing). With except to pigment printing a washing and subsequent drying step follows.
- 63. Worldwide approx. 50% of textile printing is done with the pigment printing technology. The pigments used have no affinity to the fibre. Therefore, a binder and fixating agents must be added to the printing paste. The advantage of pigment printing is that the process can be done without a subsequent washing step needed for all other printing technologies. A typical printing paste recipe for pigment printing contains water, emulsifier, thickening agent, pigment dispersion, softening agent, binder, and fixation agents.

4.2.4 Finishing

- 64. To meet requests for special "effects" the pre-treated and/or dyed/printed textile material (fibre, yarn or fabric) is submitted to one or more functional finishes. These processes may be chemical (e.g. stiffening, softening, water and soil repellent, antimicrobial, mothproofing, antistatic finishing, fire retardant finishing) or mechanical treatment (smoothness, roughness, shining). In chemical finishing the auxiliaries are applied from aqueous solutions/dispersions mainly by means of foulards (padding machines) to the textile. In most cases the padding liquor fulfils a multifunctional task (the above mentioned auxiliary types are combined in one padding step e.g. softening and crosslinking agents are combined). Drying of the padded auxiliary is carried out by temperatures of approx. 120 °C; in some cases a curing step has to be carried out at temperatures between 150 °C and 180 °C.
- 65. Besides this impregnation method with the help of padding devices, spraying or printing techniques as well as exhaustion processes and foam application are common.

4.2.5 Coating and laminating

- 66. Usually, coated and laminated textiles consist of a textile substrate, which typically will be a woven, knitted, or non-woven textile fabric combined with a thin, flexible film of natural or synthetic polymeric substances.
- 67. A coated fabric usually consists of a textile substrate, on which the polymer is applied directly as a viscous polymer liquid, a melt, or a coating powder. The coating substances are applied via a blade or similar aperture, spraying, and printing techniques.
- 68. A laminated fabric usually consists of one or more textile substrates, which are combined with a pre-prepared polymer film or membrane by adhesives or heat and pressure.
- 69. The coating agents, their by-products, and crack-products can cause a considerable off-gas load. Emissions of ammonia, formaldehyde (e.g. ex melamine resins), and residual monomers are typical. Effluents can be loaded with highly concentrated residual coating pastes.
- 70. The coating process is an important production step to improve the stability of textile floor coverings (carpet back coating). Additives (foam stabilisers, flame retardants, antistatic agents etc.) are added to the foam. Mainly foams based on styrol butadiene lattices are used.

5 WATER CONSUMPTION

- 71. Wastewater in textile finishing is generated from
- aqueous pre-treatment steps
- residual baths from exhaust processes (esp. exhausted dye baths)
- washing and rinsing steps
- after-treatment baths (soaping or reductive after-treatment subsequently to dyeing etc.)
- residual padding liquors, residual printing pastes, and residual coating pastes
- cleaning the machines.
- 72. Due to differences in processing equipment and requirements of the handled orders, type of dye, washing and rinsing procedures, etc. the wastewater volumes per processed unit vary considerably.
- 73. In the following data on water consumption resp. waste water amount are compiled:
- 74. Water consumption in France is 100 up to 150 m³ per tonne of fabric as shown in Table 3 [ITF, 1999]. Water consumption in German finishing industry is between 20 to 350 m³ per tonne of fabric (average: 120 m³/t) [Böhm et al. 1997, 2000; Hillenbrand et al. 1999].
- 75. The wastewater volume for different categories of German finishing mills is summarized in Table 4 [UBA-BREF 2002].
- 76. The TVI Enquete acquired the data compiled in Table 5 [TVI-Enquete, 1997].

Table 3: Water Consumption during finishing

| Substrate | Water consumption [m³/t] | | | | |
|-------------------|--------------------------|---------|--|--|--|
| | Average (1) | Maximum | | | |
| Cotton | 100 – 150 (250 – 350) | 200 | | | |
| Wool (piece) | 50 – 100 (200 – 300) | 150 | | | |
| Polyamide (piece) | 50 – 100 (125 – 150) | 150 | | | |
| Polyester (piece) | 50 – 100 (100 – 200) | 150 | | | |
| Acrylic (piece) | 50 – 100 (100 – 220) | 150 | | | |

⁽¹⁾ Figures in italic are reported from the TGD [EU, 2003] for water consumption during finishing

Table 4: Specific waste water flow in German textile finishing industry [UBA-BREF, 2003]

| Category | Number of | min-max | Average | Median |
|---|-----------|----------|---------|--------|
| | TFI | [L/kg] | [L/kg] | [L/kg] |
| TFI mainly finishing floc material | 2 | 10-34 | 22 | 22 |
| consisting of CV, PES, PAC and/or CO | | | | |
| TFI mainly finishing CO yarn | 3 | 105-120 | 111 | 108 |
| TFI mainly finishing PES yarn | 4 | 65-148 | 101 | 96 |
| TFI mainly finishing yarn consisting of | 5 | 66-212 | 128 | 120 |
| WO, PAC and /or CV | | | | |
| TFI mainly finishing knit fabric consisting | 17 | 21-216 | 92 | 79 |
| of CO | | | | |
| TFI mainly finishing knit fabric consisting | 12 | 0.4-42 | 9 | 2 |
| of CO having a relevant printing section | | | | |
| TFI mainly finishing knit fabric consisting | 11 | 35-229 | 101 | 83 |
| of synthetic fibres | | | | |
| TFI mainly finishing knit fabric consisting | 1 | 63 | 63 | 63 |
| of WO | | | | |
| TFI mainly finishing woven fabric | 12 | 52-618 | 151 | 96 |
| consisting of CO | | | | |
| TFI mainly finishing woven fabric | 6 | 139-283 | 221 | 242 |
| consisting of CO and/or CV having a | | | | |
| relevant printing section | | | | |
| TFI mainly finishing woven fabric | 2 | 141, 296 | 219 | 219 |
| consisting of WO | | | | |
| TFI mainly finishing woven fabric | 1 | 7 | 7 | 7 |
| consisting of PA | | | | |
| TFI finishing carpets | 2 | 15, 36 | 25 | 25 |

TFI = textile finishing industry

Table 5: Specific water consumption of different types of textile finishing industries in Germany from 1988-1996 (average and range) – [TVI Enquete, 1997]

| Type of textile | 1988 | 1988 | 1992 | 1992 | 1996 | 1996 |
|--------------------|---------|---------|---------|--------|---------|--------|
| finishing industry | average | range | average | range | average | range |
| | [L/kg] | [L/kg] | [L/kg] | [L/kg] | [L/kg] | [L/kg] |
| Flocs/yarn | 79 | 18-151 | 67 | 31-124 | 69 | 10-185 |
| Knit fabric | 168 | 100-313 | 139 | 54-250 | 97 | 20-133 |
| Woven fabric | 118 | 29-190 | 146 | 90-302 | 103 | 38-280 |
| Textile printing | 194 | 56-375 | 179 | 65-330 | 179 | 70-229 |

6 WASTE WATER TREATMENT

77. The branch of textile finishing is characterised by many small and medium-sized enterprises (SMEs), which discharge predominantly (in Germany approximately 90%) to municipal wastewater plants. Only a few companies in Germany treat their wastewater more extensively. A recent study in Germany revealed the following data. Out of a total of 127 textiles finishing companies 14 (11%) plants discharge their wastewater directly into surface waters and 113 plants into municipal wastewater plants [Böhm et al, 1997; Hillenbrand 1999] (see Table 6).

Table 6: Waste Water Treatment in the Textile Finishing Industry in Germany

| In-house waste-water treatment | D | Direct discharge | | Inc | direct dis | charge |
|-----------------------------------|---------|-----------------------------|--------|-------------------------|------------|---------------------------------------|
| | (discha | (discharge to water bodies) | | (discharge to municipal | | - |
| | | 1 | 1 | waste water tr | | · · · · · · · · · · · · · · · · · · · |
| | Yes | No | number | Yes | No | Number |
| Settling tanks | 12 | 2 | 14 | 55 | 58 | 113 |
| Sieves | 6 | 8 | 14 | 29 | 84 | 113 |
| Neutralisation | 5 | 9 | 14 | 51 | 62 | 113 |
| Precipitation | 2 | 12 | 14 | 12 | 101 | 113 |
| Recycling of waste water into | 3 | 11 | 14 | 10 | 103 | 113 |
| production | | | | | | |
| Other treatment | | | 6 | | | 10 |
| Of which: biological treatment | | | 2 | | | 5 |
| Companies that initiated measures | | | 8 | | | 36 |
| Of which: treatment measures | | | 2 | | | 18 |
| Of which: Waste water recycling | | | 2 | | | 12 |
| Companies that plan measures | | | 12 | | | 38 |
| Of which: treatment measures | | | 9 | | | 19 |
| Of which: waste water recycling | | | 1 | | | 10 |

Note: The picture in Southern Europe e.g. Spain, Portugal, Greece will be quite different with many more direct dischargers [ETAD, 2002a]. Well founded more detailed European wide data are not available.

7 TEXTILE AUXILIARIES, BASIC CHEMICALS, DYESTUFFS

7.1 Textile auxiliaries and basic chemicals

- 78. In the "Textilhilfsmittelkatalog" [THM-Katalog, 2000] a survey of auxiliaries used in textile industry is given. 7000 products based on approx. 400-600 different chemical substances are compiled.
- 79. Nearly all of the auxiliaries used in textile finishing are delivered as aqueous solutions resp. dispersions. The percentage of the active ingredients in the solutions/dispersions varies in a wide range.
- 80. The mainly used basic chemicals are inorganic salts (sodium chloride, sodium sulfate etc.), lyes (sodium hydroxide etc.), acids (acetic acid, formic acid, inorganic acids etc.), and reducing and oxidizing agents (sodium dithionite, hydrogen peroxide etc.)
- 81. In Annex I an overview on the most important auxiliaries and basic chemicals used along the textile chain, their technological effect, and their chemical composition is given.

7.1.1 Surfactants

- 82. Surfactants (organic polar compounds with at least one hydrophobic part and at least one hydrophilic group) are widely spread in textile finishing industry. All types of surfactants (anionic, nonionic, cationic, and amphoteric) are in use. Anionic and non-ionic substances dominate. Surfactants in the textile industry serve mainly as detergents, wetting agents, de-aeration agents, levelling agents, dispersing agents, softening agents, emulsifying agents, spotting agents, anti-electrostatics, foaming and defoaming agents, after-treatment agents for fastness improvement, felting agents, fixing acceleration agents for continuous dyeing and printing.
- 83. Surfactants can be the essential active part of a textile auxiliary or used as an additive in textile auxiliaries or dyes, printing pastes and coating pastes (dispersing agents in dyestuffs (surfactant content 30-60 %), emulsifiers in preparation agents etc.).
- 84. Following chemical components are mainly in use:

Anionic surfactants:

alkyl sulfates, alkyl ether sulfates, alkane sulfonates, alkyl aryl sulfonates, fatty acid condensation products, alkali salts of fatty acids (soaps), lignine sulfonates, condensation products of formaldehyde and naphthaline sulfonic acid.

Non-ionic surfactants:

hydrophilic part: polyethylenoxide or polypropylenoxide; hydrophobic part: fatty alcohol, fatty amine, fatty acid amide, fatty acid, alkylphenol, alkylphenol.

Cationic surfactants:

derivatives of quaternary ammonia salts.

Amphoteric surfactants (very rare):

betain derivatives.

85. In Annex I the various application fields of surfactants in textile industry can be seen.

86. In dyeing and pre-treatment processes surfactants are commonly used in a concentration of approx. 2 g/L. A typical liquor ratio in exhaust processes is 1: 10. This means that 20 g surfactant per kg of textile are used.

7.1.2 Biocides

- 87. Biocides are used on textiles to control bacteria, fungi, mold, mildew, and algae and the problems of deterioration, staining, odours (anti odour finishing), and health concerns that they cause. They are intentionally applied in exhaust- or padding processes in textile finishing. It can be estimated that approx. less than 5 % of the textiles are finished with biocides for the consumer end-use.
- 88. Sensitivity of the fibres differs on a "case by case" basis, but textiles made from natural fibres are generally more susceptible to biodeterioration than man-made fibres [Hamlyn, 1990].
- 89. Synthetic fibres are hardly ever subject to deterioration by micro-organisms or insects, nevertheless two polymers are more sensitive than others: Polyvinyl chloride (PVC) and Polyurethanes (PUR). Animal fibres (keratin: wool, silk) are susceptible to attack by both microorganisms and insects. Cellulose fibres (cotton, linen etc) are susceptible to attack by microorganisms, but not by insects [van der Poel, 1999]. Yet, cellulose fibres are more sensitive to rot and mildew than animal fibres. Viscose and acetate fibres, both manufactured from natural cellulose, show a different behaviour concerning biodeterioration: viscose fibres are readily degraded by mildew and bacteria whereas acetate is more resistant.
- 90. Especially, fabrics exposed to outdoor conditions (tents, tarpaulins etc.), sanitary products (hospital textiles) and carpets are treated with an antimicrobial finishing. Reduction of odour nuisances (e.g. in sportswear) by means of antimicrobial finishing is another typical application field for biocides.
- 91. Besides the intentional application of biocides on textiles the following sources for biocides to be found on textiles are possible:
- Biocides in textile auxiliaries to improve their storage stability (preservation agents)
- Biocides in raw cotton fibres (insecticides (organochlorines, organophosphates, pyrethroids, and carbamates), herbicides, harvest aid chemicals)
- Greasy wool contains residues of biocidal chemicals used to prevent or treat infestations of sheep by external pests (ectoparasites), such as ticks, mites, and blowfly. Like the natural by-products they are removed in wool scouring and load the wastewater. Biocide content of the wools processed varies widely, according to the countries of origin of the wools [Lakin, 1999]:
 - Organochlorines: 0.2–5 g/t greasy wool
 - Organophosphates: 1-19 g/t greasy wool
 - Pyrethroids: 0.05-6.3 g/t greasy wool.
- Biocides applied to textiles (yarns, fabrics, semi-finished products) during transport and storage in humid and warm climate (PCP seems to be still used in Asia for this purpose)
- Biocides added during the formulation (compounding or preparation of master batches) of synthetic fibre polymers [BRE, 1998]
- 92. According to the Textilhilfsmittelkatalog [THM-Katalog, 2000] and personal information from textile auxiliary industry the following basic chemical structures are typical for biocides used in textile finishing:

Antimicrobial finishing

- Isothiazolinone derivatives
- Triclosane (5-Chloro-2-(2,4-dichlorophenoxy)phenol (mainly for anti-odour finishing in garments)
- Ouaternary ammonium compounds
- Benzimidazol derivatives (Benzimidazol carbamates (Carbendazim))
- Dichlorophen derivatives (2,2'-Methylene-bis(4-chorophenol)-esters)
- Polyhexamethylenebiguanide
- Sodium pyrithione
- 2-(Thiocyanomethylthio)benzthiazole (TCMBT) in combination with o-phenylphenole and Copper-8-hydroxyquinoline
- Tin organic compounds
- Zinc organic compounds.

Moth proofing

- Pyrethroids
- Sulcofuron derivatives.

Preservation agents for the improvement of the storage stability of textile auxiliaries

- Chlorinated and non-chlorinated isothiazolinone derivatives (partly formaldehyde donors are added); typically approx. 15 ppm for chlorinated actives and 50-100 ppm for non chlorinated actives are added
- Quaternary ammonium compounds
- Chlorinated cresol derivatives
- Chlorinated benzene
- Sodium benzoate
- Potassium sorbat
- 2-Phenylphenolate
- 2-Bromo-2-nitropropane-1,3-diol.
- 93. Main textile auxiliaries which contain preservation agents to increase the storage stability are liquid sizing agents, preparation agents, natural thickeners in printing pastes, bonding agents for pigment printing based on polymeric dispersion, coating agents based on polymers, softening agents (esp. fatty acid condensation products), finishing agents containing silicone compounds, and auxiliaries based on proteins.
- 94. In the carpet industry biocides play an important role to impart wool fibre lifetime. Against a range of textile pests mothproofing agents on the basis of synthetic pyrethroids (permethrine and cyfluthrin) are used. Permethrine-based formulations account for approx. 90 % of the market, sulcofuron (halogenated diphenylurea derivatives) are currently not used to any significant degree [EU-BREF, 2002].
- 95. According to another source the following biocides are typical for the textile industry [Rossmoore, 1995]:
- 2,2'-Dihydroxy-5,5'-dichlorodiphenylmethane
- 2-Phenylphenol
- Sodium-2-phenyl-phenolate.
- Quaternary ammonium salts
- Copper-8-quinolinolate
- Dichlorophen
- Zinc naphthenate
- Thiobendazone
- Organotin compounds
- 2,4-Dichlorobenzyl alcohol

- 2-Bromo-2-nitropropane-1,3-diol.
- 96. To achieve an antimicrobial finishing biocides are applied to the textile similar to other auxiliaries. Mainly continuous padding processes or discontinuous methods similar to exhaust dyeing are in use. Using the exhaust technique the biocide formulations are applied in a concentration of 3 10 g per kg textile (Product Data Sheets of antimicrobial finishing agents and [Bioexpo, 1998]). In exhaust processes a fixation rate of 70-80 % is typical; but fixation rates up to 100 % can also be reached [ITF, 1999].
- 97. As a realistic worst case for the application amount of moth repellents on wool, a default value of 1% w/w (i.e. 10 kg/t) can be proposed if no further data is available [Debon, 1999] (see Annex II).
- 98. A typical recipe for an antimicrobial finishing of awnings (padding technique) according to a Product Data Sheet is given below:
- 40-120 g/L fungicide preparation
- Liquor pick-up: 60 %
- Drying between 110 °C and 150 °C
- Hydrophobic agents and easy care agents can be added to the padding liquor.

7.2 Dyestuffs and optical brighteners

- 99. Dyestuffs may be classified according to their chemical composition [Zollinger, 1987]:
- azo
- antrachinone
- sulfur
- triphenylmethane
- polymethine
- di- and triarylmethine
- indigoid
- phthalocyanine
- nitro and nitroso dyes.
- 100. Worldwide more than 60 % of the dyestuffs used in textile finishing are based on azo dyes [Hübner, 1997].
- 101. At the industrial level a classification of the dyestuffs according to their performances in the dyeing processes is preferred [Ebner, 1988]. Main classes are:

acid dyes: anionic dyes with affinity to protein, polyamide and acrylic-functional groups of

substrates

cationic dyes: cationic salt of a dye base with affinity to protein fibres and synthetic acrylates

direct dyes: dyes with a substantivity to cellulose fibres.

disperse dyes neutral dyes, which are sparingly soluble in water and which are applied to polyester,

cellulose ester and polyamide fibres

reactive dyes: dyes with the property of forming covalent bonds with the fibres (for cellulose fibres

and wool fibres)

sulfur dyes: water insoluble dyes based on sulfur chemistry, which are normally applied in the

reduced form (for cellulose fibres)

vat dyes: water insoluble dyes; the soluble reduced (leuco) form is used in the dye bath. The reduced form is subsequently re-oxidized on the fibres (for cellulose fibres).

- 102. All dyestuff classes currently used in finishing cannot be replaced, because each one has its peculiar benefits if compared to others. For example, in the case of the dyeing of cellulose, direct, reactive, vat, and sulfur dyestuffs are commonly used. Reactive dyestuffs allow bright shades; their fastness properties are excellent. On the other hand, in many cases direct dyestuffs are used because of the easiest process and low cost, even if colourfastness is much worse.
- 103. It has to be taken into account that a dye-formulation contains approx. 10-80% pure dyestuff. The higher value is for dyestuffs delivered in powder form, the lower value is for liquid formulations [ETAD, 2002b]; the major part of the formulation consists depending on dyestuff class and application field of non biodegradable dispersing agents (e.g. naphthalenesulfonic acid formaldehyde condensation products or lignin sulfonates), standardizing agents (salts), and additives (anti-freeze agents etc.). Dyestuffs are delivered in powder form, granulates, pastes and as liquids (aqueous solutions/dispersions).
- 104. Optical brighteners can be roughly classified according to her application performance in three categories:
- anionic compounds which contain sulfuric acid groups, similar to acid dyes, effective on cotton, wool, and polyamide yarns
- cationic and amphoteric compounds with a similar behaviour as basic dyes, effective mainly on polyacrylonitrile, cellulose and polyamides
- compound without solubilising groups, similar to disperse dyes, effective on polyester, polyamide and cellulose acetate.
- 105. The fluorescent whitening effect can be reached by means of the following basic chemical structures [Müller, 2001]
- Stilbene
- Triazinylflavonate
- Triazolylflavonate
- Pyrazoline
- Cumarine and chinolone
- Azolylethene
- Naphthalimide.

7.3 Consumption of textile auxiliaries, basic chemicals and dyestuffs

106. A survey of typical specific consumption levels for different kinds of textile finishing industries in Germany is compiled in Table 7.

Table 7: Consumption of dyestuffs, textile auxiliaries, and basic chemicals in textile finishing; according to [UBA-BREF, 2003]

| Kind of textile finishing industry (TFI) | Dyestuffs | Textile auxiliaries | Textile basic chemicals |
|--|----------------|------------------------|-------------------------|
| | [g/kg textile] | [g/kg textile] | [g/kg textile] |
| TFI mainly finishing cotton yarn | 25 | 70 | 430 |
| TFI mainly finishing polyester yarn | 18-36 | 80-130 | 95-125 |
| TFI mainly finishing wool, polyacryonitrile and/or CV yarn | 13-18 | 60-90 | 180-325 |
| TFI finishing knit fabrics mainly consisting of cotton | 18 | 100 | 570 |
| TFI finishing knit fabrics mainly consisting of man- made fibres | 15-50 | 45-150 | 50-280 |
| TFI finishing woven fabrics mainly consisting of cellulose fibres | 11 | 183 | 200 |
| TFI finishing woven fabrics mainly consisting of cellulose fibres with relevant printing section | 88 | 180 | 807 |

TFI= Textile finishing industry

107. Regarding a typical textile finishing mill many basic chemicals and auxiliaries and dyestuffs are used. However the consumption curve has in all cases a hyperbolic form (Figure 6 [UBA-BREF, 2003]).

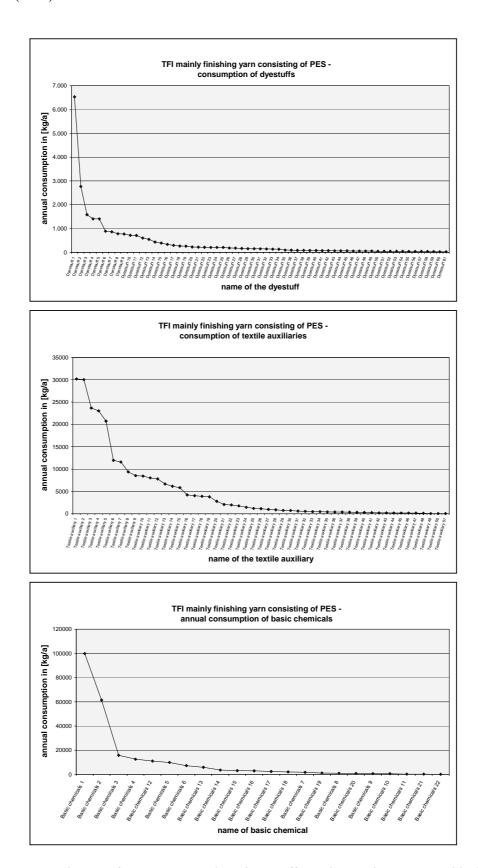


Figure 6: Typical hyperbolic curve for the consumption of dyestuffs, basic chemicals, and auxiliaries in textile finishing industry

7.4 Chemical composition of waste water ingredients

108. On basis of information in Material Safety Data Sheets, the annual consumption, site-specific data, and the chemical composition of a wastewater from a textile finishing mill, mainly finishing synthetic fibres, has been estimated (Table 8 [EnviroTex, 2002a]). Only textile auxiliaries and chemicals of the regarded textile finishing mill with an annual output of min. 100 kg are regarded; dyestuffs and fibre byproducts are not considered in the estimation.

Note: Reducing agents and oxidizing agents as well as lyes and acids will react in the wastewater; this is not considered in the calculation.

Table 8: Chemical composition of a waste water from a textile finishing mill (main ingredients)

| Substance | Estimated annual amount of the substance in the waste water [kg/a] |
|--|--|
| Sodium sulfate | 10,450 |
| Acetic acid | 10,206 |
| Fatty alcohol ethoxilate | 7,512 |
| Naphthaline sulfonic acid condensation product | 7,070 |
| Sodium hydroxide | 6,344 |
| Fatty acid ethoxilate | 6,180 |
| Sodium carbonate | 6,173 |
| Benzylbenzoate (ex dyeing carrier) | 4,680 |
| Sodium chloride | 4,641 |
| Polyacrylate | 3,879 |
| Castor oil ethoxilate | 2,400 |
| Polycarboxylate | 2,300 |
| Hydrogen peroxide | 2,093 |
| Sodium nitrate | 1,600 |
| Quaternary ammonium compounds | 1,312 |
| Sodium chlorite | 800 |
| Phosphoric acid esters | 772 |
| Sulfinic acid derivative | 600 |
| Benzyltrimethylammonium chloride | 432 |
| Di-sodiumdisulfite | 400 |
| Oxalic acid | 400 |
| Sodiumdithionite | 360 |
| Formic acid | 298 |
| Sodium meta-silicate | 288 |
| Heterocyclic nitrogen compound | 200 |
| Hydrocarbons | 180 |
| Phosphonate | 140 |
| Fatty acid condensation product | 115 |
| Alkylarylsulfonate | 106 |
| Amylase | 104 |
| Dextrose | 100 |
| Sodium acetate | 100 |
| Sodium sulfite | 100 |

8 RELEASE ESTIMATION

8.1 Distribution of releases

109. The life-cycle concept stipulates that the emission pathways from all life-cycle stages, including the disposal stage of the finished product, are analysed. They are considered, if relevant emissions occur. Along the textile chain textile finishing is first of all relevant concerning emissions to the different environmental compartments. The chemical input in textile finishing is up to 1 kg chemicals/kg processed textile. Usually only the colorants, the finishing agents including coating and carpet backing and binders and other auxiliaries in case of pigment printing remain on the textile substrates, whereas most of the other applied substances, which are necessary to enable/enhance the pre-treatment-, dyeing-, printing-, and finishing processes, are emitted to a great part to the waste water. Air emissions are a minor but not negligible source of pollution; most of the chemicals and auxiliaries are released to waste water. Concerning the organic load, 20 - 100 g organic carbon/kg processed textiles are emitted, which is 15-250 times higher than emissions to air [UBA-BREF, 2003]. Thus emissions to water are predominant.

8.2 Releases during finishing

110. It has to be mentioned that some chemicals and auxiliaries used in finishing are only used for better processing in textile finishing (e.g. levelling agents, salts, complexing agents, detergents). In wet processes they are introduced nearly to 100% into the water path. Other chemicals and auxiliaries create an effect on the textile and are fixed in a chemical/physical way on the fibres. Only a small amount of these substances will be found in the effluent or off-gas (residual liquors, non fixed substances in exhaust processes, fugitive substances in curing processes). Other substances (e.g. reactive dyes, crosslinking agents) react during dyeing/finishing. By-products from the reactions (e.g. dye-hydrolysates, formaldehyde, ammonia) will be found in the wastewater or off-gas respectively.

111. The wastewater load is characterized by

- fibre by-products (natural by-products, fibre monomers (e.g. caprolactam), fibre oligomers (e.g. polyethyleneterephthalat-trimers), fibre solvents, catalysts used in manufacturing of man-made fibres (e.g. antimony compounds in polyester fibres))
- preparation agents applied in down-stream processes
- sizing agents applied in down-stream weaving mills
- non-fixed basic chemicals, textile auxiliaries, and dyestuffs (including their by-products and impurities).

8.2.1 Releases to waste water

8.2.1.1 Pre-treatment

- 112. In textile finishing the first release to water and air occurs in the pre-treatment steps. Pre-treatment is one of the industry's largest sources of wastewater pollutants.
- 113. If the first step in pre-treatment is a wet process (desizing, scouring, bleaching, washing of manmade fibres, etc.) fibre inherent loads (fibre monomers, fibre solvents, natural fibre by-products etc.) are released mainly to the water path. The process chemicals (alkali, detergents, complexing agents, etc.) are also released to nearly 100 % to the water path.

8.2.1.1.1 Biocides in pre-treatment

114. Biocides applied as preservation agents in sizing liquors and preparation agents and during storage and transport of the textile raw material as well as biocides applied during growth of cotton are of relevance. Biocidal chemicals used to prevent treat infestations of sheep are important regarding wool scouring.

Note: in most cases wool scouring is carried out in specialized plants, not in textile finishing mills.

- 115. Especially imported fabrics can contain biocides applied for preservation during storage and transport.
- 116. According to personal information from sizing agent producers sizing agents in powder form are delivered without preservation agents (biocides). In tropical regions with high air humidity however biocidal ingredients in sizing agents (added by the size producer or the weaving mill) can be found. Information on kind and quantity of the biocides is hardly available. Laursen mentioned that 1 % preservatives on the weight of size could be added to sizing agents. [Laursen, 1997]. Sizing agents which are delivered in liquid form (polyacrylates, polyesters) contain biocides (e.g. chlorinated resp. non chlorinated isothiazolinone in an amount of 15 ppm for chlorinated types resp. 50-100 ppm for non chlorinated types (calculated on active substance).
- 117. These biocides are removed in the pre-treatment steps almost completely and are released to the wastewater of the textile plant.
- 118. More data concerning biocide content of raw wool and raw cotton fibres are compiled in Annex II.
- 119. The aqueous pre-treatment processes for cotton with exception to enzymatic desizing (scouring, bleaching, mercerizing) are carried out in relatively strong alkaline solutions mostly at elevated temperatures. The most important pesticides (phosphoric acid esters, carbamates and pyrethroides) are not stable in alkaline solutions. A study on lindane and PCP-removal in pre-treatment steps had been undertaken by Küster [Küster, 1996]. The results can be summarized as follows:
 - Lindane can be removed in cotton pre-treatment to 100 %.
 - A residue of approx 7 % of the applied PCP remains on the fibres.
- 120. The effectiveness in removal of chlorinated pesticides can be estimated therefore to at least 90%.

Note: Due to the high attachment characteristics of the biocidal compounds emissions to air are considered to be a negligible emission pathway (Luttik, 1993).

8.2.1.2 Dyeing and finishing

- 121. Releases can take place at the discharge
 - of residual baths from exhaust processes (esp. exhausted dye baths)
 - of washing and rinsing steps which follow the dyeing process
 - of after-treatment baths (soaping or reductive after-treatment subsequently to dyeing)
 - of residual padding liquors, residual printing pastes, and residual coating pastes
 - of cleaning the machines.

8.2.2 Releases to air

- 122. Emissions to air from textile finishing includes both, captured emissions released from stacks and uncaptured, fugitive emissions. The latter emissions are important concerning workplace atmosphere conditions. Main sources for captured waste gas in textile finishing are the following processes:
- Singeing
- Heat setting (esp. in mills finishing man-made fibres)
- Drying
- Printing
- Chemical finishing
- Mechanical finishing (dust generation in shearing and raising etc.)
- Coating, laminating.
- 123. Captured emissions are minimized in several finishing plants by means of an off-gas abatement. The abatement techniques are mainly based on condensation techniques, aqueous scrubbers, and electrostatic precipitation.
- 124. In pre-treatment of fabrics made from synthetic fibres often heat-setting is carried out as a first step. In this case the main release of preparation agents and volatile fibre by-products occurs via the offgas path.
- 125. Mainly fugitive emissions are relevant during aqueous pre-treatment steps and dyeing; esp. if highly volatile substances resp. substances with a high water vapour volatility are handled in an "open" form. Procedures like decanting, dispensing, dosing, measuring and weighing as well as pre-treatment and dyeing processes in "open" machines (esp. when machines are loaded or unloaded) are of specific interest concerning fugitive emissions.
- 126. It is important to know that emissions to air are caused by
- the textile materials (fibre by-products)
- the auxiliaries/chemicals
- the machines (esp. if direct heated stenters or drying apparatuses are used (fuel gas emissions like methane)).
- 127. Off-gas in textile finishing can be loaded with various chemical substances. Depending on their volatility the active ingredients in auxiliaries, impurities, and by-products in the formulations as well as reaction products of these substances are to be detected in the off-gas. The tables compiled in Annex III give an overview on the most important substances to be detected in finishing, printing, and coating processes. The classification in less and more dangerous properties follows German and European legislation.
- 128. It is of interest that off-gas emissions caused by chemicals/auxiliaries can occur during finishing (drying/curing of finishing agents like softeners, water repellents, flame retardants) as well as in all drying/heat setting/curing processes due to a carry over from volatile substances from up-stream processes (esp. from dyeing or printing). Typical substance classes to be regarded from this point of view are:
- Carriers
- Levelling agents
- After-treatment agents
- Wetting agents
- Hydrocarbons ex printing pastes

- Acetic acid
- Perchloroethylene (if dry-cleaning is carried out)
- Conditioning agents.

8.3 Releases during other life-cycle stages

- 129. Having regard to Chapter 7 it is obvious that substances remain intended (dyestuffs, optical brighteners, functional finishing agents) and non-intended on the textiles delivered to the consumer. Therefore releases may occur during other life-cycle stages, e.g. the final use of textile articles and the recycling and disposal of textile articles.
- 130. To assess emission, service life of treated articles need to be known. Some preliminary values are presented in Table 9.

| Table 9: | Service | life | of some | articles | [Ciba, | 2001] |
|----------|---------|------|---------|----------|--------|-------|
|----------|---------|------|---------|----------|--------|-------|

| Articles | Service life (years) |
|------------------------------|----------------------|
| Clothes on contact with skin | 1 |
| Others clothes and bed linen | 2 - 5 |
| Household linen | 5 - 10 |
| Bedding (mattress) | 10 |
| Carpets | 8 - 20 |
| Wall-to-wall carpet | 5 - 30 |
| Sunblind | 8 - 15 |
| Tents | 5 - 20 |
| Awning | 2 |

- 131. The amount of released substances and the way of release (water, air, soil) is not well investigated up to now.
- 132. For garments the washing in household washing machines have to be considered. Therefore the greatest part of non-intended substances, which are only weakly fixed to the textile, will be emitted to the water path. The amount of washing cycles in household depends on several parameters and is not known. Substances, which are intended to fix on the textiles, will be emitted to a great part during disposal. Disposal can be done by deposition in landfill or by incineration. Typical rates for these disposal methods are not known. For textiles used under outdoor conditions release of the substances to water and soil is to be considered depending on the water solubility of the substances.
- 133. For all substances with a high volatility (normally non-intendedly applied substances) a 100 %-emission to air can be assumed.
- 134. Data on recycling of textiles (reuse as garments, reuse in spinning mills or non-woven manufacturing, and the reuse of man-made fibres in polymer processing) are not available. This item is therefore not taken into account in this document.
- 135. Regarding waste elimination, a generic model for releases from landfills is under development and might be used once the model is available.

9 BRANCH SPECIFIC PARAMETERS

9.1 Daily production volume ($Q_{textile}$) of a generic point source

- 136. Statistical data for wastewater, dilution factors and production quantities for the textile finishing industry in Germany were obtained and statistically evaluated in a research project of the Umweltbundesamt [Böhm et al. 1997, 2000]. A comprehensive questionnaire was sent to companies in this branch and the data received were used to define the key default values so far applied in the EU exposure assessment in the aquatic compartment, e.g. the production volume per day. The return rate of the questionnaire was about 60%, so that the survey can be regarded as representative for Germany and the data could be evaluated statistically. As a result of this study the realistic worst case for the daily production volume of a generic German textile finishing plants can be determined to be 13 t/d. This value is approved by expert judgement [EnviroTex, 2002b].
- 137. After personal information [Peyrache, 1999] the daily production in textile finishing in France is estimated to 1,500-1,600 t/a resp. 6-7 t/d. In the US an average daily production of 9.1 t can be assumed [US, 2002].
- 138. The daily production volume ($Q_{textile}$) of 13 t/d for all type of fibres should be taken as realistic worst case for the PEC calculation, when no detailed in the best case statistically based data for the daily production volume are known.

9.2 Number of working days

139. The median of number of working days in 1995 was 225 days per year (arithmetical mean: 228 days per year) [Böhm et al. 1997, 2000]. One-, two- and three-shift operation is common in the European finishing industry.

9.3 Application amount $(Q_{product})$

- 140. The application amount (mass of substance used per mass of fabric) is besides the fixation rate and substance losses due to residual liquors (see Chapter 9.4) a basic parameter to calculate the relevant emissions.
- 141. If emissions are calculated on the basis of a daily production volume (see Chapter 10), it has to be taken into account that in nearly no case only one dyestuff is used to dye the daily production. Auxiliaries behave similarly. Normally several types of auxiliaries, which belong to the same class (e.g. levelling agents, repellents) are used.
- 142. The amount of dyestuffs used per site and day depends on the quantity of substrates and the amount of lots, which are dyed per day. The kind of auxiliaries changes also: e.g. very often 2-5 different levelling agents, 1-3 different carriers, 1-3 different detergents are used. Most of the auxiliaries are specific for definite substrates (PES, PA, CO etc.); therefore the amount of different auxiliaries per auxiliary type increases with the increase of substrate types.
- 143. For dyestuffs the study of Böhm et al. [Böhm et al. 1997)] determined the following:

The daily production of a generic point source is generally not dyed with only one dyestuff per day. It could be evaluated, that the median share of processed coloured textiles per day using the main dyestuff is 30%. This percentage is used for correcting the generic daily production volume when emissions from dyestuff are calculated: $F_{dyestuff} = 0.3$.

- However this is a rough estimation. Annually 200-300 different dyestuff types are used in textile finishing plants. In most cases only dyestuffs for dark shades are used predominantly.
- For auxiliaries and basic chemicals a factor 0.3 ($F_{auxiliary} = 0.3$) might be also a realistic correction factor.
- 146. If releases in pre-treatment are regarded, it is necessary to know how many different kinds of articles are finished per day. Kind and quantity of fibre by-products (preparation agents, sizes, biocides) depend on the article types (e.g. polyester knit wear; cotton woven textile etc.). For commission finishers the quantity of articles is much higher than for integrated mills.
- 147. However, due to the fact, that a worst case estimation has to be carried out, the scenario of an integrated mill, which has similar articles with no significant differences in fibre by-products is regarded. Therefore a factor (see above) is not introduced for emission calculation in pre-treatment.

9.3.1 Auxiliaries applied in upstream processes

148. The amount of auxiliaries, which are carried off from upstream processes to finishing varies due to the different type of auxiliaries. For preparation agents values between 0.5 and 3 weight % are typical; as a default value 2 weight % (20 kg/t) can be assumed. Sizing agents are applied in a range between 2-20 weight % on the warp yarns; as default a value 10 weight % (100 kg/t) on the fabric can be estimated. For biocides applied in up-stream processes see Chapter 7.1.2 and Annex II.

9.3.2 Basic chemicals used in finishing

149. The mass of basic chemicals per mass of fabric depends strongly on the chemicals, the foreseen effect of the chemicals, the processes, and the textile substrates. To give default values it would be necessary to present further details, which is not the focus. Typical recipes and input values for basic chemicals are given in the UBA-BREF [UBA-BREF, 2003].

9.3.3 Textile auxiliaries

150. In a rough estimation it can be assumed that in exhaust processes an auxiliary is added in an amount of 20 kg/t textile to the bath (2 %). In continuous and semi-continuous dyeing an amount of 30 kg/t textile can be roughly estimated (besides basic chemicals mainly complexing agents, antifoaming agents, antimigration agents and wetting agents are used in the padding liquors). Normally padding liquors for functional finishing (softeners, easy-care etc.) contain the auxiliary in an amount of approx. 5-50 kg/t textile. A typical value is 20 kg/t textile (see [UBA-BREF, 2003]).

Note: for some effects (e.g. easy-care, flame retardants) the application amount can be much more higher.

9.3.4 Dyestuffs

151. In a realistic worst case dyestuff formulations in powder form, which contain the dyestuff component in a range between 25-80 %, are used in an amount of 5 % (50 kg/t textile) for all dyeing techniques (discontinuous, continuous and semi-continuous dyeing). For liquid dyestuff formulations (amount of dyestuff components: 10-40 %) 10 % (100 kg/t textile) can be assumed as a realistic worst case. However it is to be mentioned that these data are typical for deep shades. Therefore information from the dyestuff manufacturer concerning the maximum depth of shade should be given in the chemical dossier.

9.3.5 Printing

152. Printing pastes are concentrated mixtures of different basic chemicals, auxiliaries and dyestuffs. Typical recipes are summarized in the UBA-BREF [UBA-BREF, 2001]. The amount of printing paste applied on the textile depends strongly on the pattern to be achieved; an amount of 0,75-1 kg printing paste per kg textile can be assumed as typical. Due to relatively high losses of printing pastes (residual liquors, cleaning of the equipment) the amount of dyestuffs used per kg textile is higher compared to the abovementioned dyeing techniques.

9.3.6 Coating

153. Application amount of polymer dispersions in coating processes is in most cases more than 100 kg/t textile. Depending on the thickness of the coating layer to be achieved, the application amount can vary strongly and can be much more higher than 100 kg/t textile.

9.3.7 *Summary*

154. The above-mentioned values concerning the application amount of basic chemicals, auxiliaries and dyestuffs (amount of product per mass of textile = $Q_{product}$) for different textile technologies are compiled in Table 10. Unless no data are available these figures are taken as default values.

Table 10: Typical application amounts (Q_{product})

| Product | Process | Application |
|-------------------------|---------------------------------|-----------------------------|
| | | amount |
| | | Q _{product} [kg/t] |
| Preparation agents | Upstream processes to finishing | 20 |
| | | (2%) |
| Sizing agents | Weaving | 100 |
| | | (10%) |
| Basic chemicals | Finishing | varies strongly; no |
| | | default value |
| | | possible |
| Auxiliaries | Finishing, exhaust processes | 20 |
| | | (2%) |
| Auxiliaries | Finishing semi-continuous and | 30 |
| | continuous processes | (3%) |
| Auxiliaries | Padding liquors functional | 20 |
| | finishing | (2%) |
| Dyestuffs (powder form) | Dyeing, printing | 50 |
| | | (5%) |
| Dyestuffs (liquid) | Dyeing, printing | 100 |
| | | (10%) |
| Printing paste | Printing | 750-1000 |
| | | (75-100%) |
| Coating paste | Coating | >100 |
| | | (>10%) |

It is to be mentioned that in most cases auxiliaries are aqueous solutions/dispersions. The amount of active ingredients can vary strongly.

9.4 Rate of release to waste water and degree of fixation

9.4.1 Auxiliaries applied in upstream processes

155. On the basis of a realistic worst case scenario for auxiliaries used in upstream processes (e.g. spinning and weaving) to improve the technological behaviour of the fibres, yarn and fabrics a 100 % release in textile finishing (mainly in pre-treatment processes) can be estimated. Therefore as default value for the fixation rate $F_{\text{Fixation}} = 0$ can be assumed.

9.4.2 Basic chemicals

156. Basic chemicals, which are not creating an effect on the textile (inorganic salts, acids, lyes, reducing and oxidising agents are released to approx. 100 %. As default value for the fixation rate $F_{Fixation} = 0$ can be assumed. However it is to be mentioned that the chemicals can react during application and in the wastewater (e.g. lyes can be neutralised by acids in the water path).

9.4.3 Auxiliaries in pre-treatment

157. Auxiliaries used in pre-treatment (detergents, complexing agents, desizing agents etc.) are not intended to fix on the textile. The degree of fixation $F_{fixation} = 0$.

9.4.4 Exhaust processes

158. In exhaust processes the release rate of the substances depends mainly on the rate of fixation.

9.4.4.1 Textile auxiliaries

- 159. The degree of fixation for auxiliaries and dyestuffs depend on the affinity of the chemical to the fibre, the liquor ratio, temperature, time, pH, additives, kind and quantity of rinsing processes etc.. Therefore thorough knowledge about optimum conditions is necessary to minimise losses to the wastewater.
- 160. For textile auxiliaries, which are not intended to fix on the textile and to create an effect, it can be assumed in a rough estimation that the fixation rate is 0 %. This is surely a worst case scenario: some auxiliaries (esp. carriers in PES dyeing) show considerable fixation rates up to 50 %. As default value for the fixation rate $F_{\text{Fixation}} = 0$ can be assumed.
- 161. For auxiliaries, which are intend to fix on the textile in exhaust processes, a fixation rate of 80 % can be taken as default value. It has to be mentioned that for optical brighteners and auxiliaries used in the after-treatment of dyeing processes the fixation rate can exceed 90 %.

9.4.5 Padding techniques, printing and coating

162. In contrast to exhaust processes where the rate of release depends only on the degree of fixation, for impregnation techniques (padding processes) printing and coating residual liquors have to be regarded additionally.

- 9.4.5.1 Padding of functional finishing agents (softening agents, repellents etc.)
- 163. The amount of residual liquors depends on
 - the structure of the company (in commission finishing with its high variety of processes normally higher amounts of residual liquors are observed in comparison to integrated finishing mills)
 - construction of the padding device
 - lot sizes (if only small lots are handled, the amount of residual liquors is much higher).
- 164. For a first estimation it can be assumed that residual liquors release 10 % of the total padding liquors. $F_{residual\ liquor} = 0.1$.

The degree of fixation in this case is $F_{fixation} = 1$.

- 9.4.5.2 Padding of dyestuffs (continuous and semi-continuous dyeing)
- 165. For a first estimation 10 % can be taken as default value for the loss due to residual liquors.

Note: after impregnation, in continuous and semi-continuous dyeing, the surplus of (non-fixed) dyestuff is washed out. Therefore in this case fixation rate of the dyestuffs (Table 11; fixation rate for continuous processes) and the dyestuff release by residual liquors has to be considered. $F_{residual\ liquor} = 0.1$.

9.4.5.3 *Printing*

- 166. Typical residual liquors are in a range between 20 30 %.
- For a realistic worst case estimation $F_{residual liquor} = 0.25$ would be the default value.
- 168. In all cases except pigment printing dyestuff release in washing processes which follows the printing have to be regarded additionally to the release via residual liquors. Fixation rates for dyestuffs used in printing are given in Table 11.
- With except to pigment printing the fixation rate for auxiliaries and chemicals can be estimated to $F_{fixation} = 0$. For pigment printing where no aqueous after-treatment of the printed textile is carried out the fixation rate $F_{fixation} = 1$.

9.4.5.4 *Coating*

- 170. Approx. 99 % of the coating liquors remains on the textile.
- 171. For a realistic worst case estimation $F_{residual liquor} = 0.01$ would be the default value.
- 172. The degree of fixation in this case is $F_{fixation} = 1$.

9.4.5.5 Dyestuffs

173. Normally the degree of fixation can be taken from the chemical dossier. Typical fixation rates (differences for printing, batch- and continuous dyeing are partially considered) are compiled in Table 11).

Table 11: Estimated degree of fixation for different types of dyes, processes and fibres [Commission of the EU, 1992] and additional information from [ETAD, 2002a)

| Type of Dye | Process | Type of fibre | Average degree of | Range [%] |
|---------------------------------|---------|------------------|-------------------|-----------|
| | (1) | (2) | fixation [%] | _ |
| | | | = Default value | |
| Disperse | C | CE, PES | 95 | 88 – 99 |
| Disperse | P | | 97 | 91 – 99 |
| Disperse | В | PES | 97 | 95 – 99 |
| Direct | В | CO | 88 | 64 – 96 |
| Reactive | В | WO | 95 | 90 – 97 |
| Reactive | В | CO | 75 | 65 – 90 |
| Reactive | C | CO | 80 | 70 – 95 |
| Reactive | P | | 75 | 60 – 90 |
| Vat | C | CO | 85 | 80 - 95 |
| Vat | P | | 75 | 70 - 80 |
| Vat | | CO | 90 | 85 – 95 |
| Sulfur | С | CO | 70 | 60 – 90 |
| Sulfur | P | | 70 | 65 – 95 |
| Acid, 1 SO ₃ -group | В | PA, PAN | 90 | 85 – 93 |
| Acid, >1 SO ₃ -group | В | | 95 | 85 – 98 |
| Basic | В | PAN, PES, PA, CO | 99 | 96 – 100 |
| Azoic (naphtol) | C | | 84 | 76 – 89 |
| Azoic (naphtol) | P | | 87 | 80 - 91 |
| Metal complex | В | | 94 | 82 - 98 |
| Pigment | C | | 100 | |
| Pigment | P | | 100 | 98 – 100 |
| Unknown/hardly | С | | 97 | 85 – 99.5 |
| soluble | | | | |
| Unknown/acid groups | P | | 90 | 85 – 95 |

⁽¹⁾ Processes: c = continuous dyeing; p = printing; b = batch dyeing

9.4.6 Summary

174. The above-mentioned values for the degree of fixation of chemicals/auxiliaries and dyestuffs are summarized in Table 12.

Table 12: Degree of fixation ($F_{fixation}$), amount of residual liquors ($F_{residual\ liquor}$)

| Product | Process | Degree of fixation F _{fixation} | $\begin{array}{c} \textbf{Residual liquors} \\ \textbf{F}_{residual \ liquor} \end{array}$ |
|-----------------|--|--|--|
| Auxiliaries | Upstream processes to finishing | 0 | - |
| Basic chemicals | Pre-treatment, dyeing, printing, finishing | 0 | - |
| Auxiliaries | Pre-treatment | 0 | - |

⁽²⁾ Fibres: **P** = protein; **CO** = cotton; **WO** = wool; **CE** = cellulose; **PES** = polyester; **PA** = polyamide; **PAN** = polyacrylonitrile

| Auxiliaries not intended to fix on the textile | Exhaust processes | 0 | - |
|--|------------------------------|------------------------|-----------------|
| Auxiliaries intended to fix on | Exhaust processes | 0.8 | - |
| the textile | | (in some cases higher) | |
| Auxiliaries | Padding functional finishing | 1 | 0.1 |
| Auxiliaries | Pigment printing | 1 | 0.25 |
| Auxiliaries | Printing | 0 | 0.25 |
| | (except pigment printing) | | |
| Auxiliaries | Coating | 1 | 0.01 |
| Dyestuffs | continuous and | see Table 11 | cont./semicont. |
| | discontinuous dyeing, | (amount of | dyeing: 0,1 |
| | printing | residual liquors has | printing: 0,25 |
| | | to be considered in | |
| | | addition) | |

10 EMISSION CALCULATION

- 175. The life stages "production" and "formulation" of the chemicals and auxiliaries used in textile finishing can be calculated by applying the appropriate A- and B-Tables of the Technical Guidance Document [EU, 2003].
- 176. The scenarios in this report are presented in the following way:

Input

[Variable/parameter (unit)] [Symbol] [Unit] S/D/O/P

These parameters are the input to the scenario. The S, D, O or P classification of a parameter indicates the status:

- S Parameter must be present in the input data set for the calculation to be executed. The applicant presents this value.
- D Parameter has a default value. The assessor on good grounds can change them.
- O Parameter is the output from another calculation.
- P Parameter value can be chosen from a "pick-list" (Table).

Output

[Symbol] [Description]

- 177. The emission estimation is performed on a local scale except for emissions from articles during service life. The calculation of the local emission of a substance to surface water is described in the Chapter 10.1. The air pathway can be calculated via an emission factor concept, which is well established in Germany (see Chapter 10.2). If relevant, the "soil" and also the "air" pathway can be calculated by the respective A- and B-Tables of the Technical Guidance Document (EU, 2003).
- 178. Emissions from articles during their service life are described in Chapter 10.3.

10.1 Calculation of emissions to water

179. It should be noted that ESDs are intended to provide information to make estimates of emissions into the different compartments of the environment where release initially occurs. Regarding the aqueous emission pathway it is not purpose of ESDs to consider the downstream reduction potential of wastewater treatment plants. This aspect is taken into account in the exposure evaluation.

10.1.1 Pre-treatment

180. The local emission of substances (preparation agents, sizing agents, biocides from imported fabrics/fibres), which are emitted in pre-treatment processes to water during a working day, is calculated as follows:

| Variable/parameter (unit) | Symbol | Unit | Default | S/D/O/P |
|--|-------------------------|--------------------|--------------|---------|
| Input: | | | | |
| Mass of textile processed per day | $Q_{textile}$ | t d ⁻¹ | Chapter 9.1 | D |
| Mass of auxiliary (preparation agents, sizing agents, biocides) per mass of fabric | $Q_{product}$ | kg t ⁻¹ | Table 10 | D/S |
| Content of active substance in preparation | $C_{\text{substance}}$ | - | 1 | D/S (1) |
| Degree of fixation | F_{fixation} | - | 0 (Table 12) | D/S |
| Output: | | | | |
| Local emission of substance per day to waste water | Elocal _{water} | kg d ⁻¹ | | О |

⁽¹⁾ If the content of active substance in the preparation is not available, it should be assumed as 100 %.

Model calculation:

$$Elocal_{water} = Q_{textile} \times Q_{product} \times C_{substance} \times (1-F_{fixation})$$
 (1)

10.1.1.1 Example of calculation

181. The daily emission of a sizing agent to the water path is calculated as follows:

 $\begin{array}{lcl} Q_{fabric} & = & 13 \ [t/d] \ (see \ Chapter \ 9.1) \\ Q_{sizing \ agent \ formulation} & = & 100 \ [kg/t] \ \ default: \ Table \ 10 \end{array}$

 $C_{\text{sizing agent}} = 1$

 $F_{fixation} = 0$ default: Table 12

 $Elocal_{water} = Q_{fabric} \times Q_{sizing agent formulation} \times C_{sizing agent} \times (1-F_{fixation})$

Elocal_{water} = $13 \text{ t/d} \times 100 \text{ kg/t} \times 1 \times 1 = 1,300 \text{ kg/d}.$

10.1.2 Exhaust processes

182. The local emission of a substance (basic chemicals, dyestuffs, auxiliaries as softening agents, repellents, biocides etc.) used in exhaust processes to surface water during a working day is calculated as follows:

| Variable/parameter (unit) | Symbol | Unit | Default | S/D/O/P |
|---|------------------------|--------------------|----------------------|---------|
| Input: | | | | |
| Mass of textile processed per day | $Q_{textile}$ | $t d^{-1}$ | Chapter 9.1 | D |
| Fraction of fabric treated with one auxiliary, basic chemical or dyestuff | $F_{product}$ | - | 0.3 (Chapter 9.3) | D |
| Mass of auxiliary/basic chemical/dyestuff-preparation per mass of fabric | $Q_{product}$ | kg t ⁻¹ | Table 10 | D/S |
| Content of active substance in preparation of auxiliary, basic chemical or dyestuff | $C_{\text{substance}}$ | - | 1 | D/S (1) |

Degree of fixation $F_{fixation}$ - Table 12 D/S **Output:**Local emission of dyestuff per day to waste water $Elocal_{water}$ $kg d^{-1}$ O

(1) If the content of active substance in the preparation is not available, it should be assumed as 100 %.

Model calculation:

$$Elocal_{water} = Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times (1-F_{fixation})$$
 (2)

10.1.2.1 Example of calculation

183. The daily emission of a reactive dyestuff (powder form) for finishing cotton fabrics to the water path is calculated as follows:

 $Q_{fabric} = 13 [t/d] see Chapter 9.1$

 $F_{dye} = 0.3$

 $Q_{dye} = 50 [kg/t]$ default: Table 10

 $C_{dye} = 0.5$

 $F_{fixation} = 0.85$ default: Table 11

 $Elocal_{water} = Q_{fabric} \times F_{dye} \times Q_{dye} \times C_{dye} \times (1\text{-}F_{fixation})$

 $Elocal_{water} = 13 \text{ t/d} \times 0.3 \times 50 \text{ kg/t} \times 0.5 \times 0.15 = 14,6 \text{ kg/d}$

10.1.3 Padding processes, printing, coating

184. The local emission of a substance (basic chemicals, dyestuffs, auxiliaries as softeners, repellents biocides etc.) used in padding processes and printing to surface water during a working day is calculated as follows:

| Variable/parameter (unit) | Symbol | Unit | Default | S/D/O/P |
|---|------------------------------|--------------------|----------------------|---------|
| Input: | | | | |
| Mass of textile processed per day | Q _{textile} | t d ⁻¹ | Chapter 9.1 | D |
| Fraction of fabric treated with one auxiliary, basic chemical or dyestuff | F_{product} | - | 0.3 (Chapter 9.3) | D |
| Mass of auxiliary/basic chemical/dyestuff- preparation per mass of fabric | Q _{product} | kg t ⁻¹ | Table 10 | D/S |
| Content of active substance in preparation of auxiliary, basic chemical or dyestuff | $C_{\text{substance}}$ | - | 1 | D/S (1) |
| Degree of fixation | F_{fixation} | - | Table 12 | D/S |
| Amount of residual liquors | $F_{\text{residual liquor}}$ | | Table 12 | D/S |
| Output: | | | | |
| Local emission of dyestuff per day to waste water | Elocalwater | kg d ⁻¹ | | O |

⁽¹⁾ If the content of active substance in the preparation is not available, it should be assumed as 100 %

Model calculation:

$$\begin{aligned} Elocal_{water} &= \{Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times (1 - F_{fixation})\} \\ &+ \{Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times F_{residual \ liquor}\} \end{aligned} \tag{3}$$

10.1.3.1 Example of calculation

 Q_{fabric}

185. The daily emission of a reactive dyestuff to the water path (continuous dyeing of cotton fabric; liquid dyestuff) is calculated as follows:

```
F_{dve}
Q_{\text{dye}}
                         100 [kg/t] default: Table 10
C_{dve}
                   = 0.2
F_{\text{fixation}}
                                       default: Table 11
                         0.8
                         0.1
                                       default: Table 12
F_{residual\ liquor} =
Elocal_{water} = \{Q_{fabric} \times F_{product} \times Q_{product} \times C_{substance} \times (1 - F_{fixation})\}
                           + \{Q_{fabric} \times F_{product} \times Q_{product} \times C_{substance} \times F_{residual liquor} \}
                          \{13 \text{ t/d} \times 0.3 \times 100 \text{ kg/t} \times 0.2 \times 0.2\}
Elocal<sub>water</sub> =
                           + \{13 \text{ t/d} \times 0.3 \times 100 \text{ kg/t} \times 0.2 \text{ x } 0.1\} = 23.4 \text{ kg/d} \text{ (bitte nachprüfen)}
```

10.2 Calculation of emissions to air

= 13 [t/d] see Chapter 9.1

186. The emission potential concerning off-gas of finishing recipes, which are dried/cured on a stenter, as well as the emission potential of preparation agents can be calculated in an easy way following the so-called emission factor concept which has been developed in Germany in co-operation between the public authorities at national and federal states level, the German Association of Textile Finishing Industry (TVI-Verband) and the Association of Textile Auxiliary Suppliers (TEGEWA) [Bavaria, 1994; LAI, 1997; Schmidt, 1995]. The emission factor concept defines substance emission factors and textile substrate-based emissions factors.

Substance emission factor:

- 187. The substance emission factor is defined as the amount of organic and inorganic substances in gram, which can be released under defined process parameters (curing time, temperature, substrate) from one kg of auxiliary. Typical substance emission factors are compiled in the UBA-BREF [UBA-BREF, 2000].
- 188. There is to differentiate between:
 - fc indicating the total emissions of organic substances expressed as total content of carbon
 - and fs indicating the emission of a specific substance in case of toxic or carcinogenic organic substances or in the case of particular inorganic substances like ammonia, hydrogen chloride.
- 189. The substance emission factors have to be provided as product information (further to information in the Material Safety Data Sheets) from the supplier (chemical industry) to the user (textile finishing industry). All substances according to class I 3.1.7 TA-Luft exceeding 500 ppm in the auxiliary have to be declared. In addition, information on substances classified under item 2.3 TA-Luft (carcinogenic substances) exceeding 10 ppm is obligatory [TA-Luft, 1986]. They are either measured or calculated by a concept of the chemical industry [TEGEWA, 1994].

Textile substrate-based emission factor:

- 190. The textile material based emission factor is defined as the amount of organic and inorganic substances in gram which can be released under defined process parameters from one kg of textile material in
 - WFc: g organic C/kg textile substrate
 - WFs: g special substance/kg textile substrate in case of more toxic or carcinogenic organic substances or in the case of particular inorganic substances like ammonia, hydrogen chloride.
- 191. The emission potential of each finishing recipe can be calculated on the basis of the individual substance emission factors, the concentration of the auxiliaries in the recipe and the liquor pick-up.
- 192. The total process emissions of the finishing recipe WF, referred to the sum of auxiliary input in a formulation, are obtained by adding up the emissions of the individual input auxiliaries within the same classes (fs and fc).
- 193. Examples for the calculation of textile substrate-based emission factors for typical recipes are given in Table 13.
- 194. Information on substance based emission factors a prerequisite for the above mentioned calculation of textile substrate based emission factors is given by the textile chemical industry [TEGEWA, 1994; LAI, 1997]

Table 13: Two examples for the calculation of emission factors of a finishing recipe

| Recipe | Auxiliaries | FK | FA | Substrate | T [°C] | fs [g/g] | fc [g/g] | FK*FA | FK*FA | WFs | WFc |
|----------|---------------------|--------|---------|-----------|--------|----------|----------|-------|-------|--------|--------|
| | | [g/kg] | [kg/kg] | | | | | *fs | *fc | [g/kg] | [g/kg] |
| Recipe 1 | Fatty acid ester | 20 | 0.65 | CO | 170 | - | 0.0152 | | 0.2 | - | - |
| A | Polysiloxane | 20 | 0.65 | CO | 170 | =. | 0.0052 | =. | 0.07 | - | - |
| В | Reactant cross- | 100 | 0.65 | CO | 170 | 0.0041 | 0.0009 | 0.27 | 0.06 | - | - |
| | linking | | | | | FO | | FO | | | |
| | agent/catalyst | | | | | | | | | | |
| C | Stearylurea- | 20 | 0.65 | CO | 170 | 0.0165 | 0.0162 | 0,21 | 0.21 | - | - |
| | Derivative/catalyst | | | | | FO | | FO | | | |
| Total 1 | | - | - | - | - | - | - | - | - | 0.48 | 0.54 |
| | | | | | | | | | | FO | |
| Recipe 2 | Softening agent | 50 | 1 | CO | 150 | - | 0.005 | | 0.25 | - | - |
| D | Easy-care | 12 | 1 | CO | 150 | - | 0.010 | - | 0.12 | - | |
| | crosslinking agent | | | | | | | | | | |
| | (formaldehyde- | | | | | | | | | | |
| | free) | | | | | | | | | | |
| E | Easy-care catalyst | 12 | 1 | CO | 150 | - | 0.008 | - | 0.1 | | - |
| Total 2 | | | | | | | | | | - | 0.47 |

FK: Liquor concentration in g auxiliary/kg liquor FA: Liquor pick-up in kg liquor/kg textile substrate

Substrate: textile good to be finished

CO: cotton

T: Finishing temperature in °C

fs: Substance emission factor of an auxiliary in g emission/g auxiliary

fc: Total carbon substance emission factor of an auxiliary in g emission/g auxiliary

WFs: Textile substrate-based emission factor of a recipe in g emission/kg textile substrate = $\Sigma(FK*FA*fs)$ WFc: Textile substrate-based total carbon emission factor of a recipe in g emission/kg textile substrate =

 $\Sigma(FK*FA*fc)$

FO: Formaldehyde

195. The local emission of a substance to air during a working day is calculated as follows:

| Variable/parameter (unit) | Symbol | Unit | Default | S/D/O/P |
|--|----------------------|--------------------|-------------------|---------|
| Input: | | | | |
| Mass of textile processed per day | Q _{textile} | t d ⁻¹ | Chapter 9.1 | D |
| Mass of auxiliary/basic chemical/dyestuff- preparation per mass of fabric | Q _{product} | kg t ⁻¹ | Table 10 | D/S |
| Fraction of fabric treated with one auxiliary, basic chemical or dyestuff | $F_{product}$ | - | 0.3 (Chapter 9.3) | D |
| Substance emission factor of auxiliary /basic chemical/dyestuff | fs | g/g | | S |
| Output: | | | | |
| Local emission of substance per day to air | Elocalair | kg d ⁻¹ | | О |

Model calculation

 $Elocal_{air} = Q_{textile} \times Q_{product} \times F_{product} \times fs$ (4)

10.2.1.1 Example of calculation

196. The daily emission of formaldehyde ex auxiliary B (Table 13) to air is calculated as follows:

 $Q_{fabric} = 13 [t/d] (see Chapter 9.1)$

 $F_{\text{auxiliary B}} = 0.3 [g/g]$

 $Q_{auxiliary B} = 65 [kg/t] (= FK x FA; see Table 13)$

fs = 0.0041 [g/g]

Elocal_{air} = $13 \text{ t/d} \times 0.3 \times 65 \text{ kg/t} \times 0.0041 \text{ g/g} = 1.0 \text{ kg/d}$

10.3 Emissions from articles during their service life

197. Articles may have a service life longer than one year. Chemical substances in such articles may accumulate in society. Thus the emission estimation is treated in this scenario.

| Variable/parameter (unit) | Symbol | Unit | Default | S/D/O/P |
|--|-----------------|-------------------|---------|---------|
| Input: | | | | |
| Annual input of the substance in article k | $Qtot_k$ | t a ⁻¹ | | S |
| Fraction of the continent | F_{cont} | - | 0.9 | D |
| Fraction of the region | F_{reg} | - | 0.1 | D |
| Service life of article k (Table 9) | $Tservice_k$ | y | | P |
| Fraction of substance emitted over one year during service life to compartment j | F_j | - | | D |
| Emission duration per year | N_d | $d a^{-1}$ | 365 | D |
| Output: | | | | |
| Total emission to compartment j | $Etot_{k,j} \\$ | t d ⁻¹ | | 0 |
| Continental emission to compartment j | $Econt_{k,j}$ | | | O |
| Regional emission to compartment j | $Ereg_{k,j} \\$ | | | |

Model calculation:

$$\mathbf{Etot_{k,j}} = \{ F_j \times Qtot_k \times \sum_{y=1}^{Tservice_k} (1 - F_j)^{y-1} \} / N_d \qquad (5)$$

$$Econt_{k,j} = Etot_{k,j} \times F_{cont}$$
 (6)

$$Ereg_{k,j} = Etot_{k,j} \times F_{reg}$$
 (7)

10.3.1 Example of calculation

198. The calculation of the total daily emission to the water path of a chemical substance during service life of an article $(Qtot_k)$ with a service life of 2 years is shown below. It is assumed that 10 % (a fraction of 0.1 = Fwater) of the substance is released from the article per year to the water path.

Compartment j = water

 $\begin{array}{lll} Qtot_k & = & 2,000 \text{ t/a} \\ Tservice_k & = & 2 \text{ y} \end{array}$

 F_{water} = 0.1

 $= \{0.1 \text{ x } 2,\!000 \text{ t/a x } (1\text{-}0.1)^0 \} + \{0,\!1 \text{ x } 2,\!000 \text{ t/a x } (1\text{-}0.1)^1 \} / 365 \text{ d/a}$ = (200 t/a + 180 t/a) / 365 d/a = 1.04 t/a $Etot_{water} \\$

Etot_{water}

 $Econt_{water} \\$ = 937.0 kg/d= 104.1 kg/d**Ereg**_{water}

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12 GLOSSARY

Auxiliary: A textile auxiliary is a preparation of chemical substances, mostly delivered in an aqueous solution (e.g. softening agents, repellents, antimicrobial finishing agents containing biocides etc.) used in finishing processes.

Basic chemical: Chemicals as lyes, acids, salts and oxidizing and reducing agents.

Beam: Any of a series of machines for dyeing that use a perforated beam through which the dye bath is circulated.

Beck: Any of a series of machines for scouring (cleaning), dyeing, etc., goods while in the form of rope or continuous belt. A roller gradually moves the cloth through the bath in a slack condition.

Carding: Fibres are separated and aligned in a thin web, then condensed into a continuous, untwisted strand called a 'sliver'.

Combing: Processing cotton or wool stock through a series of needles (or combs) to remove short fibres and foreign matter.

Desizing: Removal of size material from greige (gray) goods to prepare for bleaching, dyeing, etc.

Drafting: A process that uses a frame to stretch the yarn. This process imparts a slight twist as it removes the yarn and winds it onto a rotating spindle.

Drawing: Straightening and paralleling the fibres after combing or carding.

Greige: Fabrics in unbleached, undyed state prior to finishing. Also referred to as "gray" or "grey" goods.

Jet dyeing: A tubular machine utilising water jets to circulate fabric in a dye bath.

Jig: An open vat that passes full width cloth from a roller through a dye liquor and then on to another roller.

Knitting: Process for making a fabric by interlocking in series the loops of one or more yarns. Types include: jersey (circular knits), tricots (warp knits), and double knits.

Liquor pick-up: Mass of padding liquor [kg] impregnated to the textile per mass of textile to be impregnated [kg] \times 100 %

Liquor ratio: mass of textile [kg] to be dyed per volume of water used in dye bath [L]

Mercerising: A process given to cotton yarns and fabric to increase lustre, improve strength and dye ability. Treatment consists of impregnating fabrics with cold concentrated caustic soda solution under tense stress.

Padding: Impregnation of the textile in a padding machine (foulard) and removal of the liquor surplus by means of a squeeze roller

Scouring: removal of natural and acquired impurities from fibres, yarns, or fabrics through washing in alkaline solutions.

Singeing: A fabric or yarn is passed over an open gas flame at a high speed to burn off the loose surface fibres.

Sizing: Applying starch, PVA or CMC etc. to warp yarns to minimise friction during weaving.

Spinning: A process by which a large strand of fibres is drawn out to a small strand and converted into a yarn. After drawing out (or drafting), twist is inserted, and the resulting yarn is wound into a bobbin.

Texturising: it is often used to curl or crimp straight rod-like filament fibres to simulate the appearance, structure, and feel of natural fibres.

Tufting: A process used to create carpets, blankets, and upholstery.

Warping: A warp is a set of length-wise yarns in a loom through which the crosswise filling yarns (weft) are interlaced.

ANNEX I

(Overview on the most important auxiliaries and basic chemicals, their technological effect, and their chemical composition used along the textile chain)

| Process | Auxiliary | Effect | Chemical composition |
|---|---|---|---|
| Manufacturing of man-made fibres, coning, texturizing, spinning, twisting, winding, warping, weaving, knitting | Preparation agents (preparation agents for primary spinning, lubricants, conditioning agents, coning oils, warping oils, twisting oils, knitting oils) | Increasing processability, protection of fibres/yarns; adjusting of friction properties; impart of antielectrostatic properties; improve of coning, texturizing etc. | Mineral oils, common fatty acid esters, ethylene oxide-propylene oxide adducts, hindered fatty acid esters, polyolesters, polyester-polyethercarbonates, silicones, additives (emulsifiers, antistatic agents, corrosion inhibitors, anionic/non-ionic surfactants) |
| Sizing | Sizing agents, sizing additives | Protection of warp yarns during weaving (Applied in weaving mills) | Macro-molecular natural or synthetic products (starch, modified starch, modified celluloses, polyvinyl alcohol, polyacrylates, polyesters) Additives (oils, waxes, starch solubilizing agents (peroxides)) |
| Pre-treatment | | | |
| All pre-treatment steps | Fibre protecting agents | Protection of the fibre and reduction of affection of the fibre during pre-treatment processes | Protein fatty acid condensates and Guanidinium derivatives |
| Desizing | Desizing agents | Removal of sizing agents | Enzymes (amylases) for enzymatic desizing; mono- and di-persulfates for oxidative desizing; surfactants, complexing agents |
| Scouring (kierboiling) | Scouring auxiliaries | Removal of fibre by-products (fats, waxes, pectines, inorganics etc.) from cellulose fibres in cellulose materials or blends of cellulose fibres with synthetic fibres | Strong alkali; alkaline-resistant and electrolyte resistant surfactants (fatty alcohol ethoxylates, alkane sulfonates), complexing agents |
| Bleaching | Bleaching auxiliaries | Bleaching, whitening. | Peroxide, sodium chlorite, sodium hydroxide, dithionite and dithionite derivatives, complexing agents, surfactants stable in acidic or alkali conditions, silicates, polycarboxylic acids, sugar polymers as peroxide stabilizers, nitrates (anti-corrosion), polyacrylamide (crease-preventing) sodium sulfite, enzymes (catalases) to remove peroxide surplus |

| Process | Auxiliary | Effect | Chemical composition |
|---|--|---|--|
| Mercerising | Mercerising auxiliaries | Increase in dyestuff uptake and tensile strength of textiles by means of alkali treatment under tension | Strong alkali (sodium hydroxide; ammonia); wetting agents, stable in highly concentrated lyes (low molecular weight alkyl sulfates, alkane sulfonates), antifoaming agents as shorter-chain alkyl phosphates, complexing agents |
| Causticizing | Causticizing auxiliaries | See mercerising (no tension applied to textile) | See mercerising |
| Carbonizing | Carbonizing auxiliaries | Removal of vegetable impurities with acid or acid salts | Strong sulfuric acid, acid-stable wetting agents (alkyl arylsulfates, alkane sulfonates, fatty alcohol ethoxylates) |
| Optical bleaching | Fluorescent brighteners | Whitening | Stilbene, pyrazoline or benzeneazole derivatives |
| Dyeing/Printing | | | |
| Dissolving of dyestuffs | Dyestuff solubilizing and hydrotropic agents | Promotion of the dissolution of dyestuffs in water | Alcohols, polyols, fatty alcohol ethoxylates, esters |
| Dissolving of dyestuffs | Dispersing agents Protective colloids | Promotion of the formation and stability of dyestuff and pigment dispersions | Naphthalene sulfonic acid formaldehyde condensates, naphthaline sulfonates, lignosulfonates, fatty alcohol ethoxilates, alkylsulfonates, alkylaryl sulfonates, polyacrylates |
| Exhaust dyeing, padding processes | Wetting agents De-aeration agents | Increase of wetting capacity of the dye liquors; improve of dye penetration in padding processes; increase of dye absorption | Alkyl sulfates, alkane sulfonates, alkylaryl sulfonates, salts of sulfosuccinic acid esters, fatty alcohol ethoxilates, alcohols of higher valence, phosphoric acid esters, hydrocarbons, sequestring agents |
| Levelling | Retarding agents Migration agents Compensating agents Penetrating agents | Promotion of an even distribution of dyestuffs in the textiles | Alkyl -, alkyl aryl -, alkyl amine - and alkyl aryl amine ethoxylates, fatty acid esters and amides, fatty acid ethoxilates, fatty acid condensates, sulfonated PES-derivatives, polyvinyl pyrrolidone, quaternary ammonium salts, alkyl sulfates, alkyl aryl sulfonates |
| Exhaust dyeing (esp. PES, PES/WO) | Carriers | Acceleration of dye absorption, dye diffusion esp. for PES and PES/WO dyeing | Aromatic hydrocarbons, chlorinated aromatic compounds, benzoic acid esters (benzylbenzoate) phthalic acid esters, alkyl phthalimides, alkylphenolethoxilates |
| Skein dyeing of piece goods | Crease preventing agents | Crease preventing esp. during skein-dyeing of piece goods | Polyglykolethers, polyamide, polyacrylates, fatty alcohol ethoxilates, phosphoric acid esters, fatty acid esters |

| Process | Auxiliary | Effect | Chemical composition |
|----------------------------------|--|--|--|
| Exhaust dyeing | Dyestuff protecting agents, boildown | Protection of dyestuffs during application from destruction by | Buffers and/or oxidizing substances (nitrobenzene |
| | protecting agents | foreign matters with a reducing effect | sulfonate), urea, alkylaryl sulfonates |
| Padding | Padding auxiliaries Antimigration agents | Prevention of undesired migration of dyestuffs in or onto the textile | Polyacrylates, polyacryl amides, EO/PO-adducts, alkyl phosphates, alkyl aryl ether sulfates, alginates, polyacrylates, EO/PO-adducts, guar derivatives, polyacrylamide |
| | Antifrosting agents Wet pick-up increasing substances | Prevention of frosting effects in pad-steam processes. Increase of dye yield in reactive pad batch processes | polymers and copolymers. Foaming surfactants as ethylene oxide adducts. Polyacrylates, EO/PO adducts, alkyl aryl ether sulfates, |
| Continuous dyeing, printing | Fixing acceleration for continuous dyeing and printing | Acceleration of dye fixation and diffusion, increase of dyestuff yield | Aromatic ethers, fatty acid ethoxylates, polyglycols |
| After-treatment | After-treatment agents for fastness improvement | Improve of rubbing fastness, wet fastness and light fastness | Soaping after-treatment with detergents or dye-affinitive polymers. Cationic fixing agents for direct and reactive dyes (polyquaternary ammonium compounds, cationic formaldehyde condensates. Polysulfonates for improvement of polyamide dyeing with anionic dyestuffs. Reducing agents for PES. Heterocyclic compounds to improve light fastness (benzophenone, benzotriazole, benztriazine derivatives) Organic copper compounds resp. benzophenones for improvement of light fastness of PA resp. PES |
| Pigment dyeing, pigment printing | Bonding agents (also for pigment dyeing) | Fixing of inorganic and organic pigments onto the textiles (pigment printing) | Film-forming substances (styrene butadiene copolymers, polyacrylates, acrylate copolymers, polyurethane |
| Printing paste manufacturing | Thickeners | Adjusting of viscosity required in printing pastes | Alginates, galactomannanes, modified starch, polyacrylates, polysaccharide combinations, additives, esp. mineral oils |
| Printing paste manufacturing | Emulsifier | Dispersion of the pigments in the printing paste | Alkylarylethoxilates (APEO), fatty alcohol ethoxilates, isopropanol, N- methylpyrrolidone |
| Pigment printing | Fixation agents | Crosslinking of bonding agents | Melamine derivatives, urea formaldehyde condensates |

| Process | Auxiliary | Effect | Chemical composition |
|---------------------------------------|--------------------------------------|--|---|
| Printing | Agents to remove printing thickeners | Removal of printing thickeners | Alkylamine ethoxilates, fatty acid ethoxilates, fatty alcohol ethoxilates |
| Printing | Printing and edge adhesives | Printing adhesives fasten the goods to be printed onto the printing blanket | Water-soluble adhesives (starch, starch derivatives, vegetable gum, polyvinyl alcohol, polyvinylcaprolactam, polyacrylate etc.). Water-insoluble compounds |
| | | Edge adhesives (edge stiftening agents) for the hardening of edges, so that they do not role up in case of treatment in broad form (also used in pre-treatment and dyeing) | (polyvinyl acetate, polyacrylic acid esters). Polyvinyl alcohol, polyvinyl chloride, polyacrylic acid esters, polyvinyl acetate |
| Dyeing and printing | Oxidizing agents | Oxidizing of reduced forms of vat dyes, leucoester, vat dyes, and sulfur dyes | Peroxo compounds, sodium perborate, sodium persulfate, sodium chromate, salts of m- nitrobenzene sulfonic acid, bromite |
| | | Stripping (removal) of dyes and auxiliaries from the fibre | Sodium chlorite |
| Dyeing and printing | Reducing agents | Reduction of vat and sulfur dyes in order to transform them into the water soluble form | Vat Dyes: sodium dithionite, sulfinic acid derivatives Sulfur dyes: sodium sulfide, sodium dithionite, glucose and mixtures thereof. |
| | | Removal of dispersion dyes (reductive after-treatment) Destroy of dyes in case of faulty dyeing (stripping) | Sodium dithionite, thiourea dioxide. Sodium dithionite, sodium or zinc formaldehyde sulfoxylates, thiourea dioxide |
| Discharge printing | Discharging agents Discharging | Discharging agents are printed onto a pre-dyed textile material for the destruction of the dyes and thus cause a pattern | Reducing and oxidizing agents (see above) |
| | assistants | | Anthraquinone derivatives |
| Dyeing, resist printing | Resist agents | Reduced or completely prevention of dyeing/printing | Dyeing: inorganic salts, tannins, alkyl aryl -, aryl-, alkane sulfonates, aromatic sulfonates, anionic or polyanionic compounds |
| | | | Printing: aluminium and tin salts, alkali compounds |
| Dyeing and printing with mordant dyes | Mordants | Improvement of dye affinity of the fibre | Quaternary ammonium |
| Dyeing, colour correction | Brightening agents | Partial removal of the dye already absorbed and fixed | compounds, Al-, Cr-, Fe-salts Polyvinylpyrrolidone, polyglycol ether, cellulase, alkyl aryl sulfonates, alkyl amine ethoxylates, reducing agents and oxidizing agents |

| Process | Auxiliary | Effect | Chemical composition |
|--------------------------|---|--|---|
| Dyeing, fibre protection | Fibre-protective agents | Prevention or reduction of damage to the fibre during dyeing, finishing | Protein hydrolysates, polyglycol ether, protein fatty acid condensates, lignosulfonates, formaldehyde eliminating products (urea derivatives), |
| Dyeing in general | pH-regulators, acids and alkali dispensers | Adjust/control pH | guanidine derivatives Organic acids, esters, buffering salts |
| Dyeing in general | Salts | Increase of substantivity for reactive and direct dyes; levelling effect on acid dyes etc. | Sodium chloride, sodium sulfate etc. |
| Dyeing in general | Acids/alkali | Adjust pH | Organic acids (mainly acetic acid, formic acid, oxalic acid), inorganic acids (sulfuric acid, hydrochloric acid); sodium hydroxide, ammonia (in water), sodium carbonate |
| Finishing | | | |
| Optical brightening | Fluorescent brighteners | See pre-treatment | |
| Easy-care | Agents for the improvement of crease and shrink resistance Additives Catalysts | Increase of crease recovery and/or dimensional stability of textile materials | Dimethylolurea and dimethylolurea-derivatives, 1,3-dimethylol-4,5 dihydroxyethylene urea and – derivatives, melamine-derivatives, carbamates, cyclic urea compounds. Polyethylene dispersions, silicone emulsions |
| | | | Metal or ammonium salts and preparations of acids or alkalis |
| Handle | Handle imparting agents | | |
| | Weighting agents | Increase the basic weight of textiles | Pigments (kaolin, talcum); soluble compounds (urea, glycerine, salts) |
| | Filling and stiffening agents | Impart of a full handle and increase of stiffness (bending modulus) | Polyacrylates, polyvinyl acetate, polyurethane, polyvinyl alcohol, ethylenevinylacetate-copolymers, starch, modified starch |
| | Softening agents | Impart of a soft handle | Fatty acid condensation products, alkanolamides, waxes, paraffines, polysiloxanes, polyethylene, quaternary ammonium compounds |
| Anti-electrostatic | Anti-electrostatic agents | Prevention of electrostatic charging | Ethoxylation products of fatty acids, alkane sulfonates, alkyl aryl sulfonates, phosphoric acid esters, quaternary ammonium compounds, alkylamine oxides |

| Process | Auxiliary | Effect | Chemical composition |
|---|---|--|--|
| Repellents | Water repellents | Impart of a water-proof finish | Fluorocarbon resins, polysiloxanes, paraffins together with aluminium, zirconium and chromium compounds, |
| | Oil repellents | Impart of an oil-repellent finish | Fluorocarbon resins |
| | Soil repellents | Improve of soil repellent properties and removal of impurities | Polysiloxanes, fluorocarbon resins |
| | Soil release agents | Improve of soil release from textiles | Fluorocarbon resins, polyacrylates, fatty acid condensation products, polyurethane |
| Felting | Felting agents (animal fibres) | Promotion of felting during the milling operation | Fatty alcohol ethoxilates, alkyl sulfonates, fatty acid condensation products |
| Anti-felting | Anti-felting agents (animal fibres) | Reducing of shrink during washing | Reducing or oxidizing agents, chlorocyanurate, polysiloxane, polyurethane, polyamide- epoxide copolymers |
| Lustre | Lustring agents | Impart or increase of lustre (with or without connection to a mechanical treatment) | Emulsions of paraffins, waxes, polyolefins, polyglycols or polysiloxanes |
| | Delustring agents | Reduction of lustre | Pigments |
| Non-slip, ladder- proof | Non-slip, ladder- proof, anti-snag agents | Reduction of the slipping of various yarn systems and of ladders in knitwear. Prevention of snags in hosiery and other ready-made goods of continuous- filament yarns | Modified silicic acid, polyvinyl acetate, copolymers, acrylate-styrol copolymers |
| Flame resistance | Flame retardants | Reduction of inflammability and combustibility | Inorganics (e.g. ammonium salts), antimony trioxide in combination with halogenated synergists (chloroparaffins, brominated compounds), reactive P-organic compounds (e.g. derivatives of phosphonic acid dimethylester, derivatives of tetrakishydroxmethylphosphonium chloride, cyclic phosphonic acid esters) |
| Antimicrobiotics (rot-proofing, mould prevention) | Antimicrobiotic agents | Protection against microorganisms | Zinc organics, benzimidazole- derivatives, triclosane, isothiazolinone, chlorophene derivatives |
| Chemical bonding of non-wovens | Binder | Promotion of fibre bonding Additives | Polymers of acrylic acid esters, acrylonitrile, ethylene, butadiene, styrene, vinyl chloride, vinyl acetate. Latex, starch etc. Polyethers, N-methylol compounds etc. |

| Process | Auxiliary | Effect | Chemical composition |
|--|---|---|--|
| Coating | Coating agents | Production of adhesive layers on textile fabrics | Polymers of vinyl chloride, acrylic acid esters, acrylonitrile, ethylene, butadiene, styrene, vinylidene chloride, vinyl acetate. Natural latex, additives, filling materials |
| Laminating | Laminating agents | Bonding of two or more textile fabrics with other fabrics or foils | Natural or synthetic latexes, polyvinyl acetates, polyurethanes, polyacrylates, cellulose esters, polyethylene, polypropylene, polyvinyl chloride, additives |
| Textile auxiliaries for multipurpose use | Wetting agents | Increasing of wetting power | Alkyl sulfates, alkane sulfonates, alkyl aryl sulfonates, alkyl ether sulfates, alkyl esters of sulfosuccinic acids, ethoxylation products, phosphoric acid esters |
| | Anti-foaming agents | Prevention of foam in sizing, pre-treatment baths, printing pastes, dye baths and finishing baths | Phosphoric acid esters, hydrocarbons, high molecular alcohols, silicon and fluorine derivatives |
| | Foaming agents | Generation and stabilizing of foam if foam application is used | Sodium dioctylsulfosuccinate, ethoxilated tridecylalcohole |
| | Detergents, dispersing and emulsifying agents | | Soaps, alkyl sulfonates, alkyl aryl sulfonates, alkyl ether sulfates, EO-PO adducts, fatty alcohol ethoxilates, alkyl aryl ethoxilates |
| | Spotting agents | Removal of spots | Surfactants, solvents (hydrocarbons, chlorinated solvents) |
| After-treatment in yarn and fabric dyeing, raising, emerizing | Conditioning agents | Influencing of frictional behaviour and handle (softening effect) | See also preparation agents and softening agents; quaternary ammonium compounds, ethoxylation products of fatty acid- fatty amines etc. polysiloxanes, waxes, paraffines |
| Scouring, bleaching, mercerising, causticizing, desizing, dyeing, and printing. | Complexing agents | Complexing of heavy metals | Polyphosphates, phosphonates, polycarboxylates, (polyacrylates, polyacrylate-maleinic acid copolymers), sugar copolymers, hydroxy-carboxylic acids, amino carboxylic acids |

ANNEX II

(Data concerning biocide content of raw wool and raw cotton)

Table 14: Preservative chemicals on imported textiles [CEC, 1993]

| Material | Biocides | Concentration range (g/kg cloth) |
|----------|-------------|-----------------------------------|
| Wool | p, p' – DDE | 0.07 to 0.38 |
| | PCB – 28/31 | 0.15 to 0.34 |
| | Heptachlor | 0.03 to 0.12 |
| | Default | 0.38 |
| Cotton | p, p' – DDE | 0.85 to 4.5 |
| | p, p' – DDD | 0.09 to 12.8 |
| | p, p' – DDT | n.d. (not detected) to 12.4 |
| | Heptachlor | 0.13 to 0.45 |
| | Default | 12.4 |

Table 15: Constitution and rates of application of currently applied moth repellents for wool [Debon, 1999]

| Active component | Active content of formulation | | Amount of agent | Amount of agent |
|------------------|-------------------------------|---------|-----------------|-----------------|
| | [% w/v] | [% w/w] | applied [%w/w] | applied [kg/t] |
| Permethrin | 9.00 | 10.00 | 0.035 - 0.181 | 0.35 - 1.81 |
| | 10.00 | 12.05 | 0.029 - 0.150 | 0.29 - 1.51 |
| | 8.30 | 10.00 | 0.035 - 0.181 | 0.35 - 1.81 |
| Sulcofuron | 46.40 | 40.00 | 0.800 | 8 |
| | 37.95 | 33.00 | 0.970 | 9.7 |
| Permethrin/HHP* | 10.00 | 10.00 | 0.055 - 0.0825 | 0.55 - 0.825 |

^{*}HHP: Hexahydropyrimidine

As a worst case, a default value of 1% w/w (i.e. 10 kg/t) can be proposed if no further data is available.

In the last few years the Bremer Baumwollbörse analyzed raw cotton fibres from different countries. Investigations on defoliants, PCP, are summarized below [Bremen, 2000].

Table 16: Analyses Bremer Baumwollbörse (raw cotton fibres). Defoliants

| Substance | Limit values | Tests 09/11/00 | |
|-------------|--------------|----------------|----------------|
| 2,4,5-T | 0,05 ppm | Country/Region | Residues (ppm) |
| Dichlorprop | 0,05 ppm | Argentina | N.f. |
| Mecoprop | 0,10 ppm | Israel | N.f. |
| 2,4 - D | 0,10 ppm | Mali | N.f. |
| MCPA | 0,10 ppm | USA El Paso | N.f. |
| MCPB | 0,10 ppm | USA Pima | N.f. |
| Fenoprop | 0,10 ppm | Usbekistan | N.f. |
| DEF | 0,01 ppm | | |

| Tests 26/02/98 | |
|------------------|----------------|
| Country/Region | Residues (ppm) |
| Israel Acala | N.f. |
| Israel Pima | 0,008 DEF |
| Mexiko Juarez Ac | N.f. |
| Chad | N.f. |
| Turkmenistan | 0,006 DEF |
| Uzbekistan | N.f. |
| USA El Paso 1517 | N.f. |
| USA Pima | 0.010 DEF |

(Limit values according to German law for vegetable food); N.f. = not found

Table 17: Analyses Bremer Baumwollbörse (raw cotton fibres). PCP

| Tests in 1998 | | |
|------------------|-------------|----------------|
| Country/Region | <u>Test</u> | Residues (ppm) |
| Tschad | 26/02/98 | N.f. |
| USA El Paso 1517 | 26/02/98 | N.f. |

N.f. = not found

| TT 4 | • | 4000 |
|--------------|----|------|
| Tests | ın | 1996 |

| Country/Region | <u>Test</u> | Residues (ppm) |
|----------------|-------------|----------------|
| Cote d'Ivoire | 30/10/96 | N.f. |
| Mali | 30/10/96 | N.f. |
| Paraguay | 30/10/96 | N.f. |
| Senegal | 30/10/96 | N.f. |
| Chad | 30/10/96 | N.f. |
| Turkey rgd. | 30/10/96 | N.f. |
| Turkmenistan | 30/10/96 | N.f. |
| USA-Texas | 30/10/96 | N.f. |
| US Pima | 30/10/96 | N.f. |
| Usbekistan | 30/10/96 | N.f. |
| Zimbabwe | 30/10/96 | N.f. |

N.f. = not found

Table 18: Analyses Bremer Baumwollbörse (raw cotton fibres). Pesticides

Sum

Raw cotton fibres are tested for the following pesticides:

- 2,4,5-T (organochlorine compound)
- 2,4 D (organochlorine compound)
- Aldrin (organochlorine compound)
- Carbaryl (naphthylmethylcarbamate)
- DDD (organochlorine compound)
- DDE (organochlorine compound)
- Dieldrin (organochlorine compound)
- Alpha-Endosulfan (organochlorine compound)
- Beta-Endosulfan (organochlorine compound)
- Endrin (organochlorine compound)
- Hepatachlor (organochlorine compound)
- Heptachlorepoxid (organochlorine compound)
- Hexachlorbenzol (organochlorine compound)
- Alpha-Hexachlorcyclohexan (organochlorine compound)
- Beta-Hexachlorcyclohexan (organochlorine compound)
- 8-Alpha-Hexachlorcyclohexan (organochlorine compound)
- Lindane (organochlorine compound)
- Methoxychlor (organochlorine compound)
- Mirex (organochlorine compound)
- Toxaphene (Camphechlor) (organochlorine compound)
- Trifluralin (fluorinated compound)

Tests in 2000 [ppm] Country/Region

| country/region | | | | | | |
|----------------|----------|-------|------------|---------|----------|--------|
| | Date | DDT's | <u>НСН</u> | Lindane | Dieldrin | |
| Egypt | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Argentina | 09/11/00 | 0.034 | N.f. | N.f. | N.f. | 0.0340 |
| Benin | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Israel | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Camerun | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Mali | 09/11/00 | 0.048 | N.f. | 0.028 | N.f. | 0.0760 |
| Sudan Barakat | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Sudan Acala | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Syria | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Togo | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Chad | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| USA El Paso | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| USA Pima | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Usbekistan | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| Zimbabwe | 09/11/00 | N.f. | N.f. | N.f. | N.f. | 0.0000 |

N.f. = not found

Tests in 1998 [ppm] Country/Region

| | | | | | <u>Sum</u> |
|----------|--|--|--|---|--|
| Date | DDT's | <u>НСН</u> | Lindane | <u>Dieldrin</u> | |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | 0.0013 | N.f. | N.f. | N.f. | 0.0013 |
| 26/02/98 | 0.0640 | N.f. | N.f. | N.f. | 0.0640 |
| 26/02/98 | 0.3500 | N.f. | N.f. | N.f. | 0.3500 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| 26/02/98 | N.f. | N.f. | N.f. | N.f. | 0.0000 |
| | 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 26/02/98 | 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 N.f. 26/02/98 0.0013 26/02/98 0.3500 26/02/98 N.f. | 26/02/98 N.f. N.f. 26/02/98 0.0013 N.f. 26/02/98 0.0640 N.f. 26/02/98 0.3500 N.f. 26/02/98 N.f. N.f. | 26/02/98 N.f. N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. N.f. 26/02/98 0.0013 N.f. N.f. N.f. 26/02/98 0.0640 N.f. N.f. 26/02/98 0.3500 N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. N.f. N.f. N.f. N.f | 26/02/98 N.f. N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. N.f. 26/02/98 0.0013 N.f. N.f. N.f. N.f. 26/02/98 0.3500 N.f. N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. N.f. 26/02/98 N.f. N.f. N.f. N.f. N.f. |

N.f. = not found

ANNEX III

(Overview on the most important substances to be detected in the off-gas of finishing, printing, and coating processes)

Table 19: Substances with less dangerous properties which may be present in waste gas

| Substance | Possible Source | | |
|-------------------------------------|--|--|--|
| Aliphatic hydrocarbons (C1-C40) | Preparation agents, wetting agents, printing | | |
| | pastes | | |
| Aromatic hydrocarbons | Carriers, Machine cleaning | | |
| Ketones | Various textile auxiliaries | | |
| Alcohols (low molecular) | Various textile auxiliaries | | |
| Esters (low molecular) | Various textile auxiliaries | | |
| Siloxanes | Softening agents | | |
| Carboxylic acids (e.g. acetic acid) | pH-adjustment | | |
| Fatty acids | By-product in surfactants | | |
| Fatty alcohols | By-product in surfactants | | |
| Fatty esters | By-product in surfactants | | |
| Fatty amines | By-product in surfactants | | |
| Aminoalcohols | By-product in surfactants | | |
| Dioles, polyoles | By-product in surfactants | | |
| Glycol ethers | By-product in surfactants | | |
| Aliphatic, aromatic ethers | Various textile auxiliaries | | |

Table 20: Substances with more dangerous properties which may be present in waste gas

| Substance | Possible source |
|--|---|
| Acroleine | Decomposition of glycerol |
| Acrylates (methyl, ethyl, butyl) | Coating agents and binders for non-wovens |
| Acrylic acid | Polymers, thickeners |
| Aliphatic amines | Polymers (esp. polyurethanes) |
| Ammonia | Foaming agents, thickeners |
| 2- aminoethanol | Wetting agents, softeners |
| Benzyl alcohol | Carriers |
| Biphenyl | Carriers |
| Bis (2-aminoethyl)-1,2-ethanediamine, N, N | Softeners |
| Butine-1,4 diol | Fluorocarbon resins |
| Epsilon-Caprolactam | Polyamide 6 powder/textiles |
| Chlorinated aromatic hydrocarbons | Carriers |
| Chloroethanol | Decomposition of flame retardants |
| | (chlorinated P-ester) |
| Chloroparaffines | Flame retardants |
| Dichloroethene | Polyvinylidenechloride |
| Diethylenetriamine | Softeners |
| Di(ethylhexyl)phtalate | Dyeing auxiliaries/polymer dispersions |
| Diglycidylether | Epoxide resins |

| Substance | Possible source |
|---|---|
| Diisocyanatetoluene, 2,4- | Fluorocarbon resin (extender), polyurethane |
| Diisocyanatetoluene, 2,6- | Fluorocarbon resin (extender), polyurethane |
| N,N-Dimethylacetamide | Fibre solvent (m-aramide) |
| Diphenylmethane-2,4 diisocyanate | Extender, polyurethane |
| Diphenylmethane-4,4' diisocyanate | Extender, polyurethane |
| Dipropylenetriamine | Softeners |
| Acetic acid-(2-ethoxiethyl)-ester | Softeners/fluorocarbon resins |
| Ethoxyethanol | Softeners/fluorocarbon resins |
| Ethanedialdehyde (glyoxal) | Crosslinkers |
| Ethylenediamine | Softeners |
| Fluoroorganics, low molecular | Fluorocarbon resins |
| Formic acid | Various textile auxiliaries |
| Hexamethylendiamine | Polycondensation products |
| Hexamethylenediisocyanate | Fluorocarbon resins, polyurethane |
| Hexanone, 2- | Fluorocarbon resins |
| Hydrogen chloride | Catalyst |
| Isocyanatomethyl-3,5,5-trimethylcyclohexyl- | Fluorocarbon resins, polyurethane |
| Isocyanate | |
| N-Methylpyrrolidon | Fibre solvent (m-aramides), machine |
| | cleaning |
| N-alkylmorpholine | Non-wovens coating |
| Oxalic acid | Bleaching auxiliary |
| Triethylamine | Special crosslinkers |
| Tricresylphosphate | Flame retardants |
| Trimethylphosphate | Flame retardants |
| Tin derivatives, organic, inorganic | Fluorocarbon resins, |
| | Hydrophobing agents, biocides |
| Vinylacetate | Polyvinyl acetate |
| 2-Vinylcyclohexen | Polymer dispersions |

 $Table\ 21:\quad Substances\ with\ carcinogenic\ properties\ (category\ K1,\ K2\ or\ K3\ according\ to\ [EU,2001]\ which\ may\ be\ present\ in\ waste\ gas$

| Substance | CAS- | Canc. | Possible source |
|--------------------------|-----------|----------|--|
| | Number | Category | |
| Acetaldehyde | 75-07-0 | K3 | Polyvinyl acetate, acetic acid |
| Acrylamide | 79-06-1 | K2 | Reactive polymers, flame retardants |
| Acrylonitrile | 107-13-1 | K2 | Polymer dispersions |
| Antimonytrioxide | 1309-64-4 | K2 | Flame retardants, catalyst in PES fibres |
| Arsenic trioxide | | K1 | Flame retardants (impurity of antimony |
| | | | oxide) |
| 2-Butanoneoxime | 96-29-7 | K3 | Fluorocarbon resins, polyurethanes |
| 1,3-Butadiene | 106-99-0 | K1 | Polymer dispersions |
| Chloromethane | 74-87-3 | K3 | Quaternary ammonium compounds |
| (methylchloride) | | | |
| Dichloromethane | 75-09-2 | K3 | Solvent cleaning |
| Dimethylsulfate | 77-78-1 | K1 | Quaternary ammonium compounds |
| Dioxane, 1,4- | 13-91-1 | K3 | Surfactants (ethoxilated products) |
| Ethylenimine | 151-56-4 | K2 | Flame retardants |
| Epichlorohydrine | 106-89-8 | K2 | Polycondensation products |
| (1-Chlor-2,3-epoxypropan | | | |
| 1,2-Epoxypropane | 75-56-9 | K2 | Surfactants (propoxilated products) |
| (Propyleneoxide) | | | |
| 2,3-Epoxy-1-propanol | 556-52-5 | K2 | Some antistatics |
| Ethyleneoxide | 75-21-8 | K2 | Surfactants (ethoxilated products) |
| Formaldehyde | 50-00-0 | K3 | Crosslinkers, conservation agent, stenter off- |
| | | | gas |
| Pentachlorophenol | 87-86-5 | K3 | Pesticides |
| Propyleneimine | 75-55-8 | K2 | Flame retardants and polyurethane |
| (2-Methylaziridin | | | crosslinker |
| Tetrachloroethene | 127-18-4 | К3 | Dry cleaning |
| Vinylchloride | 75-01-4 | K1 | Polymer dispersions (PVC) |
| N-vinylpyrrolidone | 88-12-0 | K3 | Polyvinylpyrrolidone dispersions |