ENVIRONMENTAL RESEARCH OF THE
FEDERAL MINISTRY OF THE ENVIRONMENT,
NATURE CONSERVATION AND NUCLEAR SAFETY

Research Report 200 94 329
UBA-FB 000325/e

Texte
14
03

ISSN
0722-186X

Best Available Techniques in Textile Industry

by

Dr. Harald Schönberger

Gottenheim

Dr. Thomas Schäfer

EnviroTex GmbH, Augsburg

On behalf of the Federal Environmental Agency

UMWELTBUNDESAMT

Publications by the Federal Environmental Agency
in the TEXTE series are available subject to advance
payment of **10,00 Euro** by bank transfer, crossed cheque
or paying-in form to

Account number 4327 65 - 104 at the
Postbank Berlin (Sorting Code 10010010)
Fa. Werbung und Vertrieb
Ahornstraße 1-2
10787 Berlin

*At the same time please direct your written order to the Firma Werbung und Vertrieb naming the **volume number** from the TEXTE series, and the **name** and **address** of the orderer.*

Publisher: Federal Environmental Agency (Umweltbundesamt)
Postfach 33 00 22
14191 Berlin
Tel.: +49/30/8903-0
Telex: 183 756
Telefax: +49/30/8903 2285
Internet: http://www.umweltbundesamt.de

Edited by: Section III 2.5
Dr. Horst Fischer

Berlin, March 2003

Report Cover Sheet

1. Report No.
UBA-FB-000325

2.

3.

4. Report Title
Best Available Techniques in Textile Industry

5. Autor(s), Family Name(s), First Name(s)
Schönberger, Harald; Schäfer, Thomas

6. Performing Organisation (Name, Address)

Schönberger, Harald; Carl-Frey-Str. 3, D-79288 Gottenheim
EnviroTex GmbH; Provinostr. 52, D-86153 Augsburg

7. Sponsoring Agency (Name, Address)

Umweltbundesamt, Postfach 33 00 22, D-14191 Berlin

8. Report Date
12.06.2002

9. Publication Date
20.08.2002

10. UFOPLAN-Ref. No.
2000 94 329

11. No. of Pages
362

12. No. of Reference
281

13. No. of Tables, Diagrams
149

14. No. of Figures
116

15. Supplementary Notes

16. Abstract

This report is the German contribution to the Reference Document on Best Available Techniques for the Textiles Industry (BREF Textiles Industry) which is the final product of the exchange of information on BAT according to Article 16.2 IPPC-Directive. These BREFs are drafted by the European IPPC Bureau (see http://eippcb.jrc.es).

For preparing this report, the concerned available knowledge in Germany in this field has been collected and documented as far as possible. To this purpose, all relevant experts from textile industries, textile research institutes, suppliers of textile machinery, suppliers of dyestuffs and textile auxiliaries, suppliers of measurement and control equipment, suppliers of environmental technology, associations and authorities) have been contacted and involved.
The structure of this report concerns the instructions given for the BREF Textiles Industry. Accordingly it has following chapters:
Chapter 1: General information
Chapter 2: Applied processes and techniques
Chapter 3: Present emission and consumption level
Chapter 4: Techniques to consider in the determination of BAT
Chapter 5: Best available techniques
Chapter 6: Emerging techniques

Out of 53 techniques described in chapter 4, according to the laid down approach, in chapter 5, 46 techniques have been selected and identified to be BAT.

17. Keywords

Textile industry, textile finishing, textile chain, wastewater, waste gas, solid waste, energy consumption,
best available techniques, integrated pollution prevention and control, IPPC Directive, information exchange,
apllied processes and techniques, emission and consumption levels, emerging techniques
Best available techniques reference document, BREF

18. Price

19.

20.

Berichts-Kennblatt

1. Berichtsnummer
UBA-FB 000325

2.

3.

4. Titel des Berichts
Beste verfügbare Techniken in Anlagen der Textilindustrie

5. Autor(en), Name(n), Vorname(n)
Schönberger, Harald; Schäfer, Thomas

6. Durchführende Institution (Name, Anschrift)

Schönberger, Harald; Carl-Frey-Str. 3, D-79288 Gottenheim
EnviroTex GmbH; Provinostr. 52, D-86153 Augsburg

7. Fördernde Institution (Name, Anschrift)

Umweltbundesamt, Postfach 33 00 22, D-14191 Berlin

8. Abschlußdatum
12.06.2002

9. Veröffentlichungsdatum
20.08.2002

10. UFOPLAN-Nr.
2000 94 329

11. Seitenzahl
362

12. Literaturangaben
281

13. Tabellen und Diagramme
149

14. Abbildungen
116

15. Zusätzliche Angaben

16. Kurzfassung

Der vorliegende Bericht ist der deutsche Beitrag für das Reference Document on Best Available Techniques for theTextiles Industry –kurz BREF Textiles Industry genannt-, das im Rahmen des Informationsaustausches nach Artikel 16.2 der IVU-Richtlinie vom EuropeanIPPCBureau (siehe http://eippcb.jrc.es) erstellt wird.

Für die Erarbeitung des vorliegenden Beitrages wurde das deutsche Know-how auf diesem Gebiet so weit wie möglich erfasst und dokumentiert. Dazu wurden alle wesentlichen Akteure (Textilindustrie, textile Forschungs-, institute, Textilmaschinenbau, Farbmittel- und Textilhilfsmittelhersteller, Hersteller von Mess- und Regeltechnik, Hersteller von Umwelttechnologie, Verbände und Behörden) angesprochen und einbezogen.
Die Struktur des deutschen Berichtes entspricht den Vorgaben für das BREF Textiles Industry. Danach besteht es aus folgenden Kapiteln:
Kapitel 1: Allgemeine Informationen
Kapitel 2: Angewandte Produktionsverfahren und Techniken
Kapitel 3: Gegenwärtige Emissions- und Verbrauchsniveaus (Input/Output)
Kapitel 4: Beschreibung von Techniken, die bei der Bestimmung der Besten Verfügbaren Techniken zu berücksichtigen sind
Kapitel 5: Definition der Besten Verfügbaren Techniken
Kapitel 6: Neue, in der Entwicklung befindliche Techniken

Von den 53 in Kapitel 4 beschriebenen Techniken sind 46 im Kapitel 5 nach einem dargelegten Ansatz als BVT definiert.

17. Schlagwörter
Textilindustrie, Textilveredlung, textile Kette, Abwasser, Abluft, Abfall, Energieverbrauch
Beste verfügbare Techniken, integrierter Umweltschutz, IVU-Richtlinie, Informationsaustausch,
Angewandte Prozesse und Verfahren, Emissions- und Verbrauchswerte, zukunftsweisende Technologien
Best available techniques reference document, BREF

18. Preis

19.

20.

TABLE OF CONTENTS

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT 153

1 GENERAL INFORMATION

1.1 Overall production of textiles in Germany

The textile industry has played an important role in the development of human civilisation over several millennia. Coal, iron/steel and cotton were the principal materials upon which the industrial revolution was based. Technical developments from the second part of eighteenth century onwards lead to exponential growth of cotton output, first starting in the UK, later also in other European countries, also in Germany. The production of synthetic fibres started at the beginning of the twentieth century showing also exponential growth. This development is indicated in Figure 1.1.

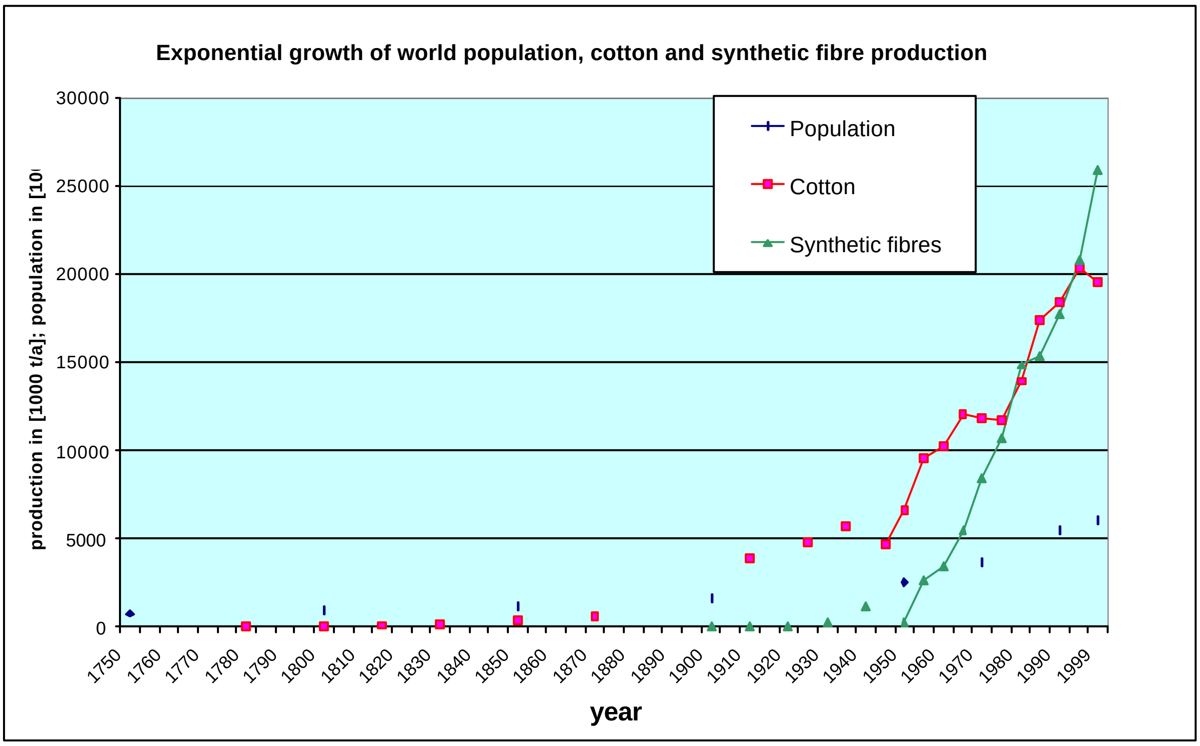


Figure 1.1: World-wide production of cotton and synthetic fibres and world population since 1750 – [Schönberger, 1998]

However, at time there is stagnation in cotton production whereas production of synthetic fibres has meanwhile overtaken it. Germany took part in this development but market competition became increasingly heavy. As a consequence, in the past ten years Germany lost about one third of its textile production (Figure 1.2). Figure 1.2 also illustrates that finishing of woven fabrics has the highest percentage of the overall production amount followed by finishing of yarn, knit fabric and textile printing. There are doubts that the annual production in 1995-1998 are in the order of 450000 – 525000 t/a because of a study carried out recently [FhG-ISI, 1997]. According to this study only 35% of the above mentioned production level could be explained although 128 textile finishing industries have been interviewed including all the bigger ones. The question could be answered whether carpet production is included or not.

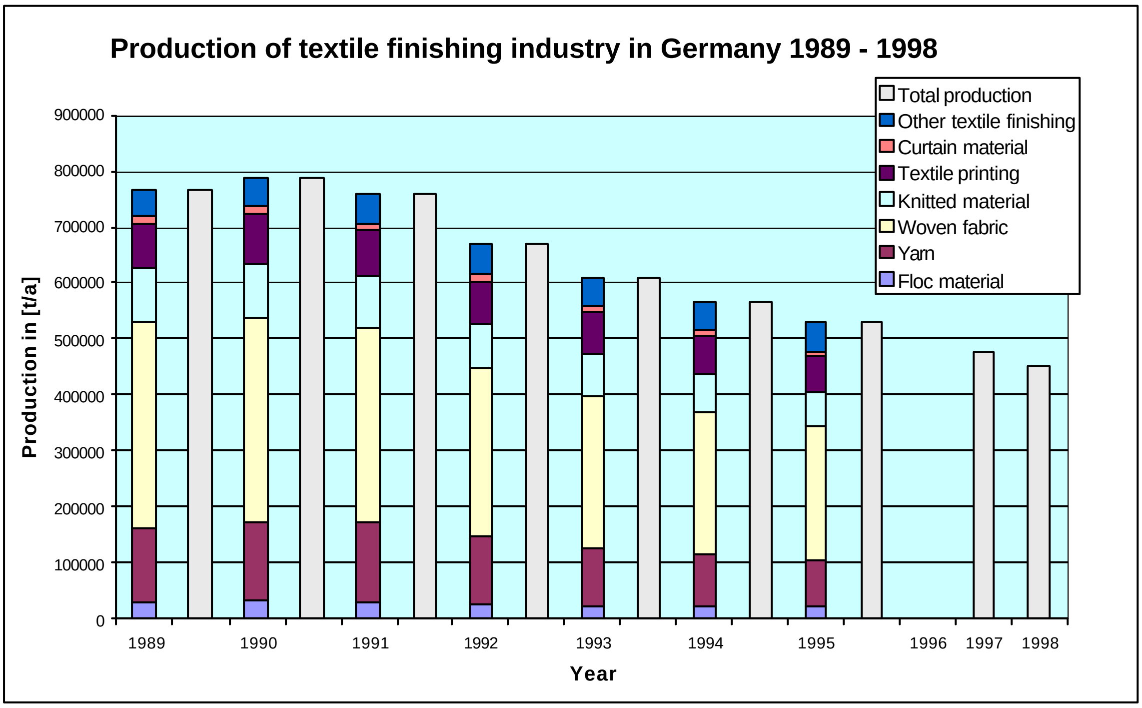


Figure 1.2: **Production of the textile finishing industry in Germany 1989 – 1998 – [TVI-Verband, 1989-1999]; for 1997-1998 numbers for total production are available only; the class „other textile finishing" covers production of ribbons, thermo-printing, coating and laminating**

The distribution of the quantities in the different product sectors of the most important textile substrates (fibre types) processed in Germany in 1999 is shown in Figure 1.3. Thereby the total annual quantity for all textile substrates (790000 t/1999) is higher than the numbers submitted in Figure 1.3 because technical textiles are also included (the sum of substrates for garments and for home textiles is about the number mentioned in Figure 1.2).

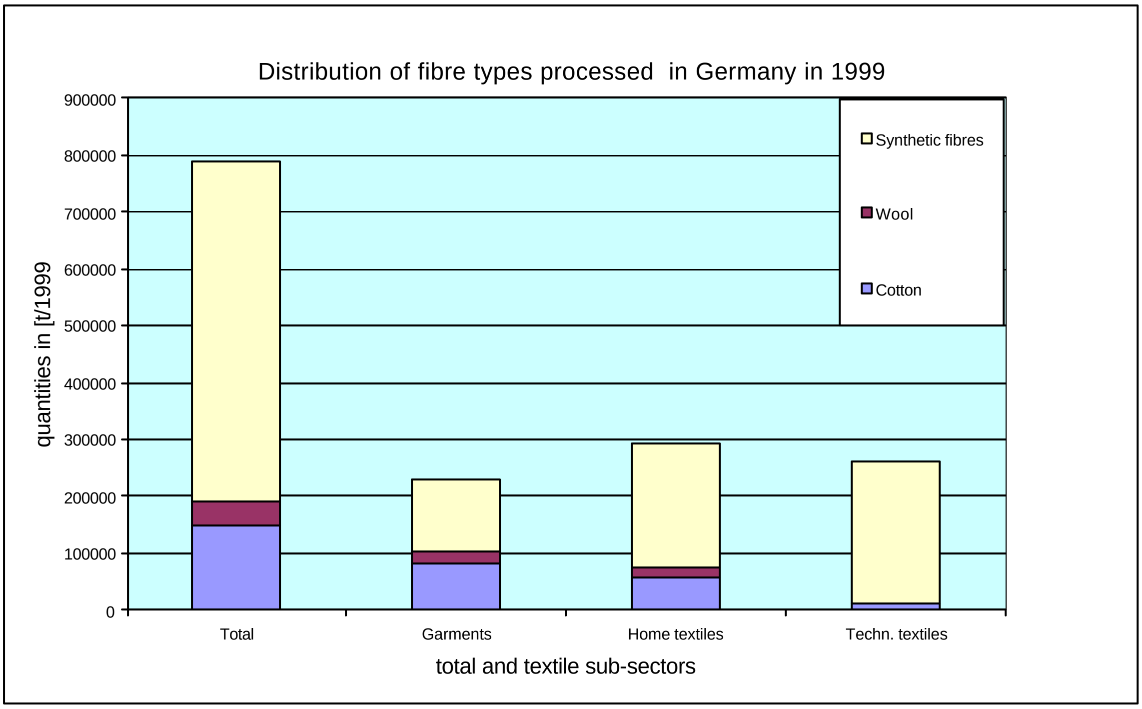


Figure 1.3: **Quantities of different substrates processed in Germany – in total and in the sub-sectors – [IVC, 1999]**

According to Figure 1.3 the synthetic fibres (including staple and filament viscose fibres) dominate the kind of processed textile substrates. Even for garments the percentage of synthetic fibres is about 50% whereas their predominant role in the sub-sector of technical textiles is not surprising.

1.2 Number of textile finishing industries in Germany and the geographical distribution

In 1999, in Germany 1230 textile industries existed comprising spinning mills, weaving mills, manufacture of textiles except manufacture of ready-made clothes, carpet manufacturing industries, fleece manufacturing industries, knit fabric manufacturing industries, industries manufacturing pullovers and cardigans, socks manufacturing industries and textile finishing industries. As this document focuses on the latter, more detailed information is submitted. According to the statistics of the concerned associations there are 155 textile finishing industries in Germany [TVI-Verband, 1999; Gesamttextil, 2000] which is half Germany had in 1970 (296 industries). However this number only includes fashion oriented industries being member of the above mentioned association for the textile finishing industry (TVI-Verband). Following kind of textile finishing industries are not included: carpet manufacturing, felt finishing industries, industries printing flags, yarn finishing industries, industries finishing technical textiles and ribbons finishing industries. In addition industries with less than 20 employees are not taken into account. A recent survey indicates that in Germany there are about 400 textile finishing industries considering all above mentioned kinds of industries. Figure 1.4 shows that nearly three quarters of the industries are located in the three Federal States North Rhine-Westphalia, Baden-Württemberg and Bavaria. Also in the Federal States Hessen, Saxony and Lower Saxony textile finishing industries are located to a relevant extent.

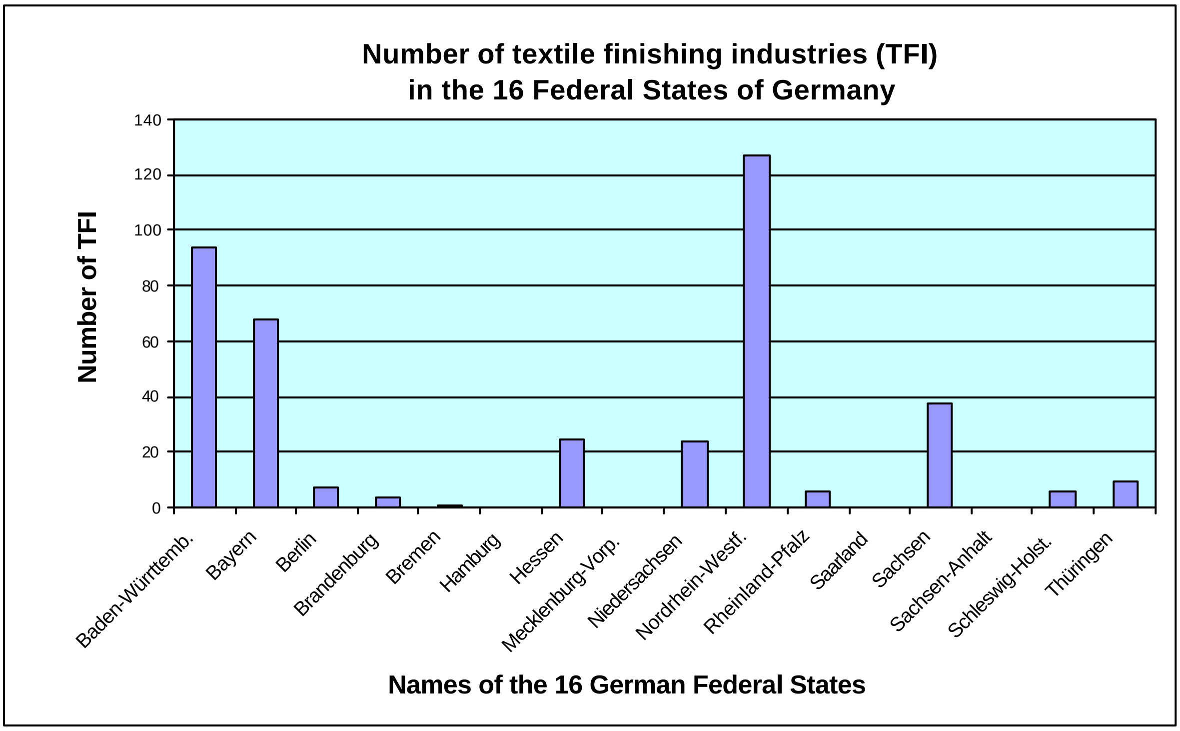


Figure 1.4: Number of textile finishing industries in Germany in 2000 and their geographical distribution according to the 16 German Federal States

1.3 Employment and investments in the German textile finishing industry

The drastic decrease of production in the past ten years correlates with employment. In addition increased productivity was also leading to less employment. Figure 1.5 shows that employment in the both in whole German textile industry and textile finishing industry reduced nearly three times from 1980 to 1998, from 304000 to 129000 employees and respectively from 45700 to 16000 employees.

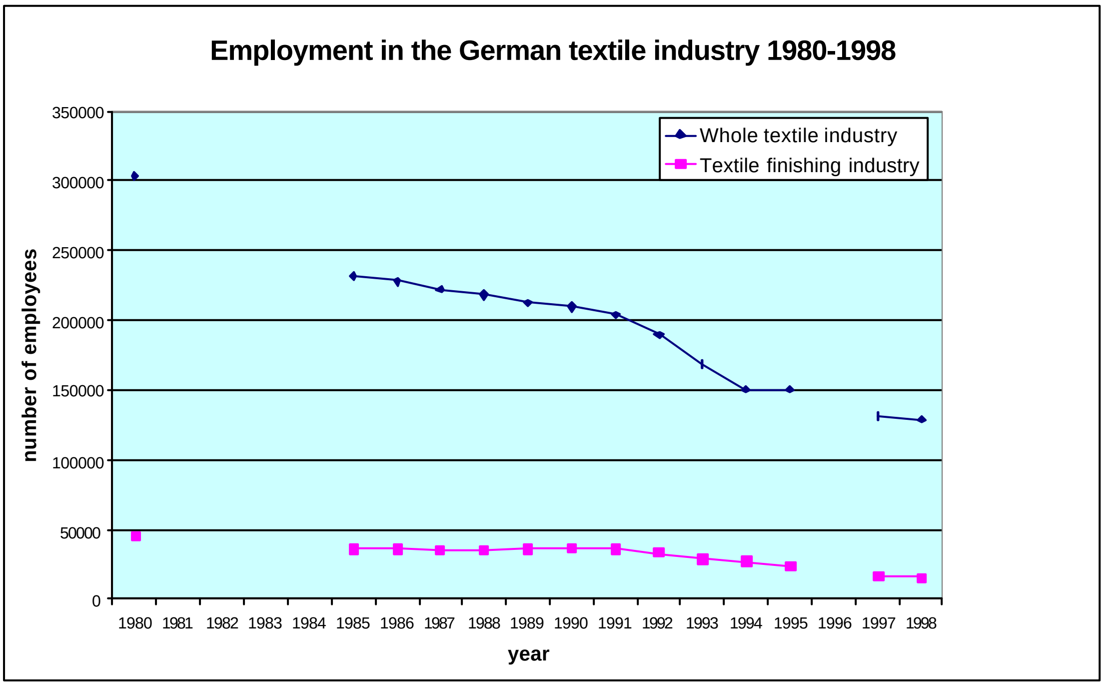


Figure 1.5: Development of employment in the German textile industry 1980-1998 – [TVI-Verband, 1986-1999]

Investments also decreased but to a significant lower percentage. In 1990, the last booming year about 165 million EUR have been invested by the textile finishing industry mainly in machinery which is about 8.5% of annual turnover. In 1998 about 80 million EUR have been invested only which is 4.7% of annual turnover.

1.4 Economic situation

Market situation is characterised by heavy competition and cheap imports mainly from Asia. As a consequence the German textile industry lost market percentages and production decreased drastically (Figure 1.2). This development finds expression in annual turnover also. Because of rate of price increases the numbers do not show it directly. In 1980 for the German textile finishing industry the annual turnover was 1650 million EUR and in 1998 1720 million EUR (Figure 1.6). These numbers do not include the textile materials value.

Figure 1.6: Development of annual turnover of the German textile finishing industry 1980-1998 – [TVI-Verband, 1986-1999]; the numbers for 1981-1984 and for 1996 are not available; because of new data base the values for 1997-1998 are significantly higher

Since the eighties the foreign trade deficit grew drastically reflecting the difficult economic environment Germany has to face (Figure 1.7). Many industries can hardly compete with standard quality products. Thus many industries go for specialities and high quality products.

Figure 1.7: Development of the import/export of textiles in Germany showing the drastically growing foreign trade deficit – [Gesamttextil, 2000; TVI-Verband, 1986-1999]; the numbers for 1981-1984 and for 1996 are not available

Looking at the cost structure of textile finishing industries the cost for consumption of materials (especially expenses for colorants, textile auxiliaries and basic chemicals) and personnel costs play the prominent role (Figure 1.8). Other costs include services from other industries and craft companies, energy costs and also 'environmental costs' like wastewater fees, fees for solid waste disposal, operation costs for wastewater (pre-)treatment plants etc. The percentage of 8% is relevant but not highly significant.

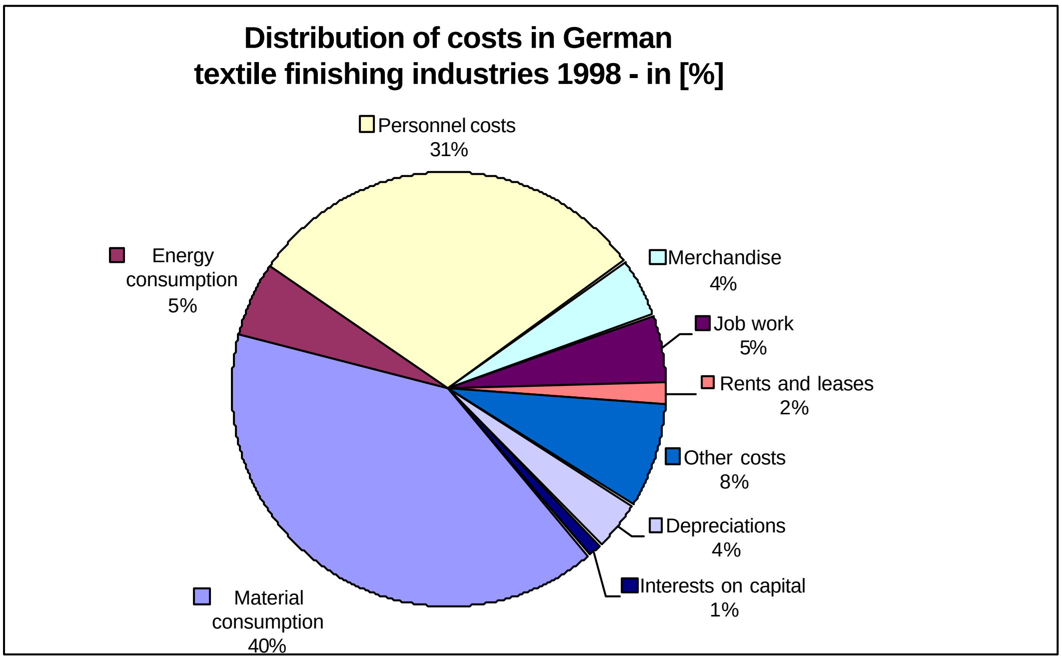


Figure 1.8: Contribution of costs in German textile finishing industries in 1998 – [Gesamttextil, 2000]

In addition the percentage for other costs has decreased remarkably from 12% in 1990 to 8% in 1998. With respect to additional measures in the textile finishing industry in order to prevent/to minimise emissions to water and to air it seems that the environmental costs are discussed intensively. The most important environmental cost factor is for water supply and wastewater disposal. In 1997, in Germany the cost for it was 2.74% average of the annual turnover with a range of 0.1 – 12.1% [TVI Enquete, 1997]. Thereby, in 1997 the absolute average cost for water supply was 0.4 EURO/m^3 (range: 0.01-2.30 EURO/m^3) in case of own water supply system (e.g. own wells) and 1.20 EURO/m^3 in case of external supply (range: 0.06-3.15 EURO/m^3) [TVI Enquete, 1997].
In 1997 the average wastewater fee was 1.80 EURO/m^3 with a range 0.50 - 2.5 EURO/m^3 [TVI Enquete, 1997].

1.5 Environmental relevance of the textile finishing industry

Evaluating the input/output-situation of textile finishing industries, an appropriate approach is to draw the system border-line site-wise and to consider the in-going and out-going mass streams on an annual base. A clear and expressive presentation of the data is possible by hand of so-called mass stream overviews (Figure 1.9).

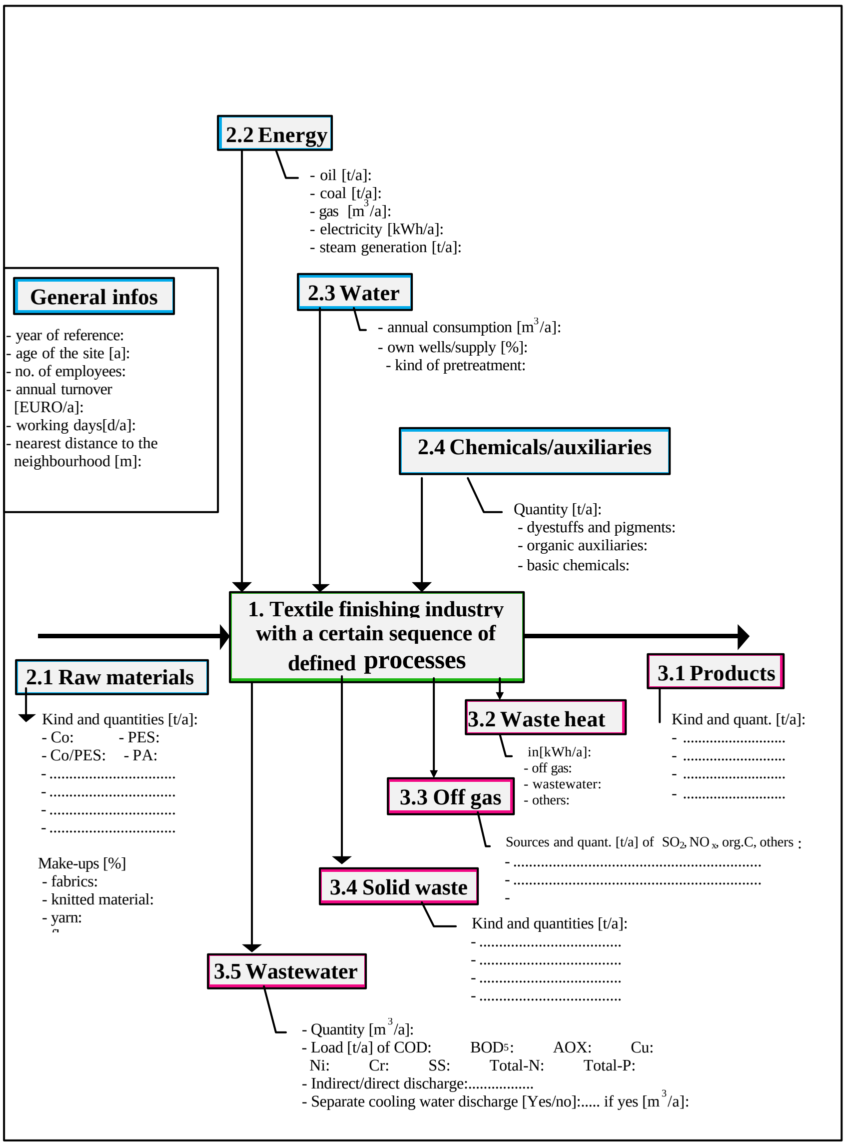


Figure 1.9: Mass stream overview for textile finishing industries

A complete mass stream overview allows the calculation of input and emission factors. By hand of these factors similar industries can be compared and categories can be formed respectively. In addition, on base of organic carbon, a quantitative comparison of emissions to water and emissions to air is possible.

In the textile finishing industries wastewater discharge is of highest environmental relevance. It contains most of the chemical load followed by emissions to air (especially from stenter frames in case of raw fixation of synthetic fibres or final finishing) and energy consumption.
In addition attention has to be paid to storage and handling of chemicals and minimisation and disposal of solid wastes.

Figure 1.10 illustrates that the textile finishing industry is ranking number eight concerning overall wastewater flow in Germany. 94% of the industries discharge their wastewater to municipal wastewater treatment plants.

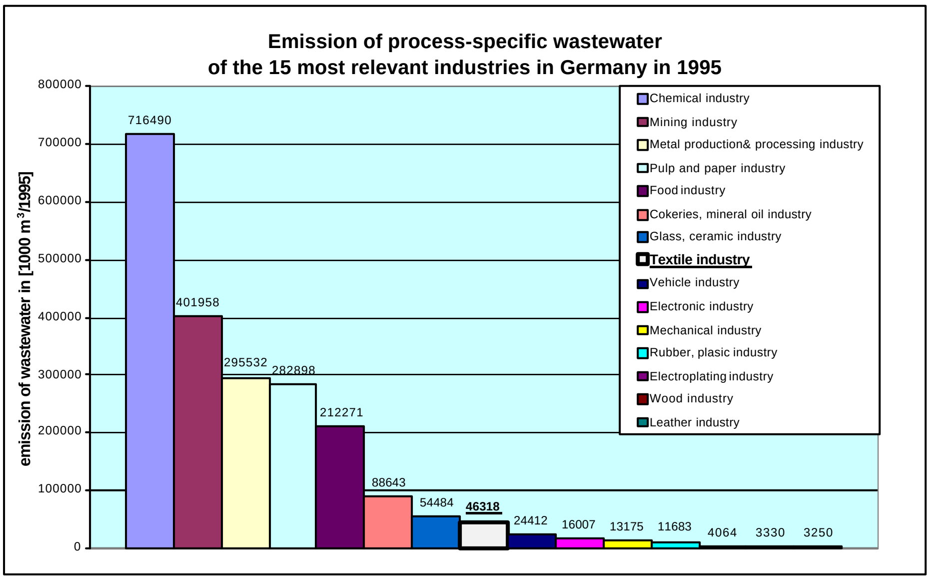


Figure 1.10: Emission of process-specific wastewater (without cooling water) –which is discharged indirectly- of the 15 most relevant industrial sectors in Germany in 1995 – according to [Stat. Bundesamt, 1998]

Regarding this so-called indirect discharge, the textile industry is number four (Figure 1.11).

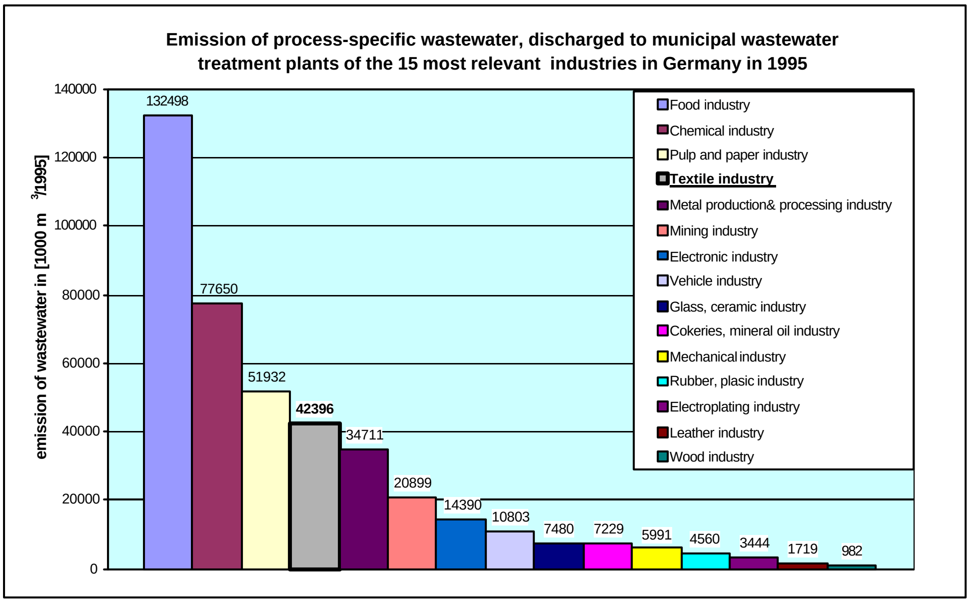


Figure 1.11: Emission of process-specific wastewater (without cooling water) of the 15 most relevant industrial sectors in Germany – according to [Stat. Bundesamt, 1998]

The specific water consumption for different types of textile finishing industries is shown in Table 1.1.

Type of textile finishing industry	1988 average [l/kg]	1988 range [l/kg]	1992 average [l/kg]	1992 range [l/kg]	1996 average [l/kg]	1996 range [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

Table 1.1: Specific water consumption of different types of textile finishing industries in Germany from 1988-1996 (average and range) – [TVI Enquete, 1997]

Recently a detailed study on water consumption and wastewater emission respectively has been finalised. In principle these study confirm the above mentioned values [Schönberger, 2000].

Most of the applied chemicals are discharged with the wastewater. Usually 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 only, whereas most of the other applied chemicals are emitted with the wastewater.

Table 1.2 contains representative examples for the input of chemical products for five different kinds of textile finishing industries.

Kind of textile finishing industry	Dyestuffs [g/kg textile]	Textile auxiliaries [g/kg textile]	Textile basic chemicals [g/kg textile]
▪ Finisher of yarn mainly consisting of polyester	18	129	126
▪ Finisher of knit fabric mainly consisting of synthetic fibres	52	113	280
▪ Finisher of knit fabric consisting of cotton	18	100	570
▪ Finisher of woven fabric mainly consisting of cellulosic fibres	11	183	200
▪ Finisher of woven fabric mainly consisting of cellulosic fibres with relevant printing section	88	180	807

Table 1.2: Input factors for chemical products for five different kinds of textile finishing industries – [Schönberger, 2000]

The chemical input is up to 1 kg chemicals/kg processed textiles which is high. As mentioned before, most of them are released to wastewater. Concerning the organic load, 20 – 100 g organic carbon/kg processed textiles are emitted which is 15-250 times higher than emissions to air. Thus emissions to water are predominant.

During textile finishing heating of water and air is required and electricity for running the machines. In addition energy is needed of drying operations. Figure 1.12 shows the overall energy consumption of the German textile finishing industry for the different sources of energy. Considering the total annual production overall specific energy consumption factors can be calculated (Figure 1.13). The latter indicates that the specific consumption remained on a rather high level and could not be reduced during fifteen years.

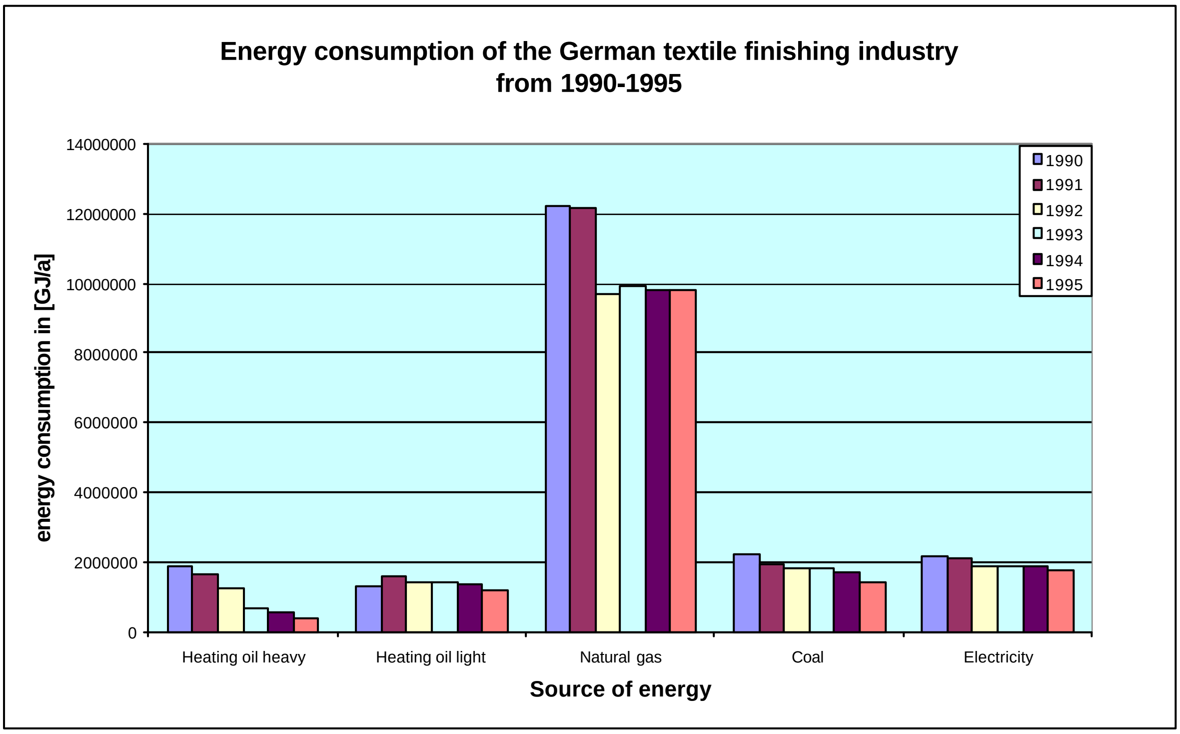


Figure 1.12: Energy consumption of the German textile finishing industry from 1990-1995 for the different sources of energy – [TVI-Verband, 1995]

The percentage of energy consumption of the textile finishing industry with respect to the overall energy consumption of all German industrial sectors is in the order of 1% [BMWi, 2000].

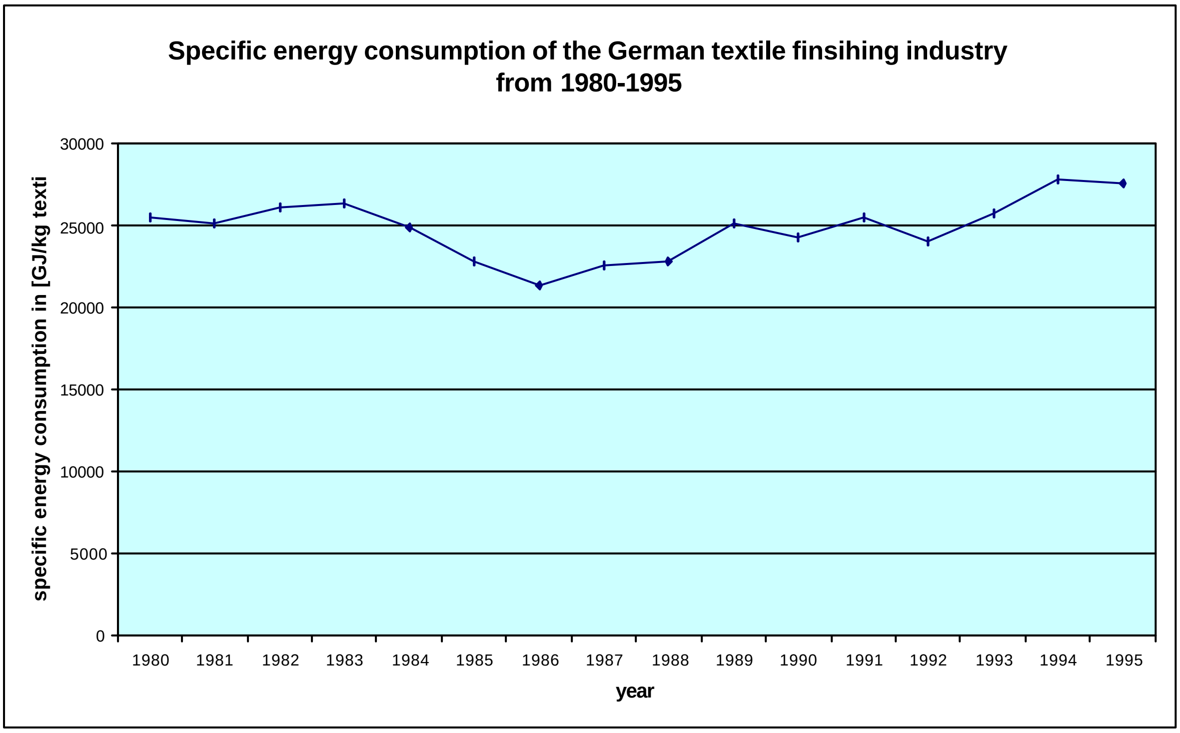


Figure 1.13: Specific energy consumption of the German textile finishing industry from 1980-1995 – [TVI-Verband, 1995]

1.6 References

[BMWi, 2000]
Bundesministerium für Wirtschaft und Technologie
Energie Daten 2000 – Nationale und internationale Entwicklung (2000)

[FhG-ISI, 1997]
Böhm, E.; Hillenbrand, T.; Landwehr, M.; Marscheider-Weidemann, F.
Fraunhofer-Institut für Systemtechnik und Innovationsforschung (FhG-ISI)
Untersuchung zur Abwassereinleitung: Statistik wichtiger industrieller und gewerblicher Branchen zur Bewertung der Umweltgefährlichkeit von Stoffen (1997)

[Gesamttextil, 2000]
Gesamtverband der Textilindustrie in der Bundesrepublik Deutschland, Gesamttextil
Jahrbuch der Textilindustrie 2000 (2000)

[IVC, 1999]
Industrievereinigung Chemiefasern e.V. (IVC)
Die Chemiefaser-Industrie in der Bundesrepublik Deutschland 1999 (2000)

[Schönberger, 1998]
Schönberger, H.
Zur Abwässerfrage der Textilveredlungsindustrie
VDI-Fortschrittsberichte, Reihe 15: Umwelttechnik (1998)

[Schönberger, 2000]
Schönberger, H.
Die gegenwärtige Verbrauchs- und Emissionssituation der deutschen Textilveredlungsindustrie
UBA-Texte 28/01 (2001)

[Stat. Bundesamt, 1998]
Statistisches Bundesamt
Umwelt, Fachserie 19, Reihe 2.2 „Wasserversorgung und Abwasserbeseitigung im Bergbau und Verarbeitenden Gewerbe und bei Wärmekraftwerken für die öffentliche Versorgung 1995 (1998)

[TVI Enquete, 1997]
Gesamtverband der deutschen Textilveredlungsindustrie, TVI-Verband e.V.
Wasser-/Abwasserenquete 1997 (1997)

[TVI-Verband, 1989-1998]
Gesamtverband der deutschen Textilveredlungsindustrie, TVI-Verband e.V.
Jahresberichte 1989-1995 und Dreijahresbericht 97-99 (1989, 1990, 1991, 1992, 1993, 1994, 1995, 1999)

[TVI-Verband, 1995]
Gesamtverband der deutschen Textilveredlungsindustrie, TVI-Verband e.V.
Jahresbericht 1995 (1995)

[TVI-Verband, 1999]
Gesamtverband der deutschen Textilveredlungsindustrie, TVI-Verband e.V.
Dreijahresbericht 97-99 und Jubiläumsschrift (1999)

2 APPLIED PROCESSES AND TECHNIQUES

2.1 General information

A great part of the ecological load esp. in the pre-treatment processes in textile finishing mills is caused by the textile raw materials themselves and textile auxiliaries applied in upstream processing steps (fibre-, yarn- and fabric-processing). To characterize the ecological impact related to textile finishing it is therefore of crucial interest to have a closer look on the whole textile chain.

Chapter 2.1 gives a brief overview on textile raw materials and the processes along the whole textile production chain. Important aspects concerning the ecological situation in textile finishing mills are mentioned shortly. Figure 2.1 can be used as a guidance for reading this chapter.

Knowledge of material input (textile raw materials, auxiliaries, chemicals, and dyes) and its inherent ecological loads is a key to understand the environmental situation in textile finishing industry. Therefore Chapter 2.2 focuses on the input situation in textile finishing.

In Chapter 2.3 a detailed description is given of the processes used in textile finishing, respectively their ecological aspects including a short look on appplication methods and drying methods.

The production of textiles affords a great variety of processing steps (Figure 2.1). 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 (Figure 2.1). The make-up (cutting, sewing, assembling) is the last step before selling in retail trade or whole trade and consumer use.

After use textiles can be recycled (reuse in fibre processing, non-woven processing etc.).

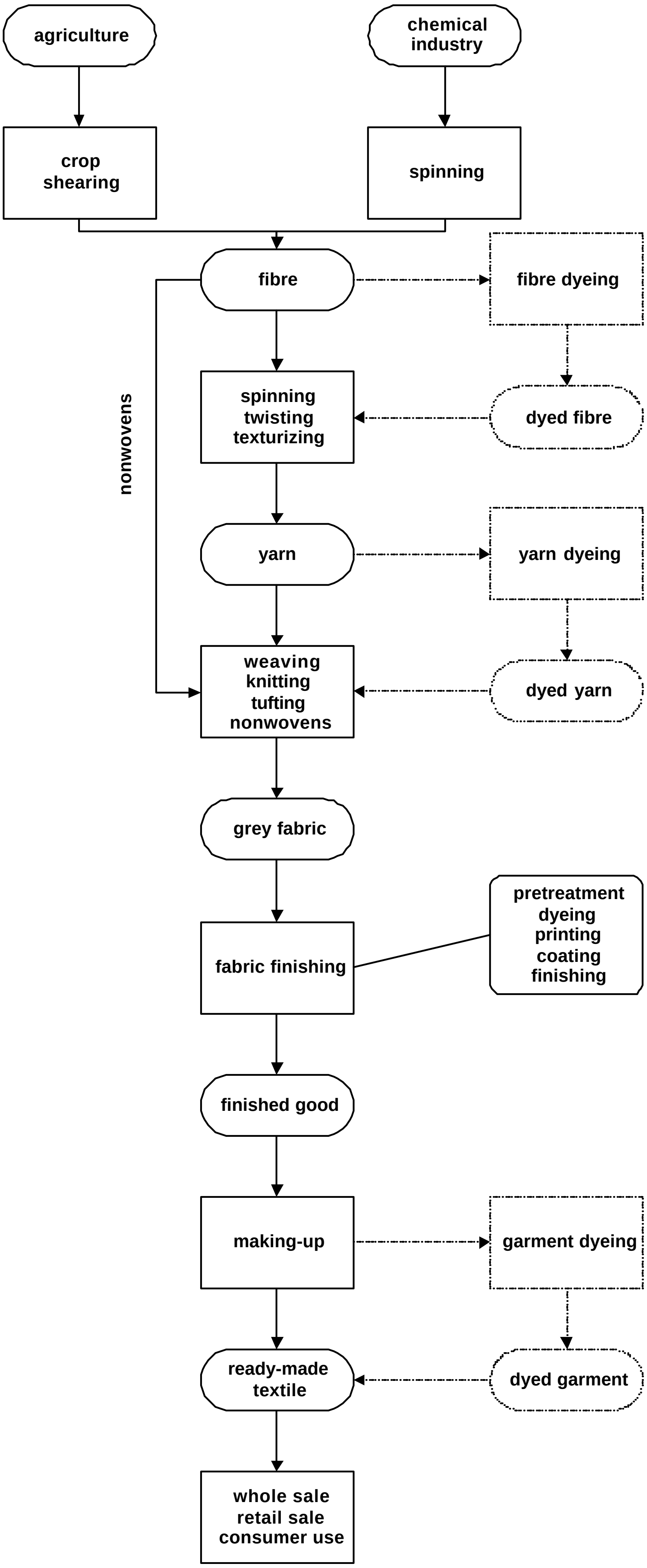


Figure 2.1: The textile chain

To explain the ecological situation in textile finishing mills (wastewater, off-gas) a simplified view on the input-output situation along the textile chain may be helpful (Figure 2.2).

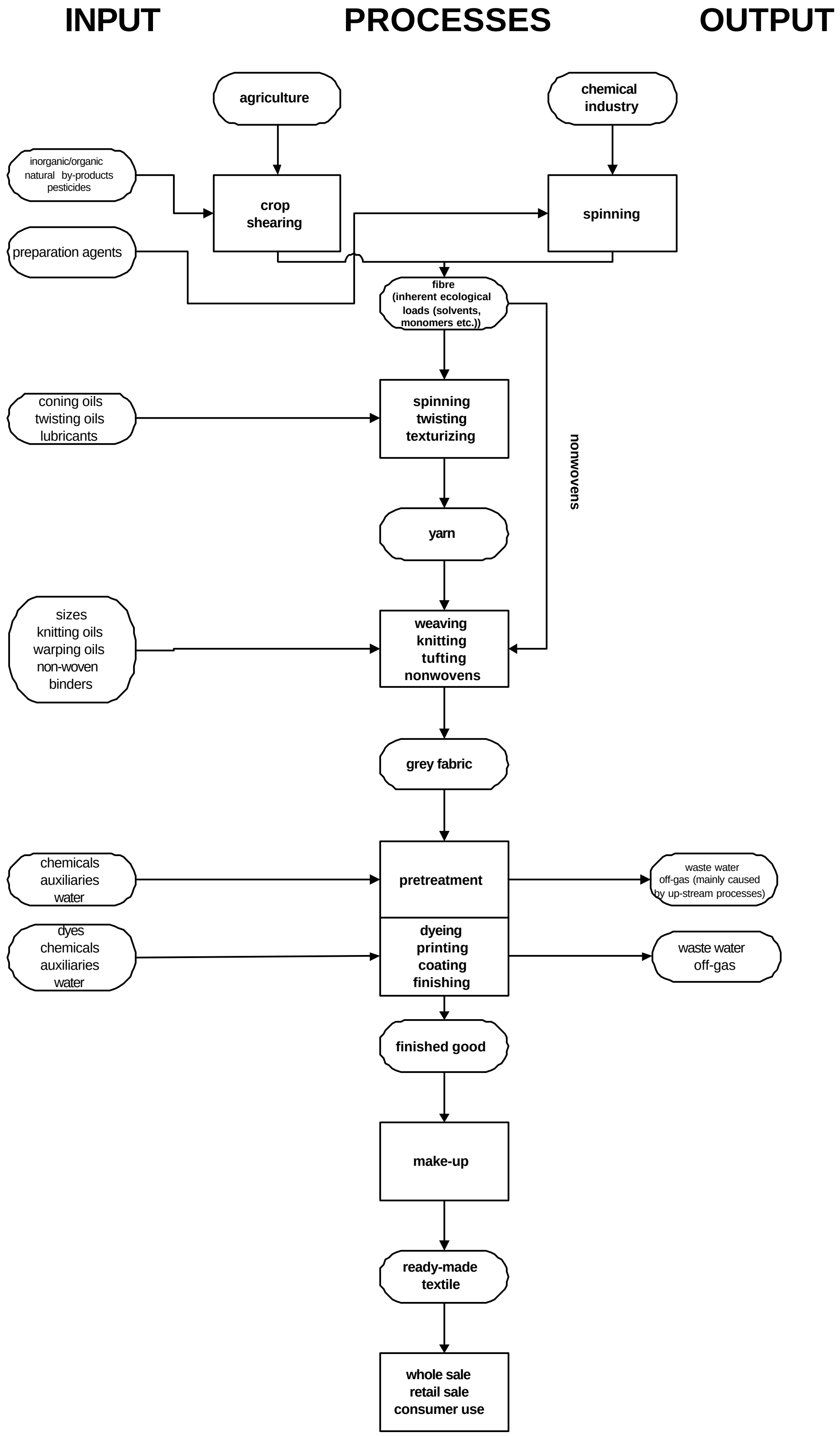


Figure 2.2: Simplified view on the input-output situation along the textile chain

2.1.1 Fibre production

Natural fibres are available from animals and plants (Figure 2.3). The most important natural fibre types are cotton and sheep´s wool.

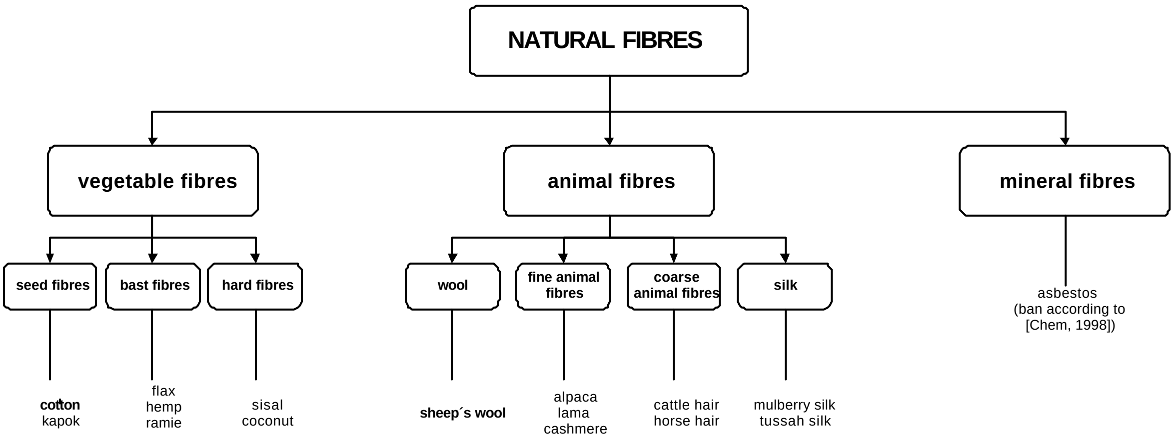


Figure 2.3: Natural Fibres [Wulfhorst, 1998]

The raw materials for man-made fibres are natural and synthetic polymers and inorganics (Figure 2.4).

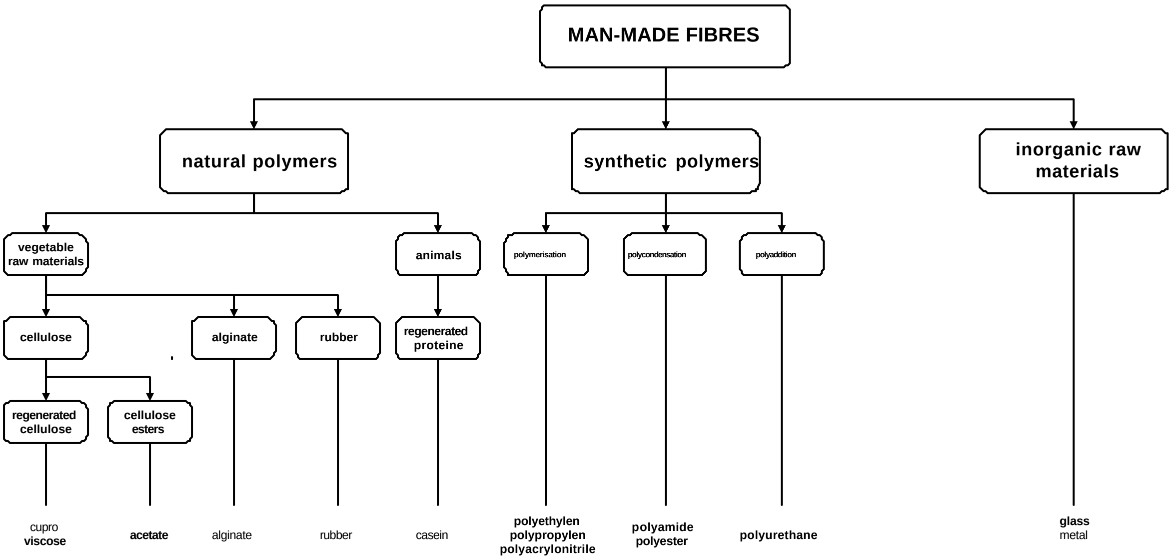


Figure 2.4: Man-made fibres [Wulfhorst, 1998]

Polyester, polyamide, polyacrylonitrile, polypropylene, regenerated cellulose (viscose), and acetate are the most important man-made fibre types in textile industry.

2.1.1.1 Man-made fibres

As a first step in man-made fibre processing filaments from the above mentioned raw materials are produced by

- melt-spinning
- dry-spinning
- and wet-spinning.

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 had passed the spinning nozzles is used. Wet-spinning is carried out by immersing the filaments into a coagulation bath. The removal of the solvents from the fibres is a diffusion controlled process.

Solvent-residues charging wastewater and off-gas are typical for man-made fibres which are produced by wet- or dry-spinning techniques.

After the spinning process the filaments are drawn to increase the orientation of the macromolecules and thereby the tensile strength of the yarns.

Man-made fibres can be used

- as filaments or multifilament yarns
- or after converting (breaking, cutting) as staple fibres (further processing is carried out like natural fibres/spun yarns).

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. A better heat retentivity, elasticity, and a more „textile“ character in comparison to flat yarns is attained.

Preparation agents 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. These preparation agents can cause the main part of ecological loads in pre-treatment processes in textile finishing mills (for details see Chapt. 2.2.1.3 and Annex I).

2.1.2 Spun yarn production

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 of the fibres, drafting, and twining of the fibres to a yarn.

Ring spinning is the most important technology (80 % of worldwide yarn production). The open end technique is the mostly used non conventional spinning technology.

Natural fibres as well as man-made staple fibres are produced into yarns with different types of spinning systems. The kind of system used depends on the fibre length, fibre thickness, and the end-use of the product. In all technologies mentioned below the last step is carried out on ring spinning or non conventional spinning machines:

- cotton spinning technologies
  (all fibre types (esp. cotton) up to 40 mm length)
- worsted spinning (wool and long staple man-made fibres (esp. polyester and polyacrylonitrile))
- semi worsted spinning (important for coarse wool and long staple man-made fibres (esp. for polyamide and polyacrylonitrile))
- woolen spinning (universal technique for wool and fine man-made fibres).

The differences between these techniques are based on type and number of the spinning preparatory steps (drafting, combing etc.).

Some yarn qualities are twisted (two or more yarns are twined up).

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 wastewater and off-gas in finishing (esp. in pre-treatment processes).

2.1.3 Fabric formation

2.1.3.1 Weaving

Weaving means to interlace two ore more yarn systems crosswise and perpendicular. On the weaving machine (loom) the weft yarn is inserted into the lengthwise oriented warp yarns (shed). Before the weaving process starts some preparatory processes have to be carried out. At first, the loom beam has to be prepared. The warp yarns have to be assembled with the help of direct warping machines or sectional warping machines. Sectional warping is used for small highly patterned qualities. With respect to ecology it is important that warping oils are sometimes used in sectional warping and that, in most cases, beam warping is related to the sizing process.

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 (Annex I) forms a protective film on the warp yarn, protruding fibre ends causing loom stops are minimized. Sizing is done with help of sizing machines (slashers). 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 dryed and assembled to the loom beam. 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.

Due to different machinery manufacturers and different fabric qualities (fineness of yarns, fabric density, fabric pattern etc.) different kinds of looms are used in weaving mills:

- Eccentric looms (simple weave patterns)
- Dobby machines (more kind of weave patterns)
- Jacquard machines (most kind of weave patterns).

The weft insertion is carried out with the following techniques:

- Shuttle
- Projectile
- Rapier
- Water jet
- Air jet
- Special weft insertion techniques
- Circle weave technique.

The size add-on on the warp yarns depends – besides some parameters of the yarn – on the type of weaving machine used, respectively, on the weft insertion rate.
Woven textiles are used in all textile sectors (apparel, home textiles, and technical textiles).

2.1.3.2 Knitting

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 (Annex I) used in the process are of ecological interest in downstream processing steps (esp. pre-treatment in textile finishing mills).

2.1.3.3 Nonwovens

Fabrics made of fibres without an intermediate yarn processing are called nonwovens. A great variety of processes is used (Figure 2.5).

The application of nonwovens varies in a great range:

- interlinings,
- backings for coatings,
- dishclothes,
- diapers,
- filters, geo-textiles, and other technical textiles.

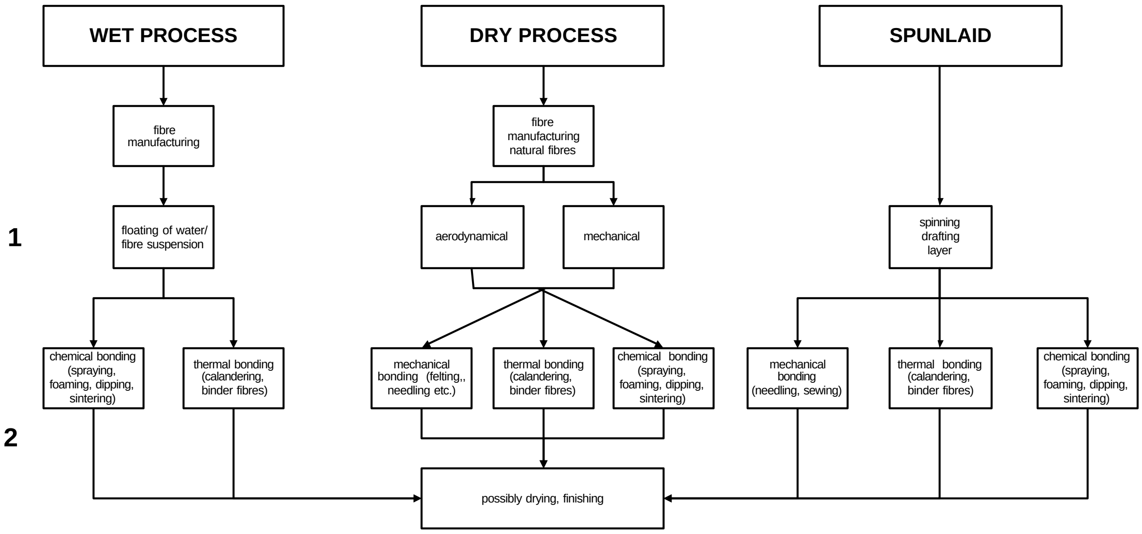


Figure 2.5: Nonwoven processing [Wulfhorst, 1998; Rouette, 1995]
1: Production of non-bonded fleece 2: Bonding technologies

In nonwoven 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 materials are negligible.

2.1.3.4 Tufting

Carpet industry uses the tufting technology. Pile threads (in loop form) are introduced with needles into a backing. The piles are fixed with a back coating on the substrate. Loop pile materials and cut pile materials are produced.

2.1.3.5 Braiding

Braiding goods are of less importance compared to the above mentioned methods of fabric formation. Braided goods are used as ropes, healds, and in composite materials etc..

2.1.4 Finishing (Overview)

To reach the consumers or technical demands, textile raw materials have to be finished. 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 water proof and/or flame resistant finishing for industrial textiles are fulfilled in textile finishing. Therefore, the finishing step has a great influence on the added value and utility value of the textile.

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 textile. However, fabric finishing dominates (Figure 2.6).

Before further processing in the finishing mill all by-products from the grey textile which could interfere the downstream processes (dyeing, printing, and finishing) must be removed. The pre-treatment steps play a key role for all the subsequent finishing processes. The main part of ecological loads in pre-treatment steps (wastewater and off-gas) are caused by the different fibre by-products (Chapter 2.2). The kind and amount of pre-treatment steps are substrate specific and depend on the end-use (consumers demand) of the material. For standard recipes used in pre-treatment see Annex II.

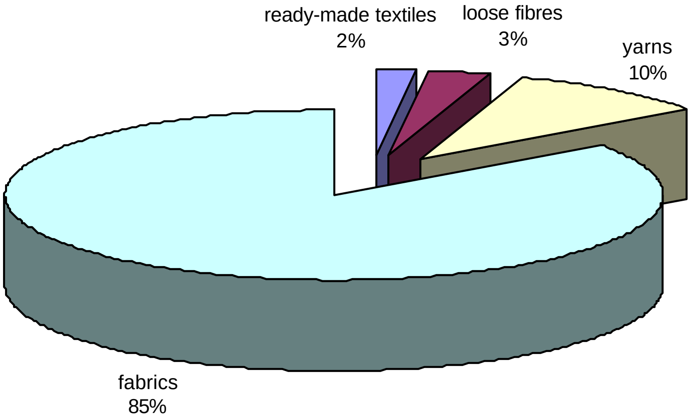


Figure 2.6: Finishing of textiles [BFBW, 2000]

Especially in the apparel industry the demands on the products change quickly (up to four times a year) due to fashion. For the German textile finishing industry with her highly sophisticated products short delivery times (just in time production) is the dominating factor in dispatching and production.

2.1.5 Make-up

Make-up of the textiles is the last step before selling in retail or whole trade. Make-up includes the following steps:

- cutting
- sewing
- assembling with other technologies (adhesive bonding, welding, shaping).

2.2 Input materials

2.2.1 Textile raw materials

The different types of natural and man-made fibres are mentioned in Chapter 2.1.1.

Textile raw materials and their by-products play a crucial role concerning the ecological impacts (esp. wastewater and off-gas) in textile finishing and are therefore discussed in more detail.

Especially the following items are of interest [EnviroTex, 1998; EnviroTex, 1994; EnviroTex, 1996a;

EnviroTex, 1996b; EnviroTex, 1996c]:

- natural impurities from cotton, wool, silk etc. (kind and quantities see Annex I)
- fibre solvents (in cases where man-made fibres are produced by dry spinning or solvent spinning processes)
- monomers (esp. caprolactam ex polyamide 6)
- catalysts (e.g. antimony trioxide in polyester fibres)
- sizing agents (woven textiles esp. cotton and cotton blends) (kind and quantities see Annex I)
- preparation agents (esp. woven and knitted textiles made of man-made fibres) (kind and quantities see Annex I).

The next chapters focus on the inherent ecological loads which are imported from the natural and man-made fibres into the textile finishing mills.

2.2.1.1 Cotton

The native cellulose fibre cotton consists mainly of cellulose and some other components with varying composition as shown in Annex I. The organic material in natural cotton, which is released during pre-treatment processes (pectines, proteins, waxes, seed capsules etc.), creates COD in the wastewater. Also inorganic substances (salts of K, Na, Fe etc.) are removed from cotton in the pre-treatment processes.

In cotton production besides fertilizers, fungizides, insecticides, herbizides, growth regulators, and defoliants are used. Normally the pesticides are applied in growth periods before the cotton boll is opened. Biocides can be applied to protect cotton fibres during transport and storage. According to an analysis by order of the Bremer Baumwollbörse the pesticide content in raw cotton fibres is negligible [Bremen, 2000; Dollacker, 1996].

2.2.1.2 Wool

The natural by-products of wool (grease, suint, dirt, vegetable matters; see Annex I) are removed during wool scouring. 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.

Any remaining dirt and vegetable matter on the raw wool, together with short fibre fragments, are removed either mechanically during carding or chemically by carbonizing. The washing of fabrics during pre-treatment removes preparation agents (spinning oils, combing oils, etc.).

2.2.1.3 Man-made fibres

Preparation agents, applied during fibre processing, spinning and fabric formation cause the main ecological charges in pre-treatment of textiles made of man-made fibres. The preparation agents are mainly based on the following chemistry (see also Annex I):

- Mineral oils
- Ethylene-propylene oxide adducts
- Common fatty acid esters
- Steric hindered fatty acid esters (low-emission products)
- Polyolesters (low-emission products)
- Polyester-/polyetherpolycarbonates (low-emission products).

Figure 2.7 shows the main application points and characteristic add-on levels (amount of preparation based on the dry weight of the fibres) of preparation agents and sizes.

Besides preparation agents the following inherent ecological loads are imported from man-made fibres into the pre-treatment processes in textile finishing.

Fibre	Impurities, by-products	Content
Polyamide 6	Caprolactam Oligomers	Up to1% (therefrom up to 90% extractable during wet processes, up to 50% fugitive in thermal processes)
Polyester	Antimony trioxide (catalyst) Oligomers	300 ppm Sb (approx. 80 ppm Sb can be extracted during HT-dyeing [Thier-Grebe, 2000])
Polyacrylonitrile	Solvent (mainly N,N-Dimethyl-formamide, N,N-Dimethyl-acetamide)	0,2% - 2%
Elastane	Solvent (N,N-Dimethylacetamide)	Up to 3%
m-Aramide	Solvent (N,N-Dimethyl-acetamide, N-methyl-pyrrolidone)	1% - 3%

Table 2.1: Inherent ecological loads of man-made fibres

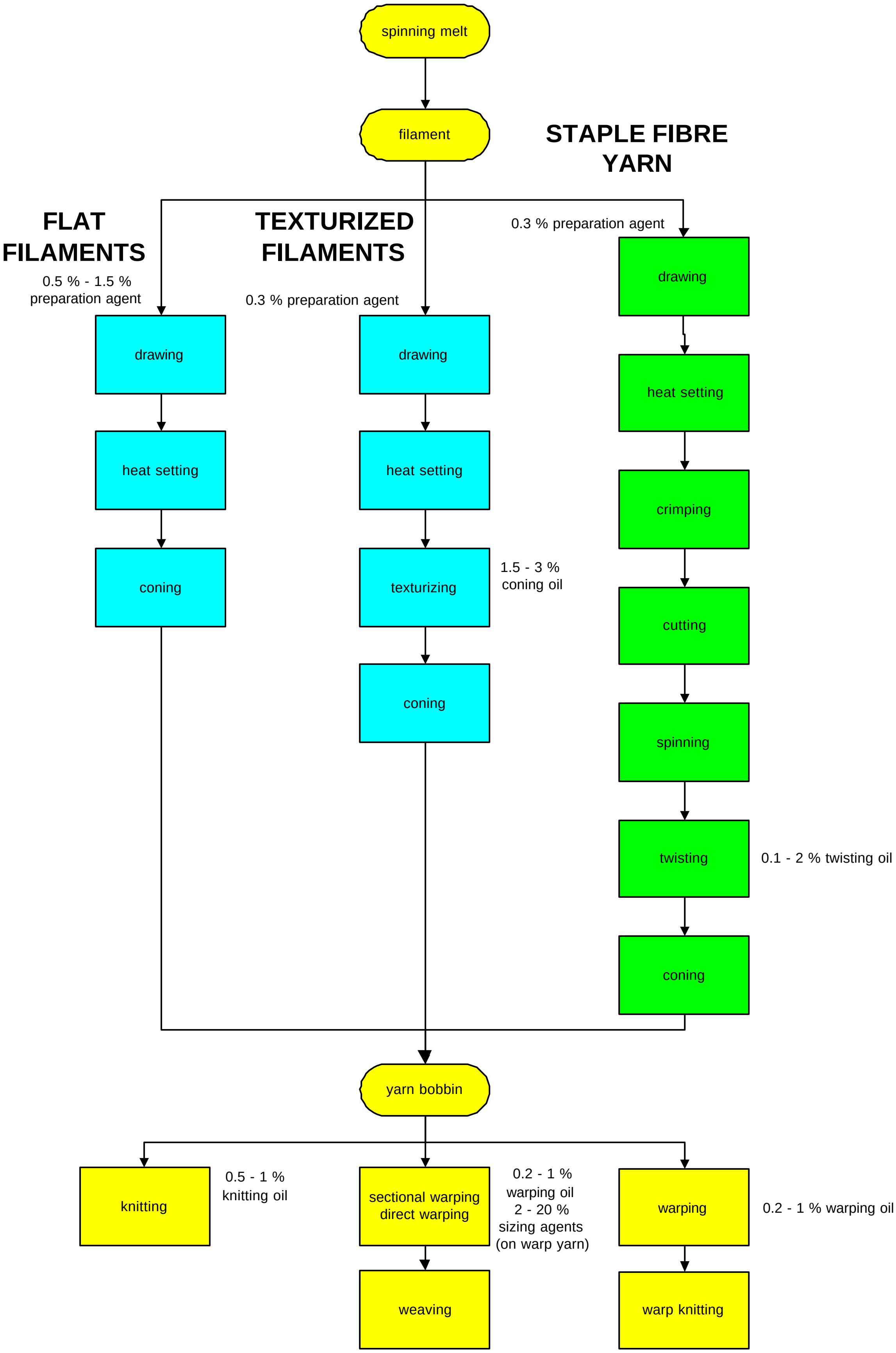


Figure 2.7: Main application points and characteristic add-on levels for preparation agents and sizing agents

2.2.2 Auxiliaries and chemicals

Integrated environmental pollution prevention and control in textile finishing has to start at „the begin of the pipe“. Besides information on textile raw materials sufficient information on the chemicals and auxiliaries used in textile finishing is necessary too.

It has to be mentioned that some chemicals and auxiliaries 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 this 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.

The consumption of chemicals, auxiliaries and dyes (1997) in German finishing industry is estimated to

- 204000 t chemicals
- 102000 t auxiliaries
- 13000 t dyes (estimation of Umweltbundesamt [BW, 1998].

The best overview on textile auxiliaries is given in the „Textilhilfsmittelkatalog“. 7000 products based on approx. 400-600 different chemical substances are listed [THK, 2000].

Table 2.2 gives an overview on the variety of textile auxiliaries and chemicals used in textile finishing, their effects, and their chemical composition. The nomenclature and structure of the „Textilhilfsmittelkatalog“ is adopted in most of the cases [TEGEWA, 1987].

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 cellulosis, 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 dipersulfates 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, 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
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

Process	**Auxiliary**	**Effect**	**Chemical composition**
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 ulfonates, polyacrylates
Exhaust dyeing, padding processes	Wetting agents Deaeration agents	Increase of wetting capacity of the dye liquors; improve of dye penetration in padding processes; increase of dye absorption	Alkylsulfates, alkanesulfonates, alkylarylsulfonates, salts of sulfosuccinic acid esters, fatty alcohol ethoxilates, alcohols of higher valence, phosphoric acid esters, hydrocarbons.
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 condensates, 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
Exhaust dyeing	Dyestuff protecting agents, boildown protecting agents	Protection of dyestuffs during application from destruction by foreign matters with a reducing effect	Buffers and/or oxidizing substances (nitrobenzene sulfonate), urea, alkylarylsulfonates

Process	**Auxiliary**	**Effect**	**Chemical composition**
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 polymers and copolymers.
	Antifrosting agents	Prevention of frosting effects in pad-steam processes.	Foaming surfactants as ethylene oxide adducts.
	Wet pick-up increasing substances	Increase of dye yield in reactive pad batch processes	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
Aftertreatment	Aftertreatment agents for fastness improvement	Improve of rubbing fastness, wet fastness and light fastness	Soaping aftertreatment 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. 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 (polyvinyl acetate, polyacrylic acid esters).
		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 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, sulfonic acid derivatives Sulfur dyes: sodium sulfide, sodium dithionite, glucose and mixtures thereof
		Removal of dispersion dyes (reductive aftertreatment)	Sodium dithionite, thiourea dioxide
		Destroy of dyes in case of faulty dyeing (stripping)	Sodium dithionite, sodium or zinc formaldehyde sulfonic acids, thiourea dioxide
Discharge printing	Discharging agents	Discharging agents are printed onto a predyed textile material for the destruction of the dyes and thus cause a pattern	Reducing and oxidizing agents (see above)
	Discharging assistants		Anthraquinone derivatives

Process	**Auxiliary**	**Effect**	**Chemical composition**
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 compounds, Al-, Cr-, Fe-salts
Dyeing, colour correction	Brightening agents	Partial removal of the dye already absorbed and fixed	Polyvinylpyrrolidone, polyglycol ether, cellulase, alkyl aryl sulfonates, alkyl amine ethoxylates, reducing agents and oxidizing agents
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), guanidine derivatives, benzophenon, benzotriazol
Dyeing in general	pH-regulators, acids and alkali dispensers	Adjust/control pH	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	

Process	**Auxiliary**	**Effect**	**Chemical composition**
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		
	Weigthing 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, ethylenvinylacetate-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
Repellents	Water repellents	Impart of a water-proof finish	Fluorocarbon resins, polysiloxanes, paraffins together with aluminium, zirkonium 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

Process	Auxiliary	Effect	Chemical composition
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 combusibility	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 tetrakis-hydroxmethylphosphonium 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.
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

Process	Auxiliary	Effect	Chemical composition
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
	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)
Aftertreatment 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

Table 2.2: Auxiliaries and chemicals used in textile finishing

2.2.3 Dyes

2.2.3.1 Classification of dyestuffs

Dyestuffs may be classified according to their chemical composition (azo, antrachinone, sulfur, triphenylmethane, indigoid, phthalocyanine, etc.) or according to their performances in the dyeing processes [Ebner, 1988].

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 colour fastness is much worse.

Table 2.3 shows the main application fields of different dyestuff types.

Dyestuff class	Sub- class	PES	CA	PAC	PA	Si	WO	Cell
Disperse		+++	+++	++	++	-	-	-
Basic (cationic)		-	~	+++	++	-	-	-
Acid	Standard	-	-	~	+++	+++	+++	-
	1:1 metal complex	-	-	-	P	+	+++	-
	1:2 metalcomplex	-	-	-	++	+	+++	-
Mordant		-	-	-	-	~	+++	-
Reactive		-	-	-	~	++	++	+++
Direct		-	-	-	++	++	P	+++
Vat	Standard	~	-	~	~	~	-	+++
	Leuco vat ester	-	-	-	~	~	~	P
Sulfur		-	+	-	-	-	-	+++
Azoic (naphtol)		+++	-	~	~	~	-	+++

Table 2.3: Dyestuff classes and their main application fields (according to [Ebner, 1988])
+++: very often; ++: often; +: in use; p: mainly in printing; ~: possible

2.2.3.2 Dyestuff specific ecological loads

In exhaust dyeing (Chapter 2.3.7.1) non fixed dyestuffs remain in the dyebath and load the wastewater depending on dyestuff type and process conditions.

Average degrees of fixation of dyestuffs in exhaust dyeing are summarized in Table 2.4.

Type of dye	Degree of fixation [%]
Reactive	55-97
Vat	75-95
Disperse	88-99
Direct	64-96
Acid (anionic)	85-98
Metal complex	82-98
Sulfur	60-95
Basic (cationic)	96-100
Mordant (Chrome)	95-98
Pigment	100

Table 2.4: Degree of fixation of the main dyestuff classes [Schulze-Rettmer, 1996]

Wastewater from dye bathes or rinsing bathes (resp. residual liquors if padding technologies are used) are loaded with the non exhausted dyes, dyeing auxiliaries, salts, alkali and acids.

It has to be taken into account that a dye-formulation contains approx. 30-60% pure dyestuff (rough estimation); 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 lignine sulfonates), standardizing agents (salts) and additives (anti-freeze agents etc.).

In Table 2.5 an overview on the main ecological loads concerning the important dyestuff classes is given (multipurpose dyeing auxiliaries used for all the dyeing techniques are not mentioned).

Dyestuff class	**Main ecological aspects**
Reactive	Partially low fixation degree, AOX source, low adsorption tendency of dyestuff hydrolysates in activated sludge treatment, high amount of salts (sodium chloride, sodium sulfate)
Vat	Reducing agents (sulfur compounds), partially halogene containing oxidizing agents
Disperse	Carriers, reductive aftertreatment (sulfur compounds)
Direct	Salt, aftertreatment with water toxic cationic agents
Metal complex	Heavy metal content in dyestuffs
Sulfur	Sulfur containing dyestuffs and reducing agents, partially halogene containing oxidizing agents
Basic (cationic)	Retarder in dyeing PAC (quaternary ammonium compounds)
Mordant (Chrome)	Chrome

Table 2.5: Main ecological loads in dyeing

2.3 Processes in finishing

2.3.1 General information

The processes in textile finishing mills can be summarized under four categories (Figure 2.8):

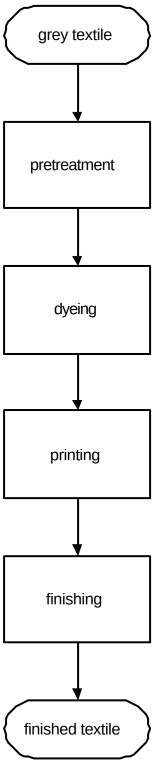


Figure 2.8: Main processes in textile finishing

Depending on the demanded end-use properties of the textile all or only some of the above mentioned processes are carried out.
Normally coating and laminating - not mentioned in Figure 2.8– take place before the last finishing step.

2.3.2 Pre-treatment

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 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.

These by-products together with the auxiliaries and chemicals used in pre-treatment cause a considerable ecological load in the wastewater as well as in the off-gas.

Pre-treatment is a key factor for all downstream finishing steps. Poor pre-treatment generates quality problems and in consequence re-works and therefore additional ecological loads in the operations downstream.

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).

Mechanical, wet, and thermal pre-treatment steps are used (Figure 2.9). 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 drycleaning processes (perchloroethylene as solvent) is in use.

Typical recipes in wet pre-treatment are summarized in Annex II.

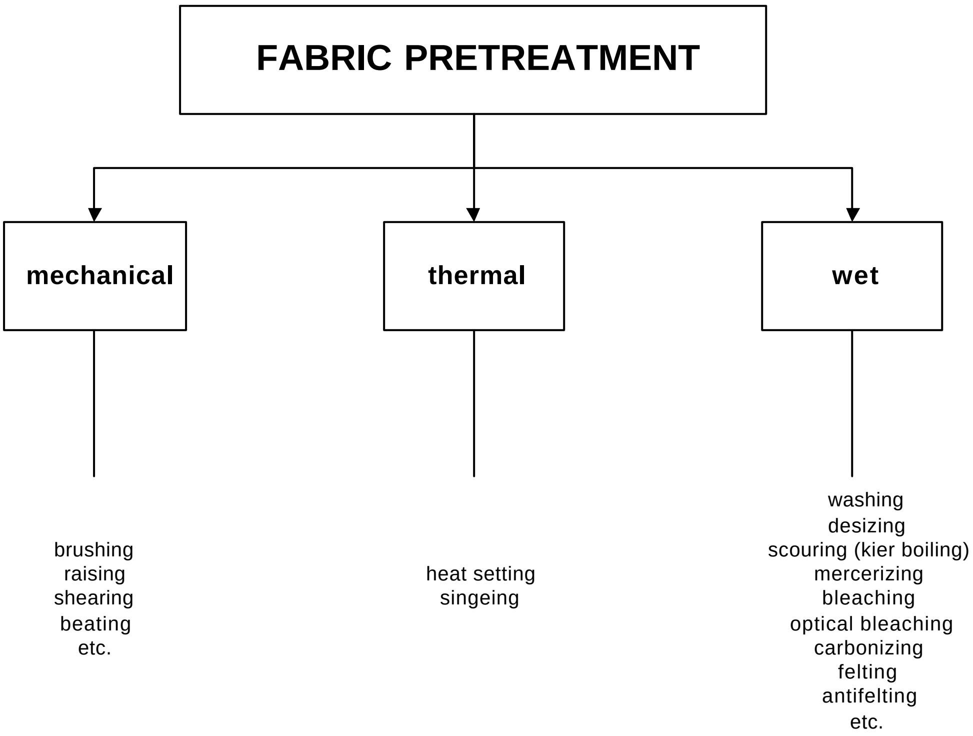


Figure 2.9: Main pre-treatment processes

Typical pre-treatment steps for cotton, wool and fabrics made of man-made fibres are summarized in Figure 2.10 (see also Annex II).

If pre-treatment starts with a wet process (washing, desizing etc.), the ecological loads due to the textile raw material are to be found to a certain degree (depending on the extraction rate) in the wastewater. If a heat setting process is done as first step (esp. in pre-treatment of synthetic materials), the main part of raw material by-products are found in the off-gas.

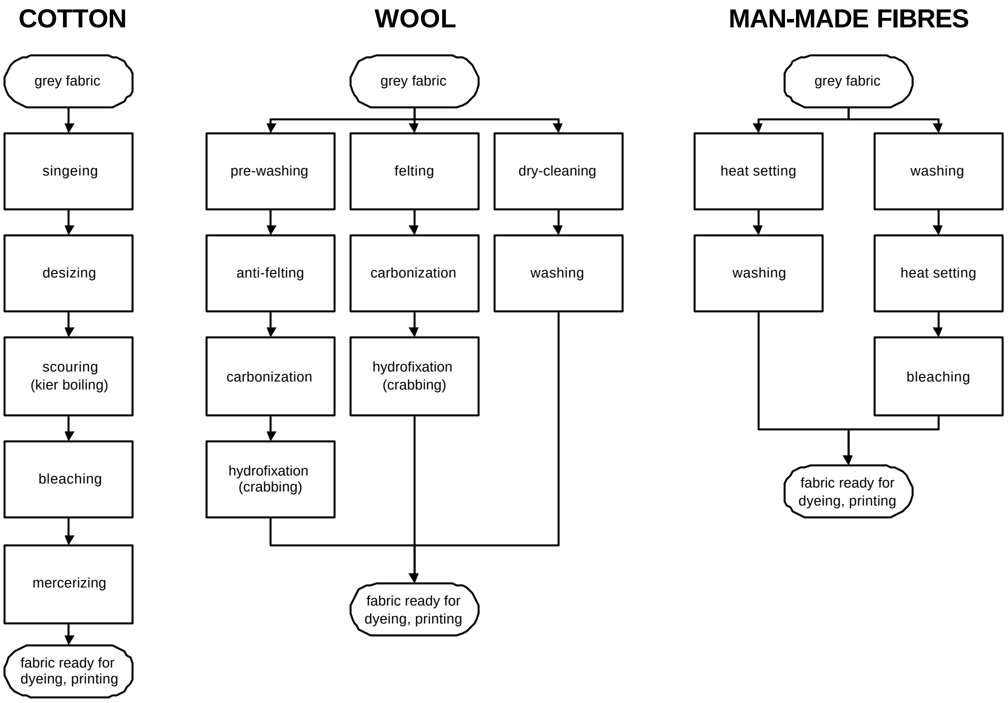


Figure 2.10: Typical pre-treatment processes for cotton, wool and man-made fibres

2.3.2.1 Mechanical processes in pre-treatment

The following mechanical pre-treatment steps are commonly used:

- brushing; removal of impurities
- beating (e.g. after singeing or carbonizing); removal of impurities
- raising (also used in mechanical finishing)
- shearing (also used in mechanical finishing).

In comparison to wet and thermal pre-treatment processes mechanical pre-treatment is accompanied with negligible environmental charges. Besides energy consumption and noise dust generation should be mentioned.

2.3.2.2 Thermal processes in pre-treatment

2.3.2.2.1 Heat setting

Heat setting (also called thermofixation) 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 (Figure 2.10), as an intermediate step after dyeing or as a last finishing step (often in combination with application of finishing auxiliaries) (Chapter 2.3.5.3).

It has to be taken into account that heat setting of grey fabrics or insufficient pre-washed textiles can lead to a considerable ecological impact to the off-gas depending on the amount and type of preparation agents and other fibre inherent ecological loads (residual fibre solvents, residual fibre monomers). In case of direct heated stenters Organic-C-load and formaldehyde content in the off-gas due to incomplete burning out of the gases (methane or propane/butane) is to be taken into consideration.

2.3.2.2.2 Singeing

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. Of ecological interest are dust and volatile organic carbon (VOC). Also a relative strong odour emission can be observed during singeing. Singeing is often combined with a device to extinguish sparks and a padding device to impregnate the textile directly after singeing with the desizing liquor.

2.3.2.3 Wet processes in pre-treatment

Wet pre-treatment includes various processes. All or only some of these processes may be required. The processes can be applied either as separate steps or as combined steps.

In wet pre-treatment batch, semi-continuous, and continuous processes can be used. Fabrics can be pretreated in open width or rope form. Regarding ecology and economy continuous pre-treatment operations are to prefer, but batchwise pre-treatment on dyeing machines is often used in those cases where a great variety of small lots are to be scheduled and handled. Besides, discontinuous pre-treatment is often preferred due to high investment costs for a continuous equipment.

Typical recipes for the most important wet processes in pre-treatment are summarized in Annex II.

2.3.2.4 Desizing

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 materials 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.

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.

The following methods are commonly used (depending on the size type):

- enzymatic desizing processes; starch
- oxidative desizing (e.g. persulfate); all size types
- washing (with/without detergents); water soluble sizing agents.

Desizing can be carried out in a continuous (pad-steam), semi-continuous process or discontinuous way.

As mentioned above, the desizing technology depends on the kind of size applied on the warp yarn. However, the commission finisher has often no or less knowlegde on the quantity and type of sizes on the fabrics; for this reason optimization of the desizing process is not always possible.

Enzymatic desizing
Fabrics sized with non-soluble starches or non-soluble starch derivates are desized with the help of enzymes (amylases) which catalyse the depolymerisation of the starch macromolecules. The operation is mainly done in a semi-continuous way. The fabric is padded with the hot desizing liquor and then stored up to 20 h under slow rotation on batching rolls for enzymatic degradation of the starch size. Afterwards the starch degradation products are washed out.

Oxidative desizing
Oxidative desizing (oxidative degradation of macromolecules mainly by means of persulfate leads to water soluble fragments) is useful because it is a non-substrate specific desizing method. A single step

process combining peroxide bleaching and oxidative desizing is possible. It has to be taken into account that oxidative desizing, if not well controlled, may attack cellulose.

Water soluble sizing agents (mostly used on man-made fibres)
Water soluble sizes (polyvinyl alcohols, modified starch, modified cellulose, polyacrylates, polyesters.) can be removed in a continuous or discontinuos way (hot water with or without detergents).

It is to be mentioned, that the desizing liquors can cause the main part of the COD-load of a finishing mill (up to 70% in mills finishing woven fabrics). Depending on the desizing technique COD-concentraions in a range from 3000 to 80000 mg O_2/l can be observed in the desizing liquors.

2.3.2.5 Scouring (kier boiling)

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. Besides alkali (mostly sodium hydroxide) complexing agents and surfactants are used in the scouring liquor.

Main ecological impact in scouring is caused by non readily biodegradable surfactants and complexing agents as well as by a high COD-load due to the organic impurities removed from the fibres. COD-concentrations from 2000 to 6000 mg O_2/l are typical.

2.3.2.6 Bleaching

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.

During bleaching natural coloured by-products on the fibres are removed resp. destroyed. Bleaching is carried out for undyed natural materials to achieve extra-white effects as well as for materials to be coloured with high brilliance or in light shades. Normally, textiles made of man-made fibres are delivered with a high degree of whitenesss. However, to achieve extra-white effects (e.g for curtains) bleaching is commonly used.

Bleaching can be carried out on loose fibres, slivers, yarns, and (mostly) on fabrics in a continuous way or batchwise.

The bleaching technologies resp. the bleaching agents vary with the textile substrate (Table 2.6):

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

Table 2.6: Bleaching agents
***: protecting agent for polyamide necessary**

Peroxide bleaching
In bleaching with hydrogenperoxide the bleaching agent is oxygene, generated from hydrogenperoxide under alkaline conditions. It is done at elevated temperatures (60 °C – 98 °C) under alkaline conditions (pH approx. 12). Main ecological impact to wastewater is caused by the strong alkali, complexing agents (phosphonates, polycarboxylic acids), wetting agents, stabilizing agents (esp. sodium silicate), and by-products removed from the cellulose. COD- content in the effluent is in a range between 3000-10000 mg O_2/l.

Chlorite bleaching
Bleaching with sodium chlorite is done under acidic conditions (pH 3 – 5) at temperatures between 70 °C and 95 °C; buffers and sodium nitrate as a corrosion inhibitor are added.

Highly toxic chlorine dioxide can be released in the process, if the pH is not well controlled. AOX generation through chlorination reactions with organic compounds has to be minimized by means of a good process control and reduction of chlorite surplus after bleaching (adding of reducing agents; mostly sulfite).

Reductive bleaching
Reductive bleaching can be carried out with sodium dithionite and sodium formaldehyde sulfoxylates.

It has to be taken into account that bleaching with sodium hypochlorite is not permitted in Germany due to high loads of AOX and free chlorine.

2.3.2.7 Mercerising

Mercerising (treatment of cotton and cotton blends with strong alkali under tension) improves the dyestuff absorption and increases tensile strength. A good handle, better dimensional stability, and a resistant lustre are achieved. Mercerising leads to a change in the crystalline structure of the cellulosis moelcules and to a swelling of the fibres.

Mercerisation is possible

- on greige goods
- after desizing
- after desizing and scouring
- after bleaching
- after dyeing.

Woven fabrics are mercerized in full width, knitted fabrics in full width or in rope form. Normally, mercerising is mostly done with a hot sodium hydroxide liquor; only one installation in Germany uses ammonia which leads to more resistant effects and a very soft handle. For typical recipes in mercerising see Annex II.

The sodium hydroxide concentration varies from 20% - 30%.

The process, done in a continuous way, consists of the following steps:

- padding of the textile with the lye
- drafting of the textile
- washing (under tension)
- acidifying, rinsing.

The main ecological impact in mercerising is the high concentrated residual lye.

2.3.2.8 Causticizing (alkali treatment)

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 °C and 15 °C. The process induces shrinking of the textiles. Ecological impacts in causticizing can be compared to mercerising.

2.3.2.9 Optical bleaching

Optical bleaching agents are fluorescent chemicals (mainly stilben and imidazol derivatives), which absorb ultraviolett light and give a bluish light to the textiles, thereby hiding the yellowish colour of by-products; a very high degree of whiteness/brightness is achieved. Optical brighteners can be regarded as „invisible“ direct dyes. Application is possible in a single step or during bleaching. Optical brightening can also be carried out during finishing. The water toxicity and relatively low degree of bioelimination of the fluorescent agents is often to be considered; however, the amount of brighteners in the effluent is on a low level.

2.3.2.10 Washing/Scouring (synthetic fabrics)

To remove preparation agents as spin finishes, coning, and warping oils, twisting oils etc. and other impurities, synthetic materials are washed with water and detergents. The efficiency depends on dwell time, water througput and the appropriate conditions concerning temperature and detergents. A high COD-load is observed in washing /scouring. If preparation agents based on mineral oils are used, the effluent is not readily biodegradable.

The intense exchange of information in the textile chain is very important to adjust the appropriate washing conditions (kind and quantity of surfactants, pH, temperature, dwell time, liquor exchange, etc.) to achieve good quality and to minimize ecological loads.

2.3.2.11 Raw wool scouring

Raw wool scouring is done on loose fibres to remove vegetable impurities, wool grease and suint (dried perspiration). Raw wool scouring – carried out in one installation in Germany - is topic of a special BREF-document [Lakin, 1999] and therefore not described here.

2.3.2.12 Carbonizing

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.

Main ecological loads are caused by the acid and the organic load in the effluent due to natural by-products removed from the fibre and by volatile crack-products in the off-gas of the burning step.

2.3.2.13 Crabbing

During crabbing („hydrofixation“) the textile material is wounded under tension, treated with hot water and chilled. Crabbing is carried out on wool worsteds in order to fix the material and reduce/prevent creases and felting properties and to wash out by-products (sizes, lubricants). Crabbing can also be carried out after dyeing.

2.3.2.14 Felting (milling; fulling)

Felting (mainly done on woollen fabrics) induces shrinkage of the textile goods made of animal hairs (mainly sheep´s wool); the material becomes denser. The character of the textile changes, esp. a full handle is achieved. Mechanical operations in a humid/warm atmosphere (alkaline or acidic liquor with help of felting agents) induce the felting process. App. 20% of textiles made of pure wool are felted. Ecological charges are caused by felting agents and by-products/impurities removed from the wool during the process.

2.3.2.15 Anti-felting

Felting (shrinkage of textiles made of animal fibres) caused by the unidirectional oriented scales on the surface of the fibres when animal fibres are mechanical stressed in wet processes (e.g. dyeing or household-washing) is in most cases an undesirable effect. In anti-felting operations the scales are minimized with the help of coating polymers, with oxidizing techniques, or with a combination of these processes.

The Hercosett process (combination of chlorine and polymer (polyamide-epoxide compound) treatment) is carried out in two installations in Germany (combed slivers are treated). This method is responsible for a relatively high AOX-load in the effluent.

In antifelting treatment of fabrics based on oxidizing techniques the chlorine generating agents (e.g. dichloroisocyanurat) are responsible for the AOX-content in the effluent.

2.3.2.16 Dry cleaning

As a first step in pre-treatment of fabrics made of wool, wool blends and elastane blends dry-cleaning is carried out in some installations in Germany. By-products from the wool and man-made fibres are removed. Perchloroethylene is used as solvent. The advantage in dry-cleaning is the high washing efficiency achieved and the non-felting properties of perchloroethylene. Dry-cleaning is done in „closed circuits“. The solvent is redistillated. Air emissions are minimized with active carbon filters.

2.3.3 Dyeing

In dyeing textiles are brought into contact with aqueous dyestuff solutions, a great variety of chemicals (salts, acids, etc.), and dyeing auxiliaries (surfactants, dispersing agents, levelling agents, etc.).

Kind and quantity of dyes, chemicals and auxiliaries are substrate specific and depend on the product quality (e.g. fastness properties) and the installed machinery.

Coloration with dyes is based on physico-chemical equilibrium processes, namely diffusion and sorption of dye molecules or ions. These processes may be followed by chemical reactions in the fibres (e.g reactive dyestuffs react with the fibres, metal complex dyestuffs generate complexes with the fibre molecules, vat- and sulfur dyes have to be re-oxidised) [Zollinger, 1987].

Dyeing is carried out in continuous and semi-continuous processes or batchwise (exhaust dyeing) (see also Chapter 2.3.7).

Exhaust dyeing
In exhaust dyeing the material is brought into contact with the dyeing liquor (water with dissolved or dispersed dyes and textile auxiliaries) in a dyeing machine. The dyes exhaust from the dyebath and absorb on the fibres. The dyeing equilibrium depends on temperature, time, pH, and textile auxiliaries. After dyeing the exhausted dyebath is discharged and rinsing, soaping, and special aftertreatment processes take place depending on the kind of substrate, quality to be achieved, and dyestuff used. Dyeing of fabrics is possible in rope form (skein dyeing) or in full width. Different kinds of dyeing machines are available (Chapter 2.3.7).

Important parameters in exhaust dyeing are:

- liquor ratio (kg textile to be dyed/l water used in dyeing bath)
- dyeing method (temperature/time curves; two bathes or one bath method in case of fibre mixtures)
- dyestuff type, auxiliaries
- exhaustion degree of dyestuffs
- amount of rinsing bathes and kind of aftertreatment needed
- energy, and cooling water consumption.

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 batchwise 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.

Continuous dyeing
In contiunous processes 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.

Main ecological loads in dyeing are caused by residual liquors from continuous and semi-continuous processes and the exhausted dye bathes, respectively, rinsing bathes. It is to be mentioned that in exhaust dyeing only dyestuffs and some other auxiliaries esp. carriers, aftertreament agents, conditioning agents) are fixed to a several degree on the textile. The other components in the dyeing liquor load the effluent.

Undesired coloration of the effluent, heavy metal content and impact of AOX ex dyestuffs as well as high degrees of COD and a high salt content are the main ecological impacts with respect to dyeing (see also Chapter 2.2.3.2). COD-concentraion is in a range of 400 to 10000 mg O_2/l (exhausted dyebaths) respectively 10000 to 100000 mg O_2/l for residal liquors.

In Germany (not at least due to a very strict legislation) the colorization of dyeing effluents (esp. if reactive dyes, which are not readily adsorbed by activated sludge, are used) is one of the greatest environmental problems in textile finishing.

Besides the impact to the water path some dyeing auxiliaries (e.g. carriers and some levelling agents) which are partially exhausted from the dye bath and fixed on the textile are released to the off-gas during subsequent drying or curing steps and are responsible for generation of volatile organic carbon (VOC).

2.3.4 Printing

Besides dyeing, colorization in textile industry is possible by means of printing technologies, mainly used for multicolour patterns. The most common printing technologies are:

- direct printing
- discharge printing
- resist printing

Direct printing is the most common approach for applying a colour pattern. It is done on white or previously dyed fabrics (generally in light colours to make the print stand out); in this case it is called overprinting.

In discharge printing a local destruction of a dye applied in a previously step takes place. If the etched areas become white the process is called white discharge. If the printing paste contains reduction resistant dyes the etched areas become coloured (coloured discharge technique). In the case of resist printing a special printing paste (resist) is printed onto the textile to prevent dyestuff fixation. In subsequent dyeing only the non-reserved areas are coloured.

Various printing paste application methods are applied:

- roller printing
- flat screen printing
- rotary screen printing
- transfer printing
- ink jet (emerging technique).

Roller printing is a technique with recessed (engraved) printing forms. In flat screen printing the printing paste is transferred to the fabric through penings in specially designed screens. The openings correspond to the pattern when the printing paste is forced through by means of a squeege. Rotary screen printing uses the same principle, but instead of flat screens the printing paste is transferred through lightweight metal foil screens which are made in the form of cylinder rolls.

In transfer printing (mainly done on PES) ecological loads during textile printing are minimized. The pattern in transfer printing are transfered from a paper support to the fabric by means of heat.

Ink jet printing on textiles can be carried out as jet printing on papers. Nowadays this technique is used for small lots and patterning.

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 (printing paste recipes see 3.3.2.3). 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 (Figure 2.11).

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. Printing paste emulsions based on white spirit creating a considerable amount of VOC during drying and fixation are no longer used in Germany. Nevertheless the printing pastes with synthetic binders can still contain app. 10% of hydrocarbons.

In printing main ecological impact to wastewater is caused by the washing process of the printed textile (with exception to pigment printing), the residual printing pastes (COD: 50000 to 300000 mg O_2/l) and by the cleaning procedures of printing equipment and printing blankets. A high ammonia content in the effluent (ex urea used as hydrotropic agent) is observed. In pigment printing emissions to air (ammonia, formaldehyde, VOC) can be observed in drying and curing.

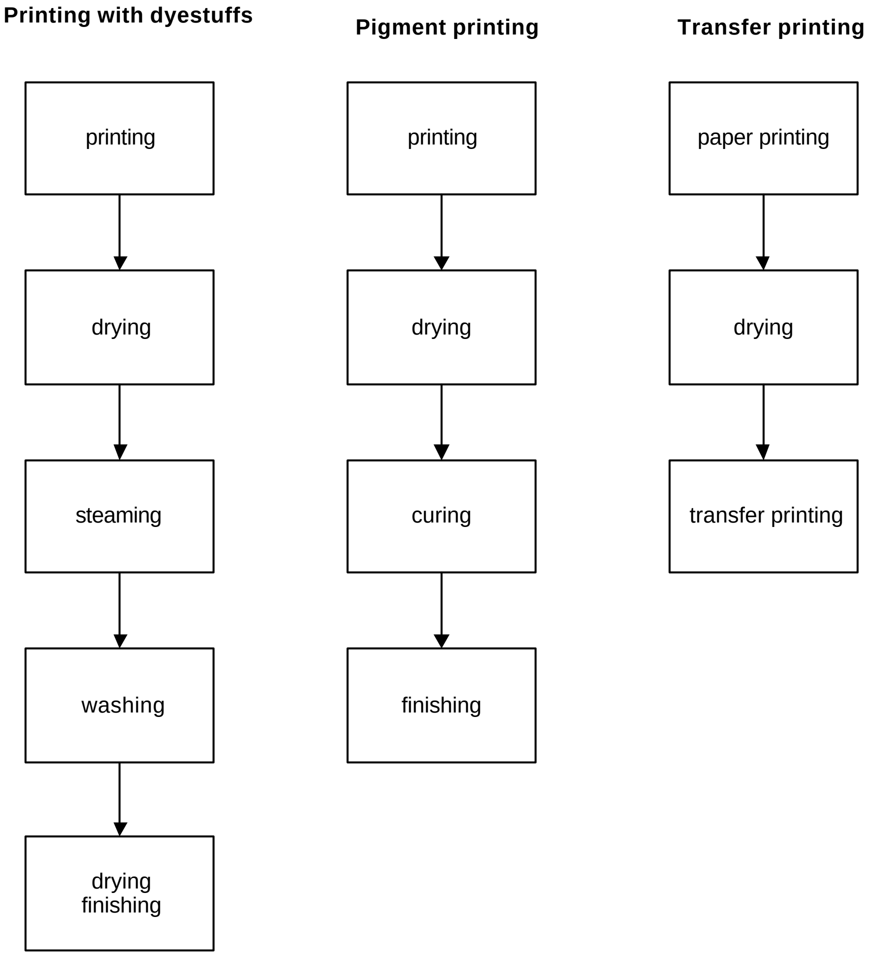


Figure 2.11: Process steps in printing

2.3.5 Finishing

Mechanical, thermal, and chemical treatments performed on fibres, yarns, and fabrics after pre-treatment, dyeing, or printing are summarized under the item finishing. Figure 2.12 gives an overview on the processes. Finishing improves the functionality and the handle of the textile.

Some finishing processes are specific for a special substrate (easy-care finishing on cotton, antistatic finishing for textiles made of man-made fibres).

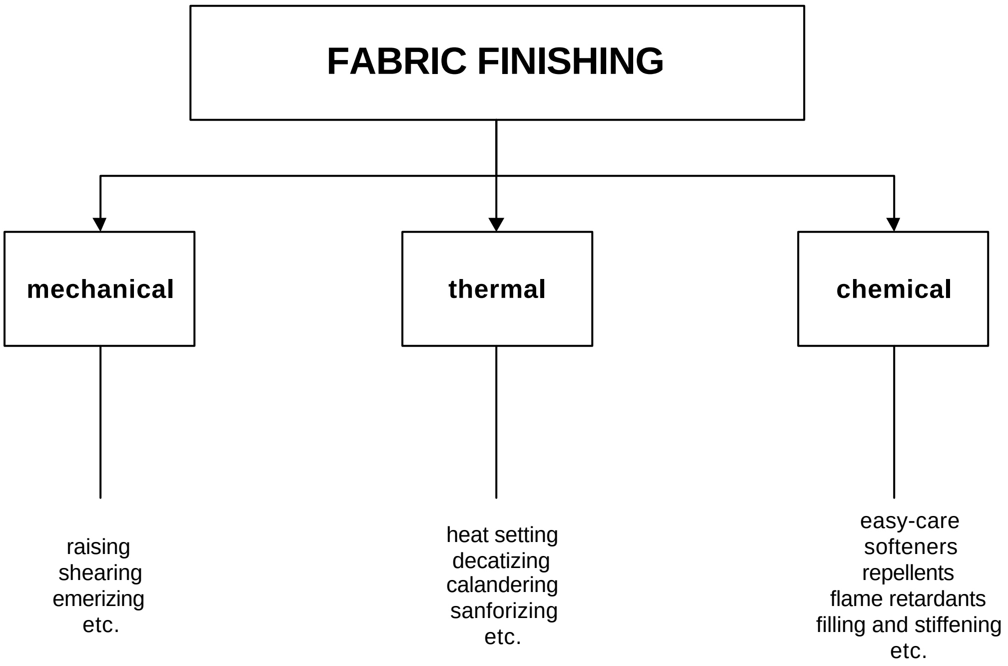


Figure 2.12: Finishing processes

2.3.5.1 Mechanical processes in finishing

In processes like raising and shearing energy consumption and dust containing off-gas have to be considered. Pressing (calandering) is carried out to give a special brightness to the textile.

From the ecological view mechanical finishing is of less interest.

2.3.5.2 Thermal processes

2.3.5.2.1 Heat setting

Heat setting can be carried out as a last finishing step but also on raw materials or as a intermediate step after washing or dyeing (see also Chapter 2.3.2.2.1).

2.3.5.2.2 Other thermal processes

Steaming, decatizing, calendering, sanforising and other processes done with heat, steam or hot water are of interest concerning energy consumption. Emissions to wastewater and off-gas are negligible.

2.3.5.3 Chemical processes in finishing

Normally in chemical finishing the finishing agent is applied to the substrate by means of a padding machine (Chapter 2.3.7). Afterwards (mostly in a continuous way) the auxiliary is dried and cured in a stenter (Figure 2.13). For typical recipes in finishing see Chapter 3.5.4.1.1.

Often a mixture of different auxiliaries is applied in one padding process to create a multifunctional effect.

The following finishing effects are of interest (not completed list):

- Easy-care (improvement of crease and shrink resistance)
- Softening
- Filling, stiffening

- Repellents (oil, water, and soil repellents)
- Flame retardants
- Antistatic finishing
- Non-slip finishing
- Antimicrobiotic finishing

Drying of the padded auxiliary is carried out by temperatures of approx. 120 °C; curing is carried out at temperatures between 150 °C and 180 °C.

In finishing the main charging load in the off-gas is generated by volatile substances either caused by impurities/by-products, residual solvents, monomers, or the auxiliaries themselves. Besides, in finishing also residues from upstream processing steps (preparation agents from spinning and fabric production, auxiliaries/chemicals and their by-products used in dyeing and printing) are to be observed. Wastewater loads in finishing are caused by highly concentrated residual liquors from the padding equipment; mainly substances with a low rate of biodegradation are to be found.

Figure 2.13: Modern stenter in textile finishing industry

2.3.6 Coating and laminating

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.

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.

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.

The basic techniques for coating/laminating fabrics require the following conditions:

- The fabric to be coated/laminated is supplied full width on a roll
- Coating or laminating zone
- Curing zone
- Rolling up

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

The coating agents, their by-products and crack-products can cause a considerable off-gas load. Emissions of ammonia, formaldehyde and residual monomers (styrole, butadiene, acrylates etc.) are typical. Effluent can be loaded with highly concentrated residual coating pastes.

2.3.7 General overview on application methods in textile finishing mills

To give an overview on the machine types mainly used in textile finishing mills some typical equipments are discussed.
It is to be taken into account that due to different local situations and different substrates and effects to be induced on the textiles resp. the consumers demand various types of application techniques are commonly used.
The wet processes in pre-treatment, dyeing and finishing, can be done batchwise or in a semi-continuous or continuous way (schematic overview in Figure 2.14-Figure 2.16).

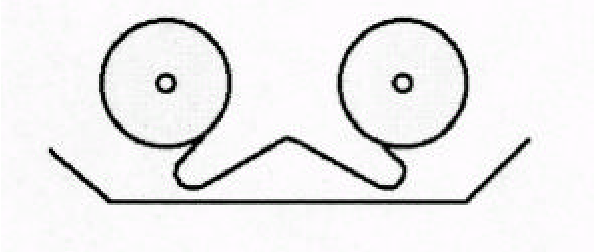


Figure 2.14: Example for a batch-wise process (Jigger). The textile is several times unrolled, dipped into the liquor and uprolled on the second batching roller

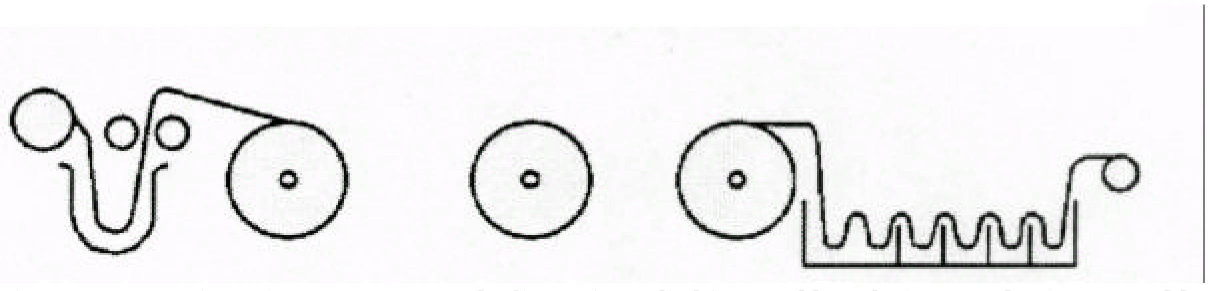


Figure 2.15: Semi-continuous processs. The liquor is applied in a padding device; surplus is removed by means of squeeze rollers; the material is stored for a few hours and subsequently washed/aftertreated

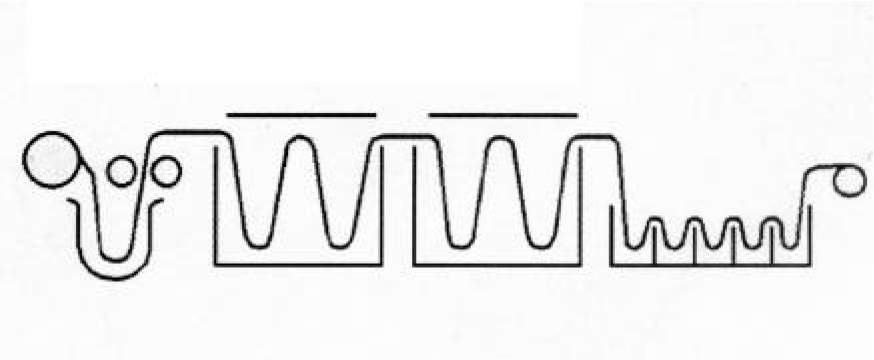


Figure 2.16: Continuous process. Impregnation, curing (e.g. steaming), and washing is carried out in one step [BFBW, 2000]

2.3.7.1 Exhaust techniques (batch techniques)

In batch techniques, used in exhaust dyeing but also for pre-treatment three types of machines (all working in a discontinuous way) have to be discussed:

- Stationary textil good - circulating liquor (beam dyeing, loose fibre dyeing, sliver dyeing, hanks and cone dyeing machines)
- Circulating textile good – stationary liquor (jiggers and winches)
- Circulating textile good – circulating liquor; (conter current flow: esp. in washing machines; direct current principle (dyeing), circulation of textile good is induced by the circulating liquor (jet, overflow) or by means of compressed air (airflow).

The liquor ratio characterizes the ratio of the textile weight (kg) to the liquor volume (l). Optimized exhaust processes are done with a minimized liqour ratio (water, energy, auxiliaries, working time are reduced).

Normally the liqour ratio decreases in the following order:

- Winch
- Beam dyeing
- Jigger
- Overflow, jets
- Airflow.

However it is to be mentioned that different kinds of textile substrates and different requests on the products implement in some cases relative high liquor ratios (esp. in processing of wool and wool blends). Very often, due to the small lots produced in Germany the machine load is not optimized and therefore the liqour ratio is higher than indicated from the machinery manufacturers.

2.3.7.2 Impregnation techniques

Padding (dipping of the textile, passing through the nip of a squeezing unit) is the mainly used impregnation technique in textile finishing (Figure 2.17).

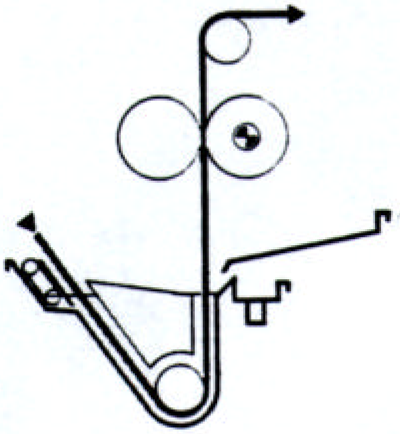


Figure 2.17: Typical padding device

Ecological impact is caused by residual liquors; therefore e.g. the volume of the padding device is to be minimized.

Other impregnation techniques are not described in detail but it is to be mentioned that some special techniques (flex nip, foam application, spraying, etc.) can be carried out with a minimized liquor pick-up and are therefore of ecological interest.

2.3.8 General overview on drying methods

Drying processes are carried out after every wet process (with exception of so called wet in wet processes which work with mechanical dewatered textiles without intermediate thermal drying step) and as a last step in finishing (often combined with heat setting) to make the textile goods ready for storage or delivery. Drying steps are in general very energy intensive. Depending on the drying temperature and the upstream processes considerable impacts to the off-gas due to volatile substances can be observed.

2.3.8.1 Mechanical dewatering (predrying)

Mechanical dewatering of textiles previous to thermal processes is of considerable interest (in an ecological and economical sense) due to a high efficency and a relative low energy consumption. The minimization of the moisture content in the textile goods allows shorter curing times in the following heat treatment. Mechanical dewatering is also used in wet/wet processes to reduce the water input to the subsequent bath.

The following methods are used:

- Squeezing mangle
- Suction devices
- Centrifugal extractors.

2.3.8.2 Thermal drying

Heat can be transferred with the following techniques:

- Convection drying (stenter, hot flue, perforated drum dryer, tumbler, yarn package drying)
- Contact drying (calender, cylinder drying machines)
- Infrared drying
- High-frequency drying.

- Indirect heating is carried out with thermo oils, steam or hot water. In direct heating mainly natural gas (methane) or propane/butane is used.

2.4 Literature

[BFBW, 2000]
Berufliche Fortbildungszentren der Bayerischen Wirtschaft
CORNELIA Web based training, Online Seminar, 2000. http://www.bfz.de

[Bremen, 2000]
Bremer Baumwollbörse, D-Bremen
http//www.baumwollboerse.de/cotton

[BW, 1998]
N.N.
Bekleidung Wear (1998) 15

[Chem, 1998]
German law
Chemikalienverbotsverordnung, 22.12. 1998

[Dollacker, 1996]
Dollacker, A.
Rolle des Pflanzenschutzes im Baumwollanbau
Melliand 74 (1996) 829-834

[Ebner, 1988]
Ebner, G.; Schelz, D.
Textilfärberei und Farbstoffe. Springer-Verlag, Berlin, 1988

[EnviroTex, 1994]
EnviroTex GmbH, D-Augsburg
Emissionen von Synthesefasern.
Bayer. Staatsministerium für Landesentwicklung und Umweltfragen,
D-München (1994)

[EnviroTex, 1996a]
EnviroTex GmbH, D-Augsburg
Wirk-/Maschenwarenprojekt.
Bayer. Staatsministerium für Landesentwicklung und Umweltfragen,
D-München (1996)

[EnviroTex 1996b]
EnviroTex GmbH, D-Augsburg
Emissionsbeitrag von Präparationen.
Bayer. Staatsministerium für Landesentwicklung und Umweltfragen,
D-München (1996)

[EnviroTex, 1996c]
EnviroTex GmbH, D-Augsburg
Emissionsverhalten elastischer Maschenstoffe bei thermischer Behandlung.
Ministerium für Umwelt, Raumordnung und Landwirtschaft, D-Düsseldorf (1996)

[EnviroTex, 1998]
EnviroTex GmbH, D-Augsburg
Minderung von Emissionen bei der Verarbeitung von synthetischen Textilmaterialien in der Textilveredlung durch integrierte Maßnahmen in der textilen Herstellungskette – am Beispiel Garnpräparation und Caprolactam.
Bayer. Staatsministerium für Landesentwicklung und Umweltfragen,
D-München (1998)

[Lakin, 1999]
Lakin, W.H. (Interlaine IPPC/Best Available Techniques Working Group)
Best Available Techniques in Wool Scouring (1999)

[Rouette 1995]
Rouette, H.K.
Lexikon der Textilveredlung. Laumann-Verlag, Dülmen (1995)

[Schulze, 1996]
Schulze-Rettmer, R.
Textilveredlung 31 (1996) 13 – 18

[TEGEWA, 1987]
Zur Nomenklatur der Textilhilfsmittel, Leder- und Pelzhilfsmittel, Papierhilfsmittel und Tenside
TEGEWA, Frankfurt/Main (1987)

[Thier-Grebe, 2000]
Thier-Grebe, R; Rabe, M.
Polyester mit neuem Titandioxid-Katalysator
Melliand 81 (2000) 977-980

[THK, 2000]
Textilhilfsmittelkatalog (THK 2000)
Melliand, TEGEWA, Deutscher Fachverlag, Frankfurt/Main (1999)

[Wulfhorst, 1998]
Wulfhorst, B.
Textile Fertigungsverfahren. Carl Hanser Verlag, München (1998)

[Zollinger, 1987]
Zollinger, H.
Color Chemistry. VCH Verlagsgesellschaft, Weinheim (1987)

3 PRESENT EMISSION AND CONSUMPTION LEVEL

In textile finishing industries, normally wastewater emissions are of highest environmental relevance. Most information is available for this emission mass stream. Quantity and composition of wastewater strongly depends on the make-up, kind of textile substrate and applied processes and chemicals respectively. However, considering wastewater emissions, it has been proven to be an appropriate approach to group textile finishing industries into various categories (Table 3.1) on base of the annual mass stream overviews (Figure 1.9). This site-wise consideration very often concerns the situation in reality. Within these categories the industries are comparable at first sight. In practice it will help to do a rough assessment of the emission level of a certain industry, also to verify given data. Thereby it has to be underlined that the data allow a rough assessment only with respect to the order of magnitude but do not allow the discussion of small differences of numbers.

Category	**Number of TFI**
TFI mainly finishing floc material consisting of CV, PES, PAC and/or CO	2
TFI mainly finishing CO yarn	3
TFI mainly finishing PES yarn	4
TFI mainly finishing yarn consisting of WO, PAC and /or CV	5
TFI mainly finishing knit fabric consisting of CO	17
TFI mainly finishing knit fabric consisting of CO having a relevant printing section	12
TFI mainly finishing knit fabric consisting of synthetic fibres	11
TFI mainly finishing knit fabric consisting of WO	1
TFI mainly finishing woven fabric consisting of CO and CV	13
TFI mainly finishing woven fabric consisting of CO and/or CV having a relevant printing section	6
TFI mainly finishing woven fabric consisting of WO	2
TFI mainly finishing woven fabric consisting of PA	1
TFI finishing carpets	2
Sum	**79**

Table 3.1: 13 categories of 79 textile finishing industries (TFI) for which data are available/presented

As far as data for the consumption of energy and chemicals are available they are also presented under the mentioned categories. With respect to the consumption of chemicals three classes are formed: dyestuffs and pigments, textile auxiliaries (definition: all products mainly containing organic compounds) and basic chemicals (all inorganic chemicals, organic aliphatic acids, organic oxidising and reducing agents and urea). Thereby it has to be pointed to the fact that the calculations have been carried out on so-called “telquel”-basis. This means the quantities of ready-formulated products, like TFI buy them from suppliers, have been taken into account including water in case of liquid formulations. This can lead to some differences; for instance in case of a TFI mainly using liquid dyestuff formulations (often the case for big TFI) the specific dyestuff consumption is higher compared to one using powder or granulates. In addition, information on consumption of chemicals is only available for a small number of TFI. The presented values are typical but from TFI to TFI there may be considerable ranges.

Subsequent to the presentation of emission/consumption levels on a site level more detailed information is presented on process level.

Data for emissions to air are submitted in a separate chapter (Chapter 3.5). It is considered to be more clear to present these data in a compact form than to present it for each kind of TFI like it is best for presenting wastewater emission data.
Information on waste is also presented in a separate chapter (Chapter 3.6).

3.1 Yarn/floc finishing

Floc material and yarn (mainly as hank or cone) are normally finished in one apparatus in which all steps consisting of pre-treatment, dyeing and finishing are carried out.

3.1.1 Site specific input/output data

3.1.1.1 TFI mainly finishing floc material consisting of CV, PES, PAC and/or CO

For this category information on wastewater emissions are available only. The values are compiled in Table 3.2. Because of low liquor ratio and small number of process baths the specific wastewater flow is low. The values in Table 3.2 are confirmed by [FhG-ISI, 1997] reporting specific flows for three further TFI between 14 and 18 l/kg.

	spec.	COD		BOD$_5$		AOX		HC		pH	L	T	NH$_4$		org.N		Cu		Cr		Ni		Zn	
	Q$_{WW}$	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	34	1945	67	850	29			12.4	0.4		14.9	40					1.2	41	0.13	5			0.71	25
TFI 2	10	1300	13	370	4												0.05	0.5	0.2	2	<0.02	<0.2	0.3	3

Table 3.2: Concentration values and textile substrate specific emission factors for wastewater from two TFI mainly finishing floc material consisting of CV, PES, PAC or CO

Cells without number mean that concerned information is not available

3.1.1.2 TFI mainly finishing CO yarn

Table 3.3 contains the concentration values and factors for wastewater emissions of three TFI mainly finishing cotton yarn. The values for specific flow are between 100 and 120 l/kg. These values are confirmed by [FhG-ISI, 1997] reporting smaller and higher values (68, 73, 78, 83, 120, 128, 149, 181, 271 l/kg). Thereby the high value of 271 l/kg (from a small TFI processing less than 0.5 t/d) has to be questioned critically. The most important factors for water consumption and wastewater flow respectively are the liquor ratio of the apparatus, the make-up of the yarn (hank or cone whereas hanks need considerably higher consumption of water), the repairing rate, the optimum loading of the apparatus (quite often the batches are too small for the used apparatus because market demands tend more and more to smaller batches) and the process sequence which mainly depends on the applied dyestuffs and the quality to be met. For instance dyeing of cotton yarn with azoic (or developing) dyestuffs requires considerably more water (more baths) than common dyeing with reactive dyestuffs. In case of reactive dyeing the COD emission factor is significantly lower (about 70 g/kg, TFI 1 and TFI 2 in Table 3.3) than in case of dyeing mainly with vat dyestuffs (nearly 100 g/kg, TFI 3). The latter needs the use of further textile auxiliaries, especially dispersing agents. All other values are inconspicuous and do not require specific comments.

Figure 3.1 shows the composition of COD load in the effluent of a TFI finishing cotton yarn. As mainly vat dyestuffs are used, the percentage of COD originating from dyestuffs is relatively high. This is not because of the dyestuffs themselves (they have a high fixation rate) but because of the dispersing agents. The latter are part of the powder or granulate formulations and have a percentage of 30-50%. They remain in the exhausted dyebath and significantly contribute to COD load in wastewater. Regarding dyeing auxiliaries, there are dispersing agents, levelling agents and washing agents which contribute most.

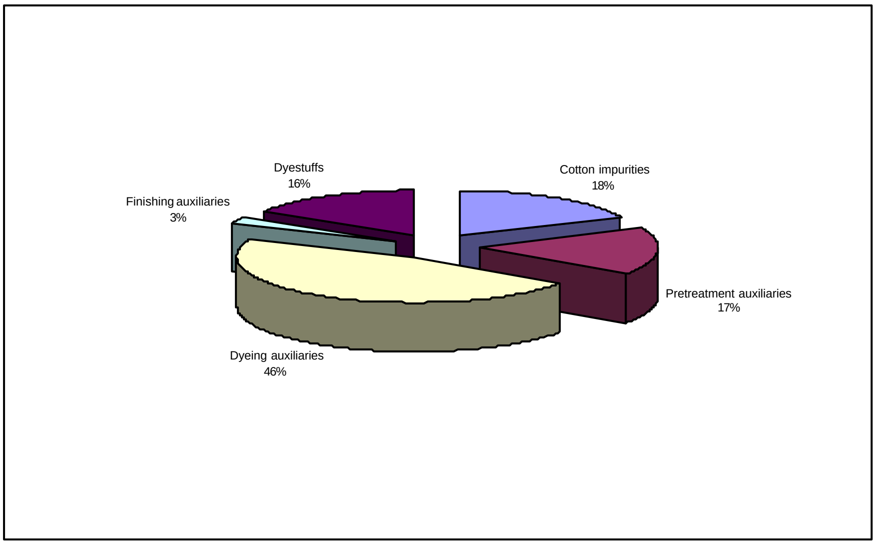


Figure 3.1: Example for the typical composition of the COD load of a TFI finishing cotton yarn (dyeing mainly with vat dyestuffs)

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. The values from a typical example are:

- dyestuffs: 25 [g/kg textile substrate]
- textile auxiliaries: 70 [g/kg textile substrate]
- basic chemicals: 430 [g/kg textile substrate]

Depending on individual conditions, the values for other CO yarn finishers may differ.

In case of mainly reactive dyeing the consumption of basic chemicals can be higher because of the high neutral salt input.

The total specific energy consumption is about 11 kWh/kg, whereas the consumption of electricity is about 2 kWh/kg (data from 2 TFI).

	spec.	COD		BOD_5		AOX		HC		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	105	690	73	260	27			<0.5	<0.05		7	27.3					0.19	20					0.32	34
TFI 2	108	632	69	160	17			1.2	0.1		6.2	33.5					0.12	13	<0.05	<6			<0.1	<11
TFI 3	120	805	97	200	24	0.36	0.04			9.8			0.6	0.07	11.1	1.3	0.13	16						

Table 3.3: Concentration values and textile substrate specific emission factors for wastewater from three TFI mainly finishing yarns consisting of CO
Cells without number mean that concerned information is not available

3.1.1.3 TFI mainly finishing PES yarn

Table 3.4 contains the concentration values and factors for wastewater emissions of four TFI mainly finishing polyester yarn. The values for specific flow vary between 65 and 148 l/kg. The higher value is for a TFI finishing yarn also in hank form which requires more water (higher liquor ratio); in addition this TFI is also processing some cotton yarn which is mercerised and dyed with azoic (development) dyestuffs both needing relatively high water consumption. The mentioned values are confirmed by [FhG-ISI, 1997] reporting for three further TFI finishing PES yarn mainly (63, 86 and 122 l/kg). The values are in the same range like for TFI finishing cotton yarn but do not show peak values like one industry there.

The finishers of PES yarn have higher COD emission factors (97-124 g/kg) than such finishing cotton because of the use of dispersing agents which are already present in the water-insoluble disperse dyestuffs and added additionally. Normally these dispersing agents consist of naphthalene sulfonates-formaldehyde condensates and lignine sulfonates which are heavily biodegradable or non-biodegradable. Also the removal of preparation agents could lead to higher COD emissions. As mentioned in Annex I, preparation agents often still contain highly refined mineral oil which is detected by the parameter mineral oil hydrocarbons. For one TFI information on hydrocarbons is available indicating the emission of mineral oil (19 mg/l for TFI 3 correlating with an emission factor of 1.2 g/kg; this factors concerns a specific COD of about 3 g/kg).

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. Typical ranges are:

- dyestuffs: 18 - 36 [g/kg textile substrate]
- textile auxiliaries: 80 - 130 [g/kg textile substrate]
- basic chemicals: 95 - 125 [g/kg textile substrate]

Depending on individual conditions, values for other PES yarn finishers may differ.

In case of applying high amounts of liquid formulations of conditioning agents the consumption of textile auxiliaries can be up to 175 g/kg.

The total specific energy consumption is in the range of 11-18 kWh/kg. The higher value is in case the TFI have also spinning, twisting and coning sections. The consumption of electricity is about 1-2 kWh/kg (data from 2 TFI).

	spec.	COD		BOD$_5$		AOX		HC		pH	L	T	NH$_4$		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	125	870	109	139	17	0.7	0.09			8.2	1.9	23.9	31.2	3.9	13	1.6								
TFI 2	65	1917	124			1.26	0.08	19	1.2			26.3												
TFI 3	66	1520	101	380	25	0.45	0.03			7.7	5.0	44.2	8.2	0.5	17.3	1.2								
TFI 4	148	655	97	169	25	0.65	0.1			8.6	3.0	34.6	7.6	1.1	9.5	1.4	0.05	7						

Table 3.4: Concentration values and textile substrate specific emission factors for wastewater from four TFI mainly finishing yarns consisting of PES
Cells without number mean that concerned information is not ava

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

Table 3.5 contains the concentration values and factors for wastewater emissions of five TFI mainly finishing yarn consisting of wool, polyacrylonitriles and their blends and some viscose and blends with WO and PAC. The values for specific flow vary between 74 and 212 l/kg which is a rather wide range. However specific COD is in the same range like TFI finishing cotton. Also the other values are in the same range like other types of yarn finishers.

Predominant is the content of chromium which can be significantly higher compared to other kind of yarn finishers because of the application of chromium complex dyes and mordant dyes fixed with dichromate. In case of high percentages of wool and depending on the dyeing method chromium concentration vary considerably. The same is for emission factors for chromium which can reach nearly 100 mg/kg (TFI 5 in Table 3.5).

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. Typical ranges are:

- dyestuffs: 13 – 18 [g/kg textile substrate]
- textile auxiliaries: 60 – 90 [g/kg textile substrate]
- basic chemicals: 180 - 325 [g/kg textile substrate]

Depending on individual conditions, the values for other WO, PAC and/or CV yarn finishers may differ.

The total specific energy consumption is in the range of 4-17 kWh/kg. The higher value is in case the TFI have also spinning, twisting and coning sections (data from 3 TFI). Thereby the consumption of electricity is about 0.9-6.5 kWh/kg, the latter value of a TFI having also the above mentioned additional processes.

	spec.	COD		BOD$_5$		AOX		HC		pH	L	T	NH$_4$		org.N		Cu		Cr		Ni		Zn	
	Q$_{WW}$	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	120	590	71	190	23																			
TFI 2	212	480	102	170	36	0.4	0.08			7.7			4.6	1	11.2	2	0.02	4	0.03	6				
TFI 3	167	584	97	265	44	0.76	0.1			6.9	4.4	41			16.6	2.8	<0.01	<2	<0.1	<17	<0.1	<17	0.63	105
TFI 4	66	782	52	355	23					7.3									0.38	25				
TFI 5	74	1023	78	220	16	0.17	0.01			6.8	1.4				22.8	1.7			1.2	89	<0.01	<0.7	0.47	35

Table 3.5: **Concentration values and textile substrate specific emission factors for wastewater from five TFI mainly finishing yarns consisting of WO/PAC/CV**
Cells without number mean that concerned information is not available

3.1.2 Process-specific input/output for TFI finishing yarn

Process-specific information is given for all kind of yarn finishers in order to avoid/to minimise repetition. Because wastewater emissions are predominant and thus of highest environmental relevance most information relates to this emission mass stream. For exhaust dyeing of viscose yarn, polyester yarn and cotton yarn detailed information is subsequently presented. Then more detailed information is submitted for the application of chemicals.
Information on emissions to air is very limited but is considered to be negligibly low.

The finishing of yarn is carried out in dyeing apparatus (mainly as hank or cone) in which all steps consisting of pre-treatment, dyeing and finishing are carried out. Such discontinuous dyeing is called exhaust dyeing. In many cases pre-treatment is not performed separately.
The pollution load of the different baths show a wide range. In the following the load of such sequences of baths is demonstrated by hand of three examples for the parameters COD, pH, conductivity, temperature and colour (determination of adsorption coefficients at wavelengths 435, 500 and 620 nm):

- exhaust dyeing of CV yarn (on cones) with reactive dyestuffs (Table 3.6)
- exhaust dyeing of PES yarn (on cones) with disperse dyestuffs (Table 3.7)
- exhaust dyeing of CO yarn (on cones) with vat dyestuffs (Table 3.8)

No. of bath	**Name of bath**	**COD [mg O_2/l]**	**pH**	**Conductivity [mS/cm]**	**Temperature [°C]**	**SAC 435 nm [1/m]**	**SAC 500 nm [1/m]**	**SAC 620 nm [1/m]**
1	Exhausted dye bath	3170	10.2	35.1	48	27	13	2
2	Rinsing bath	550	10.1	11.7	42	14	10	3
3	Neutralisation bath	1220	4.4	3.8	44	4	4	1
4	Soaping bath	4410	6.2	2.4	57	16	11	4
5	Rinsing bath	1040	7.1	0.9	59	7	5	3
6	Rinsing bath	320	7.3	0.5	60	10	8	5
7	Rinsing bath	190	7.4	0.3	49	7	6	4
8	Conditioning bath (softening)	790	4.4	0.6	35	0	0	0

Table 3.6: Sequence of emitted baths from exhaust dyeing of CV yarn with reactive dyestuffs along with values for COD, pH, conductivity, temperature and colour (spectral absorption coefficients, SAC) – [UBA, 2000]

No. of bath	Name of bath	COD [mg O_2/l]	pH	Conductivity [mS/cm]	Temperature [°C]	SAC 435 nm [1/m]	SAC 500 nm [1/m]	SAC 620 nm [1/m]
1	Pre-treatment bath	610	7.4	20	134	3.9	2.7	1.4
2	Exhausted dye bath	10320	5.0	3.4	130	290	375	125
3	Rinsing bath	1310	7.2	0.6	85	51	78	8.6
4	Reductive after-treatment	3610	9.5	6.1	89	18	11	6.3
5	Rinsing bath	615	9.2	1.4	84	6.3	4.2	2.7
6	Rinsing bath	140	8.6	0.5	66	0.9	0.7	0.3
7	Conditioning bath (softening)	2100	7.2	0.5	55	23.6	17.9	11.8

Table 3.7: Sequence of emitted baths from exhaust dyeing of PES yarn with disperse dyestuffs along with values for COD, pH, conductivity, temperature and colour (spectral absorption coefficients, SAC) – [UBA, 2001]

No. of bath	Name of bath	COD [mg O_2/l]	pH	Conductivity [mS/cm]	Temperature [°C]	SAC 435 nm [1/m]	SAC 500 nm [1/m]	SAC 620 nm [1/m]
1	Exhausted dye bath	14340	12.9	46	70	254	191	190
2	Overflow rinsing	6120	12.6	24	46	95	59	59
3	Rinsing bath	1900	12.2	12.7	34	9	8	7
4	Oxidation bath	4780	11.7	5.6	51	4	3	2
5	Rinsing bath	580	10.6	2	32	1	1	1
6	Soaping bath I	1510	10	2.3	55	4	4	5
7	Rinsing bath	230	9.3	1.5	36	2	2	2
8	Soaping bath II	860	10.1	3.4	74	4	3	2
9	Rinsing bath	47	8.9	1.2	37	1	1	1
10	Rinsing bath	27	8.5	1	31	0.5	0.5	0.4
11	Conditioning bath (softening)	1740	4.7	1.2	45	17	11	6

Table 3.8: Sequence of emitted baths from exhaust dyeing of CO yarn with vat dyestuffs along with values for COD, pH, conductivity, temperature and colour (spectral absorption coefficients, SAC) – [UBA, 2001]

It has to be underlined that the presented examples have been chosen arbitrarily in order to explain the bath sequence and the different pollution loads. The bath sequence can not be directly transferred to other finishers of yarn. There could be additional rinsing baths, in case of dyeing with vat dyes one soaping bath could be sufficient, cotton yarn could be mercerised, finishing is not carried out etc.. However the examples provide the principles; in the illustrated way or very similar exhaust dyeing of yarns with reactive, disperse and vat dyestuffs respectively is carried out in practice. In case of application of other kinds of dyestuffs such as azoic (developing) dyestuffs modified bath sequences occur.

The values in the tables of Chapter 3.1 (Table 3.2–Table 3.5) have been determined by analysing mixed wastewater of the whole TFI. Therefore the COD concentration values are much lower than the highest values of single finishing baths which are exhaust dyeing baths. Thereby the COD concentration of the exhausted dye bath from reactive dyeing is significantly lower than for dyeing with disperse and vat dyes. The main reason is the application of dispersing agents which are needed to apply the water-insoluble disperse and vat dyestuffs. Finishing baths for removing unfixed dyestuffs (soaping baths, interim purification baths, reductive after-treatment bath) also show high COD concentrations as well as colour values. The residual COD concentration of conditioning baths indicate that exhaustion of conditioning agents is not very high. In contrary rinsing baths can be very low-loaded, factor 10-100 lower than the highest polluted bath. This directly leads to the approach to optimise rinsing and to recycle low-loaded rinsing water.

3.1.3 Consumption of chemical products

Regarding the applied chemicals in TFI a common statements says that many products are in use. However the evaluation of many chemical consumption lists on an annual basis always show that the consumption curve for the single products is hyperbolic. An example for a TFI finishing PES yarn contains Figure 3.2.

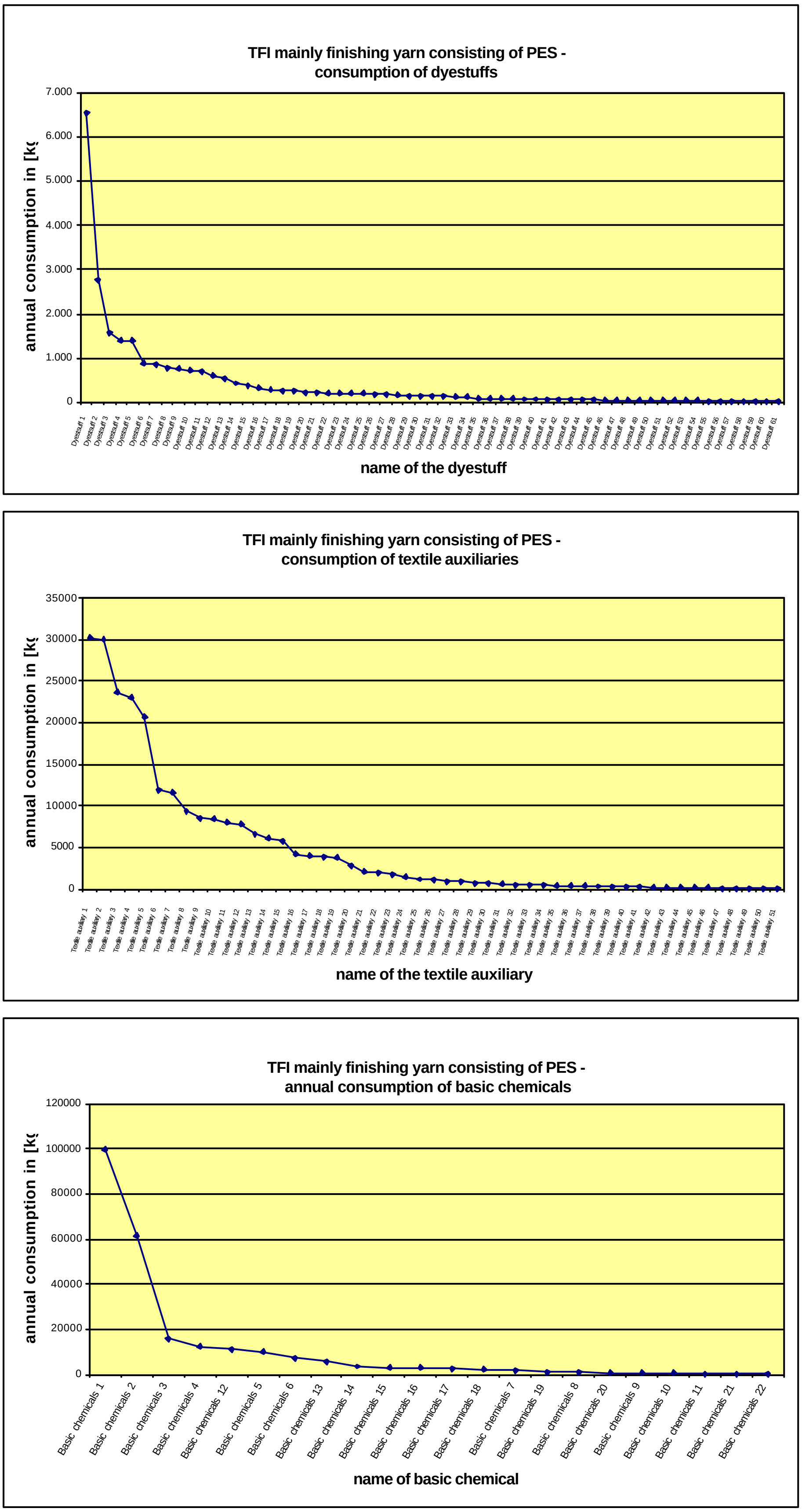


Figure 3.2: **Typical hyperbolic curve for the consumption of dyestuffs, textile auxiliaries and basic chemicals of a TFI, here for a TFI mainly finishing yarn consisting of PES – according to [UBA, 2001]**

3.2 Finishing of knit fabric

For the finishing of knit fabric the basic process sequence, already mentioned in Chapter 2, is repeated in order to enable better orientation.

3.2.1 Site specific input/output data

3.2.1.1 TFI finishing knit fabric mainly consisting of cotton

The typical process sequence for the finishing of knit fabric mainly consisting of cotton is shown in Figure 3.3.

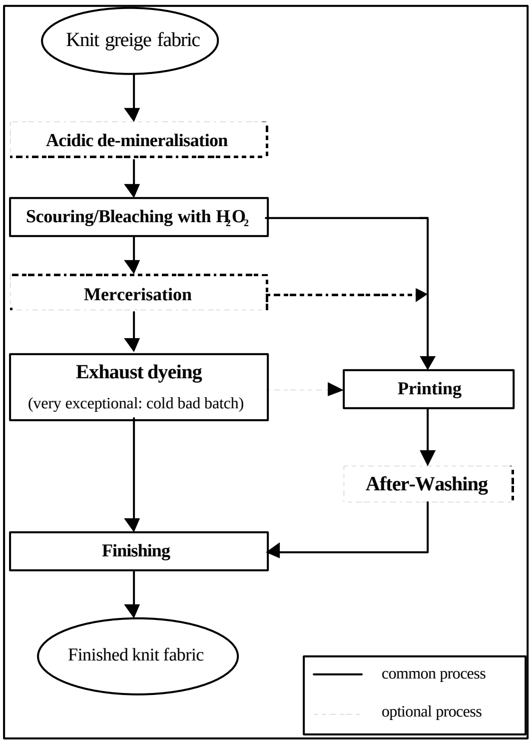


Figure 3.3: Typical process sequence for wet processes for the finishing of knit fabric mainly consisting of cotton

Thereby mechanical and thermal steps are not illustrated. The dotted lines indicate processes which are not carried out in every case. Especially acidic demineralisation is practised in a few cases only; the same is for mercerisation. Concerning printing on knit fabric mainly pigment printing is applied which does not need after-washing. The latter only is required for printing with reactive, disperse and vat dyestuffs.
In bigger TFI scouring is carried out continuously but in most cases it is a discontinuous process. Today, hydrogen peroxide is used as bleaching agent exclusively.

Table 3.9 contains the data for wastewater emissions from seventeen TFI finishing knit fabric mainly consisting of cotton are compiled. These TFI do not have a printing section. The range of specific wastewater flow is relatively small (60 – 136 l/kg) but there are two extreme exceptions at the lower and upper end of the range (21 and 216 l/kg, TFI 9 and 17 in Table 3.9). TFI 9 having 21 l/kg performs scouring and bleaching only; in addition with continuous processes which explains the very low specific wastewater flow as well as the highest COD concentration. The reasons for the very high specific wastewater flow of TFI 17 is because the high quality requirements (more rinsing steps) and the high repairing rate.

The COD emission factors are normally within a surprisingly small range (70 – 85 g/kg), only TFI 9 carrying scouring and bleaching only has a lower value (48 g/kg). For TFI 10, 11 and 16, there are higher values (107, 108 and 97 g/kg) because of finishing some woven fabric causing higher COD emissions. In addition, TFI 10 finishes some polyester knit fabric which also leads to higher COD emission factors. The latter also is responsible for hydrocarbons present in wastewater (concentration > 20 mg/l). Their origin is the removal of preparation agents mainly containing white oil (Annex I). Concentrations between 10 – 20 mg/l can also occur in case of TFI finishing cotton only but common values are below 10 mg/l. The values for heavy metals are all inconspicuously low.

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. Typical values are:

- dyestuffs:	18	[g/kg textile substrate]
- textile auxiliaries:	100	[g/kg textile substrate]
- basic chemicals:	570	[g/kg textile substrate]

Depending on individual conditions, the values for other CO knit fabric finishers may differ.

The very high specific consumption of basic chemicals is due to the application of neutral salts (NaCl or Na_2SO_4) for reactive exhaust dyeing which is about 400 g/kg.

The total specific energy consumption is in the range of 6-17 kWh/kg. The higher value is in case the TFI have also spinning and coning sections. The consumption of electricity is 1-3 kWh/kg (data from 9 TFI).

3.2.1.2 TFI finishing knit fabric mainly consisting of cotton and having a relevant printing section

Concerning TFI finishing knit fabric mainly consisting of cotton and having a relevant printing section data are presented in Table 3.10. Thereby most of the TFI perform pigment printing. Today, printing pastes for this process do not contain white spirit any more.

Except TFI 3 the presented industries do not carry out pre-treatment but print on already pre-treated knit fabric.

In case of pigment printing wastewater is only emitted during washing of printing tools (screens, blades) and washing of the printing blanket in case of rotary screen and flat screen printing. All the presented TFI do treat their wastewater and some of them recycle part of it.

Before this background, the very low specific wastewater flow is understandable which usually is far below 10 l/kg. Exceptions are TFI 3 which is carrying out pre-treatment also and TFI 6 which also practises reactive printing which needs after-washing.

Information on chemical input, energy consumption and solid waste is not available.

	spec.	COD		BOD_5		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	67	1210	81	409	27			9.3	0.6		3.5	34.0					< 0.1	< 7	< 0.1	< 7			0.2	13
TFI 2	60	1340	81	622	37			18.9	1.1		4.4	30.2					0.11	7	< 0.1	< 6			0.33	20
TFI 3	101	748	76	174	18			8.3	0.8		6.5	38.1					0.23	23	< 0.05	< 5			0.37	37
TFI 4	67			444	30			5.0	0.3		4.6	36.0					< 0.05	< 4	< 0.05	< 4			0.1	4
TFI 5	78	931	73	289	23			23.7	1.9		10.1	33.8					0.12	9	< 0.1	< 8			0.2	16
TFI 6	79	954	75	408	32			21.9	1.7		4.7	33.0					< 0.1	< 8	< 0.1	< 8			0.14	11
TFI 7	120	673	80	175	21			6.8	0.8		8.1	35.1					0.19	23	< 0.05	< 6			0.1	12
TFI 8	77	1010	77	453	35			19.2	1.5		2.9	28.6					< 0.1	< 8	< 0.1	<8			0.2	15
TFI 9	21	2281	48	788	17			11.2	0.2		2.7	39.1											0.37	8
TFI 10	71	1502	107	671	48			32.0	2.3		3.8	29.3					0.22	16	0.2	14			0.26	19
TFI 11	133	814	108	218	29			6.1	0.8		2.26	21					0.25	33	< 0.05	< 0.7				
TFI 12	75	804	60					0.9	0.07		6.3	20							< 0.1	< 8			< 0.1	< 8
TFI 13	88	911	80	390	34			14.3	1.3		6.1	24					< 0.1	< 9	< 0.1	< 9			0.12	11
TFI 14	136	439	60	127	17			6.2	0.8		5.1	31					0.11	15	< 0.1	< 14			0.12	16
TFI 15	87	658	57	259	23			18.5	1.6		11.1	30			25	2.2	< 0.1	< 9					0.2	17
TFI 16	96	1004	97	166	16	0.3	0.03						9	0.9	14.3	1.4								
TFI 17	216	390	84	112	24	0.21	5	6.1	1.3				1	0.2	22	5	0.3	65					0.3	65

Table 3.9: Concentration values and textile substrate specific emission factors for wastewater from seventeen TFI mainly finishing knit fabric mainly consisting of CO

Cells without number mean that concerned information is not available

	spec.	COD		BOD5		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	6	233	1.4					0.9	0.06		1.3	11.9					< 0.05	< 0.3	< 0.05	< 0.3			0.19	1
TFI 2	15	391	5.9					0.3	0.005		1.0	18.9					< 0.1	< 1.5	< 0.1	< 1.5			< 0.1	< 1.5
TFI 3	42	170	7.1	105	4.4			1.2	0.05		2.6	16.2					< 0.1	< 4	< 0.1	< 4			0.3	13
TFI 4	1.1	296	0.3					0.7	0.001		0.7	17.2					< 0.1	< 0.1	< 0.1	< 0.1			< 0.1	< 0.1
TFI 5	0.4	376	0.2					1.0	0.0004		3.0	10.6					< 0.05	< 0.02	< 0.05	< 0.02			< 0.1	< 0.04
TFI 6	35	17	0.6					0.2	0.007		2.6	17.2					< 0.1	< 4	< 0.1	< 4			< 0.1	< 4
TFI 7	0.4	1027	0.4					10.3	0.004		1.3	14.5					0.1	0.04	< 0.1	< 0.04			0.1	0.04
TFI 8	2	639	1.3					14.4	0.03		1.4	15.9					0.6	1.2						
TFI 9	0.9	713	0.6								0.9	13.2					0.07	0.06	< 0.1	< 0.1			< 0.1	< 0.1
TFI 10	2	666	1.3					1.7	0.003		3.3	19.0					< 0.1	< 0.2	< 0.1	< 0.2			< 0.1	< 0.2
TFI 11	2	351	0.7					0.9	0.002		1.3	17.6					< 0.1	< 0.2	< 0.1	< 0.2			0.3	0.6
TFI 12	3	1196	3.3					11.2	0.03		1.1	17					< 0.1	< 0.3	< 0.1	< 0.3			0.2	0.6

Table 3.10: Concentration values and textile substrate specific emission factors for wastewater from tewlve TFI finishing –by printing- knit fabric mainly consisting of CO

Cells without number mean that concerned information is not available

3.2.1.3 TFI finishing knit fabric mainly consisting of man-made fibres

The typical process sequence for the finishing of knit fabric mainly consisting of man-made fibres is shown in Figure 3.4. The processes in dotted lines are not practised in many cases. Heat setting is carried out optionally and can cause considerable emissions to air because of evaporation of hydrocarbons originating from preparation agents. Before dyeing the fabric is normally pre-treated by washing off preparation agents and dirt. Depending on the required quality bleaching may be performed.

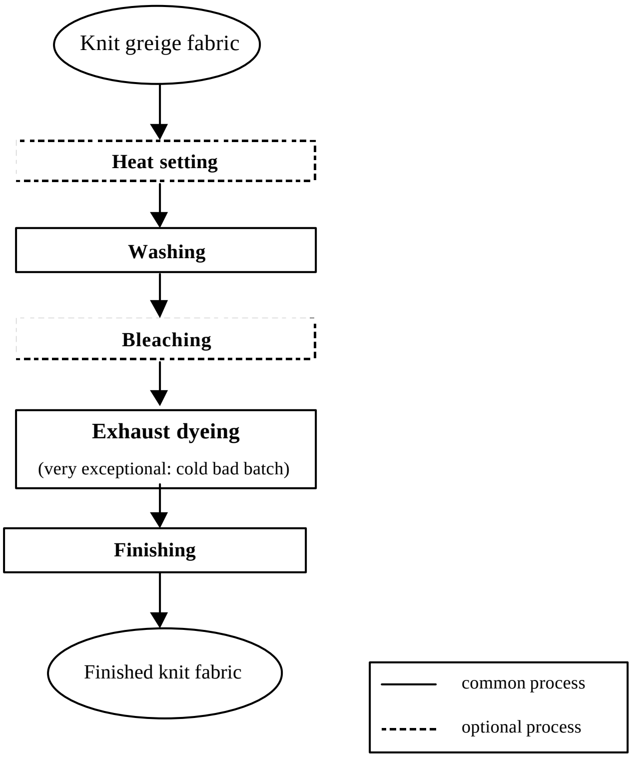


Figure 3.4: Typical process sequence for wet processes for the finishing of knit fabric mainly consisting of man-made fibres

According to Table 3.11 the range for specific wastewater flow is big (35-229 l/kg). The lower value is for cases in which finishing is carried out in automated machines with low liquor ratio and small numbers of finishing baths. The high value occurs in cases of TFI having older machines and small batches finished at non-optimal liquor ratios.

The low COD emission factors are typical for TFI finishing mainly polyamide. Due to the load of preparation agents the emission of hydrocarbons is significantly higher compared to TFI mainly finishing cotton.

Also for this kind of TFI the values for heavy metals are all inconspicuously low.

Figure 3.5 shows the composition of COD load in the effluent of a TFI finishing knit fabric mainly consisting of polyamide and polyamide/elastane blends. The percentage of preparation agents is significant, although this TFI carries out raw fixation to an high extend (thereby preparation agents, basing on mineral oil, evaporate). However, dyeing auxiliaries contribute most to the COD load because of levelling agents and washing agents. In case of polyamide 6, also caprolactam is present in wastewater; in the presented example it represents 4% of the COD load.

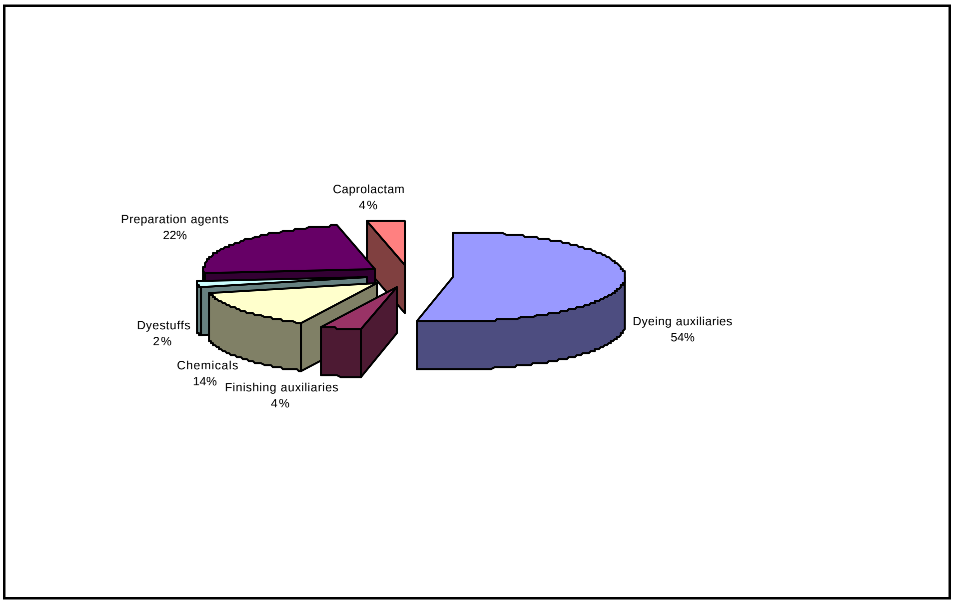


Figure 3.5: **Example for the typical composition of the COD load of a TFI finishing knit fabric mainly consisting of polyamide; the percentages are calculated by hand of data in safety data sheets and known/assumed retention factors, the values are cross-checked with the measured COD-concentration and -load**

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. The typical range is:

- dyestuffs:	15 - 50	[g/kg textile substrate]
- textile auxiliaries:	45 – 150	[g/kg textile substrate]
- basic chemicals:	50 - 280	[g/kg textile substrate]

Depending on individual conditions, the values for other TFI finishing knit fabric consisting of man-made fibres may differ.

The ranges are rather big reflecting the variety of processes and process sequence.

The total specific energy consumption is in the range of 3.5-17 kWh/kg. The higher value is in case the TFI have also spinning and knitting sections. The consumption of electricity is 1.5-6 kWh/kg; the high value is for a TFI performing spinning and knitting also, not only finishing (data from 3 TFI).

3.2.1.4 TFI finishing knit fabric mainly consisting of wool

Data on wastewater emissions are available for one TFI only. The same is for energy consumption. The precise process sequence is not known.

Table 3.12 contains the values for wastewater emissions. Specific flow and also other parameters do not indicate significant differences compared to TFI finishing cotton or synthetic fibres.

Information on applied chemicals is not available.

The specific energy consumption is very high (67 kWh/kg) whereas the specific consumption of electricity is 9.5 kWh/kg. The reason why is that energy consumption for spinning, twisting, coning and knitting is included.

	spec.	COD		BOD_5		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Konc.	E-Fac	Konc.	E-Fac	Konc.	E-Fac	Konc.	E-Fac				Konc.	E-Fac	Konc.	E-Fac	Konc.	E-Fac	Konc.	E-Fac	Konc.	E-Fac	Konc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	117	1003	117	271	32			60	7		3.2	29.3					< 0.05	< 6					0.16	19
TFI 2	173	379	65	184	32			4.9	0.8		4.1	29.1					0.06	10	< 0.1	< 17			0.05	9
TFI 3	81	1045	84	384	31			57.1	4.6		1.0	39.8					0.09	7	0.15	12			0.07	6
TFI 4	77	3590	277	855	66	4.3	0.33				2.2		2	0.15	15	1.2	< 0.09	< 7	< 0.05	< 4				
TFI 5	127	911	116	242	31	0.3	0.04	26.9	3.4						16.5	2.1	0.09	11	0.14	18				
TFI 6	89	890	79	246	22	0.34	0.03			7.3	1.7		6	0.5	18.2	1.6								
TFI 7	35	2170	76	252	9																			
TFI 8	229	384	88	95	22					9.2	1.5	36.8	18	4.1	12	2.6	< 0.1	< 22			< 0.1	< 22		
TFI 9	83	581	48	132	11						3.6													
TFI 10	43	3480	150	590	25	0.65	0.03			6	2.6				15	0.6	<0.01	<0.4			<0.01	<0.4	0.03	1.3
FFI 11	61	1870	115			0.3	0.02			7.4	0.9						0.04	2.1			<0.02	<1.2	0.08	4.9

Table 3.11: Concentration values and textile substrate specific emission factors for wastewater from eleven TFI finishing knit fabric mainly consisting of synthetic fibres
Cells without number mean that concerned information is not available

	spec.	COD		BOD_5		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	63	1470	93	367	23	0.3	0.02			6.8	0.6	31.5	9.5	0.6	23.3	1.5	0.03	2	0.09	6			0.5	32

Table 3.12: Concentration values and textile substrate specific emission factors for wastewater from a TFI finishing knit fabric mainly consisting of wool
Cells without number mean that concerned information is not available

3.2.2 Process-specific input/output for TFI finishing knit fabric

Process-specific information is submitted on

- the pre-treatment of cotton knit fabric (continuous and discontinuous processes)
- pre-treatment of knit fabric consisting of synthetic fibres (very limited information available)
- exhaust dyeing of knit fabric consisting of cotton and synthetic fibres

As already mentioned at the beginning of Chapter 3, information on emissions to air are submitted in a separate chapter (Chapter 3.5) in order to submit a compact compilation of data.

3.2.2.1 Pre-treatment of cotton knit fabric

In the following two processes are described for continuous pre-treatment which means bleaching and washing as well as three discontinuous processes. The intensity of cotton knit fabric bleaching mainly depends on the kind of cotton quality and the degree of whiteness to be achieved. For subsequent exhaust dyeing with dark shades a less intensive bleach process is necessary only (pre-bleach) whereas for pale shades and non-dyed products the whiteness must be higher and bleaching more intensive respectively.

3.2.2.1.1 Continuous pre-treatment of cotton knit fabric

Bigger TFI often have continuously working machines for the pre-treatment. In the following a process is described for continuous bleaching/washing with hydrogen peroxide. The process consists of following steps:

- Padding of the bleaching liquor with a pick-up of 130%
- Bleaching reaction in a steamer (30 min) with saturated steam at a temperature of 95-98°C
- Counter-current rinsing
- Padding of liquor containing complexing agents and washing agents with subsequent second steamer (3-5 min with saturated steam)
- Rinsing and drying (in case of non-dyed qualities, before drying softening agents are applied)

A typical recipe is given below:

Recipe	[g/kg textile]	COD of product [g O_2/kg product]	spec. COD-input [g O_2/kg textile]
Padding liquor for bleaching			
$NaOH$(100%)	8,2		
Wetting agent	6,0	1210	7,3
Complexing agents	4,4	270	1,2
Organic stabilisers	22,0	185	4,1
$MgSO_4$	2,2		
H_2O_2 (50%)	66,0		
Optical brightener	5,0	760	3,8
Washing agent	1,5	2060	3,1
Second padding liquor			
Polyphosphate	1,1		
Washing agent	1,1	1780	2,0
			sum: 21,4
Padding liquor in case of softening			
Softening agents	14,5	684	9,9
Acetic acid (60%)	1,1	645	0,7

Table 3.13: Typical recipe for the continuous bleaching/washing of cotton knit fabric

The specific COD-input can vary between 20-30 g/kg textile. In principal this example is confirmed by the standard recipe in Annex II.
The specific water-consumption and wastewater flow is about 30 l/kg (±7 l/kg).
Typical values in first rinsing water are:

- COD: 4000-8500 mg O_2/l
- Conductivity: 2.5-4.5 mS/cm
- pH: around 10.

Typical values in second rinsing water are:

- COD: 1000-3000 mg O_2/l
- Conductivity: 0.5-1.2 mS/cm
- pH: 8-10

At first order the chemicals and auxiliaries applied for bleaching/washing reach wastewater quantitatively. As already mentioned, the COD-input-factor is 20-30 g O_2/kg textile. Measurements in total wastewater showed COD output-factors between 80-100 g O_2/kg textile (Table 3.9). This means that about 60 g O_2/kg textile has been extracted from the greige cotton knit fabric.

The consumption of energy of the described process is not available.

The second process described consists of following steps:

- Padding of the de-mineralisation liquor with a pick-up of 130% (inorganic and organic acids) with subsequent reaction at 40°C and rinsing
- Padding with the bleaching liquor (H_2O_2 as bleaching agent)
- Bleaching reaction in a steamer with saturated steam at a temperature of about 97°C
- Counter-current rinsing
- Depending on the quality addition of softening agents

In principle the recipe for the bleaching liquor concerns the one given above (Table 3.13). The specific consumption of chemicals, water, steam and electricity contains Table 3.14. It is obvious that this process needs significant lower quantities of water. The input of organic auxiliaries is slightly higher. It can be expected that also here the total specific COD emission is about 80-100 g O_2/kg textile

(Table 3.9). The range is mainly caused by different specific weight and quality of processed knit fabric.

Input	unit	Typical range
Spec. consumption of inorganic chemicals	[g/kg textile]	37-41
Spec. consumption of organic chemicals, as COD (calculated with the recipe in Table 3.13)	[g O_2/kg textile]	29-35
Spec. consumption of water	[l/kg textile]	14-19
Spec. consumption of steam	[kg/kg textile]	1.1-1.6
Spec. consumption of electricity	[kWh/kg textile]	62-79
Spec. COD-output in wastewater caused by the applied chemicals (it is assumed that the wetting agents, complexing agents and organic stabilisers reach wastewater quantitatively whereas the optical brighteners and the softening agents remain to 70% and 90% respectively on the textile substrate)	[g O_2/kg textile]	16-20 (the wetting agents contribute most to the COD in wastewater)

Table 3.14: Consumption of chemicals, water and energy for a continuous pre-treatment process (bleaching/washing) of cotton knit fabric

3.2.2.1.2 Discontinuous pre-treatment of cotton knit fabric

For discontinuous bleaching/washing of cotton knit fabric, Annex II provides the standard recipes for bleaching with hydrogen peroxide (H_2O_2). For the discontinuous pre-bleaching and full-bleaching in a bleaching vessel following values are available (Table 3.15). Thereby factors can not be calculated because of missing wastewater flow for the single batches. Only the overall specific wastewater flow is known.

Parameter	**Pre-bleaching**			**Full-bleaching**		
	Exhausted bleaching bath	Hot rinsing (15 min)	Cold rinsing (25 min)	Exhausted bleaching bath	Hot rinsing (15 min)	Cold rinsing (25 min)
COD [mg O2/l]	5200-6500	4200-5400	800-1700	7800-8500	5700-6500	800-1200
pH	11.4-11.7	11.1-11.3	11.1-11.2	12.1-12.5	12.1-12.3	11.3-11.5
Conductivity [mS/cm]	6.4-9.5	5-8	1.5-3.5	16-16.8	12-12.6	2.1-1.5

Table 3.15: Data for COD, pH and L for exhausted bleaching bath and rinsing water from pre- and full-bleaching with H_2O_2 of cotton knit fabric; the overall specific wastewater flow (for the whole process including rinsing) is 30-50 l/kg

Formerly, for cotton knit fabric a combination of sodium hypochlorite and hydrogen peroxide has been applied. Because hypochlorite generates chlorinated by-products it has been phased out to a high extend. Data from 1992 show values for the combined application of hypochlorite and peroxide indicating the big difference of AOX in wastewater (Table 3.16). The applied recipe is according to the ones mentioned in Annex II. AOX in the exhausted H_2O_2-bleaching bath is up to 6 mg Cl/l because there is no rinsing after hypochlorite bleaching and the knit fabric transports the by-products to the peroxide bleaching bath.

Parameter	**NaOCl-Bleaching** Exhausted bleaching bath	**H_2O_2-bleaching** Exhausted bleaching bath	**Rinsing**
COD [mg O2/l]	1500-1800	1500-1600	70-80
AOX [mg Cl/l]	90-100	3.5-6	0.2-0.3
pH	9.3-10.2	10.5-11	8.2-8.3
Conductivity [mS/cm]	10.2-10.5	7.2-8	0.8-0.85

Table 3.16: Data for COD, AOX, pH and L for exhausted bleaching bath and rinsing water from combination bleaching with NaOCl/H_2O_2 of cotton knit fabric (LR = 1:15) – [ITV, 1992]; the overall specific wastewater flow (for the whole process including rinsing) is 30-50 l/kg)

3.2.2.2 Pre-treatment of knit fabric consisting of synthetic fibres

The availability of specific data on the input/output of processes for the pre-treatment of knit fabric consisting of synthetic fibres is limited. The components which are removed from the fibres along with quantities can be seen from Annex I. Together with specific water consumption and wastewater flow respectively the concentration of COD and hydrocarbons can be reliably estimated. Bigger industries have continuous pre-treatment processes (usually washing processes) with low specific water consumption resulting in high COD and hydrocarbon concentrations. For the latter concentrations in the g/l-order are typical.

3.2.2.3 Exhaust dyeing of knit fabric

Usually knit fabric is dyed discontinuously (exhaust dyeing). Only in some cases it is dyed semi-continuously (cold pad batch dyeing). In the future also continuous dyeing will be practised.

3.2.2.3.1 Exhaust dyeing of cotton knit fabric

Cotton knit fabric can be dyed with different kind of dyestuffs such as reactive, direct, sulphur and vat dyestuffs. Today the application of reactive dyestuffs is most common. Direct dyestuffs may be used for lighter shades and sulphur dyestuffs for dark shades. Vat dyestuffs may be used in case of very high light fastness requirements.

Table 3.17 presents typical input factors whereas distinction is made between light, medium and dark shades which reflects the specific input of dyestuffs. The high range for the liquor ratio is not due to different kind of machines but to the non-optimum loading of the soft flow machines having an optimum liquor ratio of 1:8. This occurs in case of small batches dyed in a too big machine.

		light shade	medium shade	dark shade
	unit			
Liquor ratio	1:8 - 1:25			
Dyestuff input	[g/kg textile]	0.5-4	5-30	30-80
Organic auxiliary input	[g/kg textile]	0-30	0-30	0-35
Salt input	[g/kg textile]	90-400	600-700	800-2000
Inorganic auxiliary	[g/kg textile]	50-250	30-150	30-150

Table 3.17: Typical input factors for exhaust dyeing of cotton knit fabric with reactive dyestuffs

Normally, for light shades less rinsing is required and soaping is not needed. Table 3.18 contain the data of the single emitted bath from reactive dyeing at light shade. COD values are very low, especially for rinsing water. In contrary such data are presented for a dark shade showing significant higher values for COD, conductivity and colour (Table 3.19). The values for exhaust dyeing for other shades with reactive dyestuffs will be between these extreme cases.

No. of bath	Name of bath	COD [mg O_2/l]	pH	Conductivity [mS/cm]	SAC 436 nm [1/m]	SAC 525 nm [1/m]	SAC 620 nm [1/m]
1	Exhausted dye bath	920	11	72	43	18	6
2	Rinsing bath	180	10.6	10	9	4	2
4	Rinsing bath	33	10	2.8	4	2	1
5	Rinsing bath	23	9	1	2	1	1
6	Rinsing bath	5	8.3	0.8	1	0.5	0.2

Table 3.18: Sequence of emitted baths from exhaust dyeing (light shade) of cotton knit fabric with reactive dyestuffs along with values for COD, pH, conductivity and colour (spectral absorption coefficients, SAC) LR = 1: 25; specific water consumption for the whole process: 142 l/kg (including water at loading stage and direct cooling after dyeing)

No. of bath	Name of bath	COD [mg O_2/l]	pH	Conductivity [mS/cm]	SAC 435 nm [1/m]	SAC 500 nm [1/m]	SAC 620 nm [1/m]
1	Exhausted dye bath	3400	12.1	140	328	315	320
2	Rinsing bath	2980	11.8	55	325	298	308
3	Neutralisation bath	2530	4.5	25	309	220	246
4	Rinsing bath	1060	4.7	8.3	316	185	196
5	Rinsing bath	560	5.3	2.1	316	164	154
6	Soaping bath	450	6.7	0.8	321	177	132
7	Rinsing bath	150	7.0	0.5	205	94	61
8	Rinsing bath	76	7.6	0.4	63	27	17
9	Rinsing bath	50	7.6	0.4	29	13	7

Table 3.19: Sequence of emitted baths from exhaust dyeing (dark shade) of cotton knit fabric with reactive dyestuffs along with values for COD, pH, conductivity and colour (spectral absorption coefficients, SAC) LR = 1: 8.2; specific water consumption for the whole process: 71 l/kg

In the following two more examples are submitted, one for dyeing with direct dyestuffs (light shade) (Table 3.20) and one for dyeing with sulphur dyestuffs (dark shade) (Table 3.21).

No. of bath	Name of bath	COD [mg O_2/l]	AOX [mg Cl/l	pH	Conductivity [mS/cm]	SAC 436m [1/m]	SAC 525m [1/m]	SAC 620 nm [1/m]
1	Exhausted dye bath	3000	1.5	10	9.1	50	28	19
2	Rinsing bath	160	0.18	8.2	1.2	8	3	2.8
3	Rinsing bath	50	0.07	7.4	0.6	0.3	0.02	0.02
4	Conditioning bath (softening)	900	0.2	4.8	0.8	13	9	7

Table 3.20: Sequence of emitted baths from exhaust dyeing of cotton knit fabric with direct dyestuffs (light shade) along with values for COD, AOX, pH, conductivity and colour (spectral absorption coefficients, SAC) – [ITV, 1992]

No. of bath	Name of bath	COD [mg O_2/l]	AOX [mg Cl/l	pH	Conductivity [mS/cm]	SAC 436nm [1/m]	SAC 525m [1/m]	SAC 620 nm [1/m]
1	Exhausted dye bath	4800	3.3	11.5	63	1100	1080	1130
2	Hot rinsing bath	600	0.4	10	3.2	8	8	9
3	Rinsing bath	36	0.03	8.2	0.62	0.5	0.3	0.3
4	Rinsing bath	25	0.04	8	0.34	0.3	0.1	0.2
5	Hot rinsing bath	580	0.3	8.3	1.3	3.5	3.2	3.3
6	Rinsing bath	30	0.04	7.4	0.52	0.1		0.1
7	Rinsing bath	25	0.04	7.4	0.5	0.1	0.02	0.03
8	Hot rinsing bath	390	0.25	8.2	1.5	2.8	2.6	3
9	Rinsing bath	24	0.03	7.6	0.52	0.1		0.08
10	Rinsing bath	12	0.04	7.7	0.5	0.2		0.08
11	Conditioning bath (softening)	2200	1.6	7.7	1.1	15	8	5

Table 3.21: Sequence of emitted baths from exhaust dyeing of cotton knit fabric with sulphur dyestuffs (dark shade) along with values for COD, AOX, pH, conductivity and colour (spectral absorption coefficients, SAC) – [ITV, 1992]

Table 3.19–Table 3.21 clearly indicate that from exhaust dyeing high, medium and low loaded baths occur which are emitted. This directly leads to the approach to recycle the low loaded ones without much efforts.

3.2.2.3.2 Exhaust dyeing of knit fabric consisting of synthetic fibres

Table 3.22 shows a typical recipe for exhaust dyeing of PES knit fabric including the application of a UV stabiliser for high light fastness. The conclusion is that disperse dyeing causes significant higher COD emission factors than e.g. reactive dyeing because of the dispersing agents (present in the dyestuffs itself to 40-60 weight-%) and carriers. There are no analytical data available. The same is for exhaust dyeing of other synthetic fibres.

	Input factor [g COD/kg textile]	Output factor Emission to wastewater [g COD/kg textile]
Liquor ratio	1: 10	
Exhaust dyeing		
Dyestuff input	1-100	0.5-50
Dispersing agent	6	5
Organic acid	?	?
Mixture of carriers (especially phthalic acid esters)	23	11
UV absorber	19	4
Defoaming agent	17	16
After-treatment		
NaOH (50%)		
Reducing agent	7	5
Sequestring agent	3	3
		Sum 45-95

Table 3.22: Example for the typical input and calculated output factors for exhaust dyeing of PES knit fabric with disperse dyestuffs

Explanations for the calculation:

- disperse dyestuff formulations contain 40-60% dispersing agents, therefore the output factor is 0.5-50
- very small amounts of dispersing agents and defoaming agents remain on the textile substrate, thus they reach wastewater nearly quantitatively
- carriers have affinity to PES fibres, so about 50% remain on PES fibres
- UV absorber have affinity to PES fibres and only about 20% reach wastewater
- reducing agents for after-treatment are partially oxidised (assumption: 30%), so COD contribution to wastewater is lower than the input

3.2.2.4 Consumption of chemical products

Regarding the applied chemicals in TFI a common statements says that many products are in use. However the evaluation of many chemical consumption lists on an annual basis always show that the consumption curve for the single products is hyperbolic. An example for a TFI finishing cotton knit fabric contains Figure 3.6.

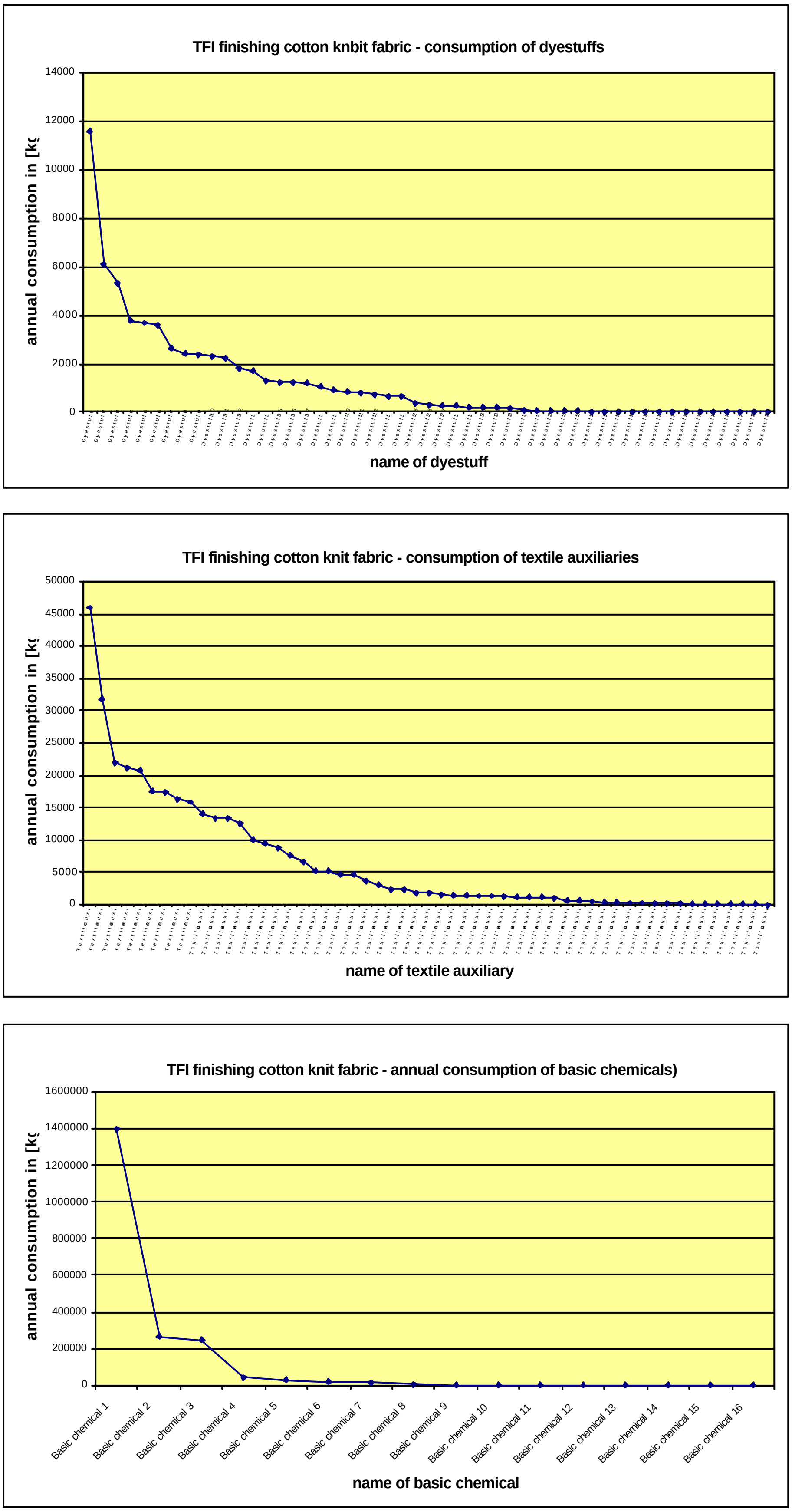


Figure 3.6: **Typical hyperbolic curve for the consumption of dyestuffs, textile auxiliaries and basic chemicals of a TFI finishing cotton knit fabric – according to [UBA, 2001]**

3.3 Finishing of woven fabric

For the finishing of woven fabric the basic process sequence, already mentioned in Chapter 2, is repeated in order to enable better orientation.

3.3.1 Site specific input/output data

3.3.1.1 TFI finishing woven fabric mainly consisting of cotton and viscose

The typical process sequence for the finishing of woven fabric mainly consisting of cotton is shown in Figure 3.7.

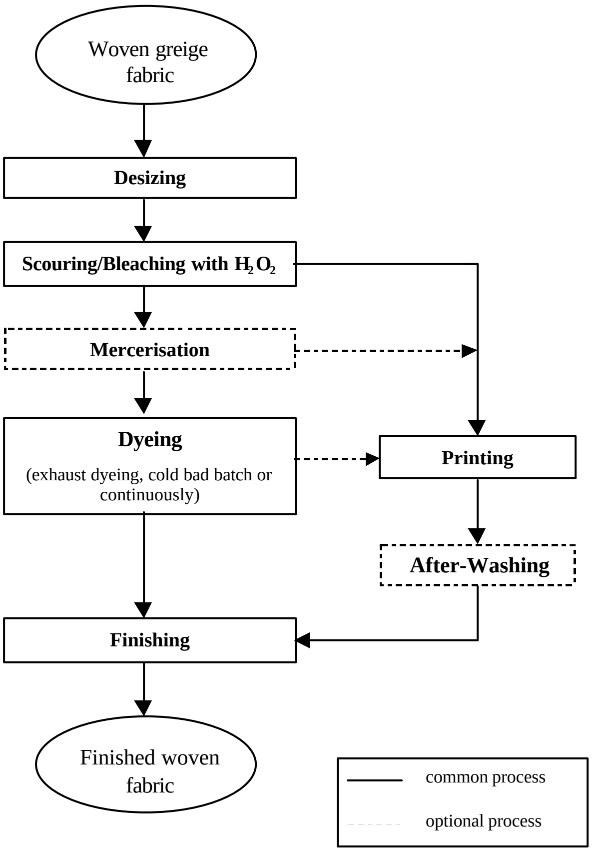


Figure 3.7 : Typical process sequence for wet processes for the finishing of woven fabric mainly consisting of cotton

In addition to the processes, mentioned in Figure 3.7, further processes may be applied exceptionally, such as pre-treatment with liquid ammonia (carried out at a very few sites in Europe only).
Pre-treatment of viscose usually requires alkali treatment and washing only, provided the sizing agents are water-soluble which is normally the case.

Pre-treatment steps, such as desizing, scouring and bleaching, very often are combined in one continuously operated treatment line. In contrary to knit fabric, woven fabric mostly is finished semi-continuously or continuously.

In Table 3.23 the data for wastewater emissions from twelve TFI finishing woven fabric mainly consisting of cotton are compiled. All these industries carry out pre-treatment continuously or semi-continuously. The same is for dyeing; however, some industries have exhaust dyeing section also.

	spec.	COD		BOD_5		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O_2/l]	[g/kg]	[mg O_2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	182	822	150	249	45	0.3	0.05			8.4	1.4	25.8	4.6	0.8	16.7	3	0.23	42	0.09	16			0.24	44
TFI 2	83	3640	303	1350	113	2.5	0.21	7.5	0.6		3.3	44.5	3.1	0.3			0.6	50	0.05	4			0.18	15
TFI 3	211	597	126	128	27	0.38				8.6	1.9		7.9	1.7	15.6	3.3	0.09	19	0.02	4				
TFI 4	99	1210	120	256	25	0.9	0.09			10.1			48.3	4.8	158	16	0.36	36						
TFI 5	52	824	43	356	19																			
TFI 6	56	2280	128	610	34	0.17	0.01			9.6	2.4		14.3	0.8	56	3.1	0.08	5						
TFI 7	132	996	132	384	51			3	0.4		0.2	20.4					0.07	9	0.1	13			0.16	21
TFI 8	93	949	89					3	0.3		4.5	34.1					0.08	7.5	0.07	7			0.3	28
TFI 9	45	4600	208	1760	79	1.1	0.05					33.7					0.25	11	0.006	0.3	0.03	1	0.18	8
TFI 10	150	672	101	307	46	0.3	0.04			10.1	2.2	41.9			25	3.7	<0.01	<1.5	<0.01	<1.5			<0.01	<1.5
TFI 11	93	1616	150	367	34	0.3	0.028										0.13	12	0.050	5	0.03	3		
TFI 12	618	334	206	66	41	0.27	0.17			8.6	1.2	30.9			16.5	10.2	0.12	74	0.022	14			1.05	649

Table 3.23: Concentration values and textile substrate specific emission factors for wastewater from twelve TFI mainly finishing woven fabric mainly consisting of CO

Cells without number mean that concerned information is not available

There is a wide range for specific wastewater flow. TFI with values of about 50 l/kg (TFI 6 and 9) have more modern and more efficient washing machines compared to TFI having values of about 200 l/kg. TFI 12 has an extremely high value (618 l/kg) because of usage of very old machines with very high water consumption. TFI with low specific water consumption and wastewater flow respectively have concerned higher COD-concentrations up to 4500 mg/l. The values for specific wastewater flow are confirmed by [FhG-ISI, 1997], reporting for 25 other TFI similar values with another very high value (415 l/kg) and two other high values (240 and 265 l/kg).

COD emission factors for finishers of woven fabric are considerably higher compared to yarn or knit fabric finishers (two to three times higher). This is mainly due to the removal of sizing agents which are present on woven fabrics up to 15 weight-%. Depending on kind of fabric and sizing agents, the load of sizing agents on the fabric varies strongly and the emission factors respectively. E.g. TFI 5 is finishing light, open fabrics with low load of sizing agents. In addition, this TFI only carries out pre-treatment. Therefore, its emission factor is very low. In contrary, TFI 2 is finishing woven fabric with a high load of sizing agents and is therefore having a high emission factor (300 g/kg). TFI finishing cotton frotté and such finishing mainly viscose fabrics have also low factors. The BOD_5 emission factors vary strongly in relation to the COD emission factors. This is due to the method of BOD_5 which can been considered a biodegradation test on ‘ready biodegradability’. Synthetic sizing agents, such as carboxymethylcellulose (CMC), polyacrylates (PA) and polyvinyl alcohol (PVA) are all not easily biodegradable; CMC and PA are non-biodegradable or only to a very low percentage. Before this background, it may be understandable that TFI 1 and TFI 2 have a COD/BOD_5 ratio of about 3:1 (percentage of biodegradable sizing agents is relatively high) meanwhile TFI 3 and TFI 4 have one of about 5:1 (percentage of heavily or non-biodegradable sizing agents is relatively high). The high ammonia concentration of TFI 4 is due to the printing section of this TFI. However, this TFI is not categorised with TFI having a relevant printing section because the percentage of printed textile substrate is lower than 30%.

The reasons for the high AOX concentration and emission factor of TFI 2 are not known.

Figure 3.8 shows a typical evaluation of the composition of the COD load of wastewater from a TFI finishing woven fabric consisting mainly of cotton. It is obvious that sizing agents and cotton impurities contribute most. In case of applying sulphur and/or vat dyestuffs, the percentage of dyestuffs is higher compared to reactive dyestuffs because of dispersing agents present in the applied formulations.

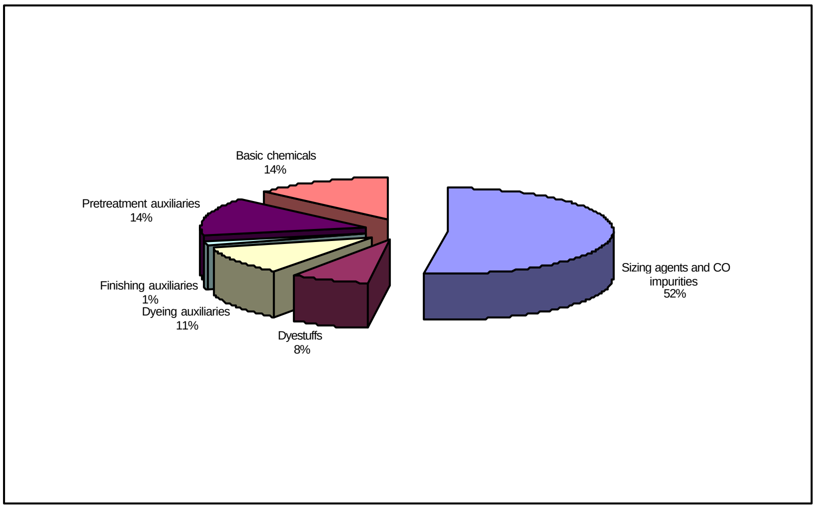


Figure 3.8: **Example for the typical composition of the COD load of a TFI finishing woven fabric mainly consisting of cotton; semi-continuous and continuous dyeing is carried out with sulphur, vat and reactive dyestuffs**

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. Typical values are:

- dyestuffs:	11	[g/kg textile substrate]
- textile auxiliaries:	183	[g/kg textile substrate]
- basic chemicals:	200	[g/kg textile substrate]

Depending on individual conditions, values for other finishers of woven fabric consisting mainly of cotton and viscose may differ.

The total specific energy consumption is in the range of 8-20 kWh/kg. The higher value is in case of TFI which have also spinning, twisting and coning sections. The consumption of electricity is about 0.5-1.5 kWh/kg (data from 8 TFI). There is very limited information on the composition of the overall energy consumption. Figure 3.9 contains an example for the finishing of viscose fabric. The example clearly indicates, that high temperature processes such as thermal treatment in stenters or condensation machines and drying operations contribute most to the overall energy consumption. Electric energy is needed at all stages and there is no dominating process.

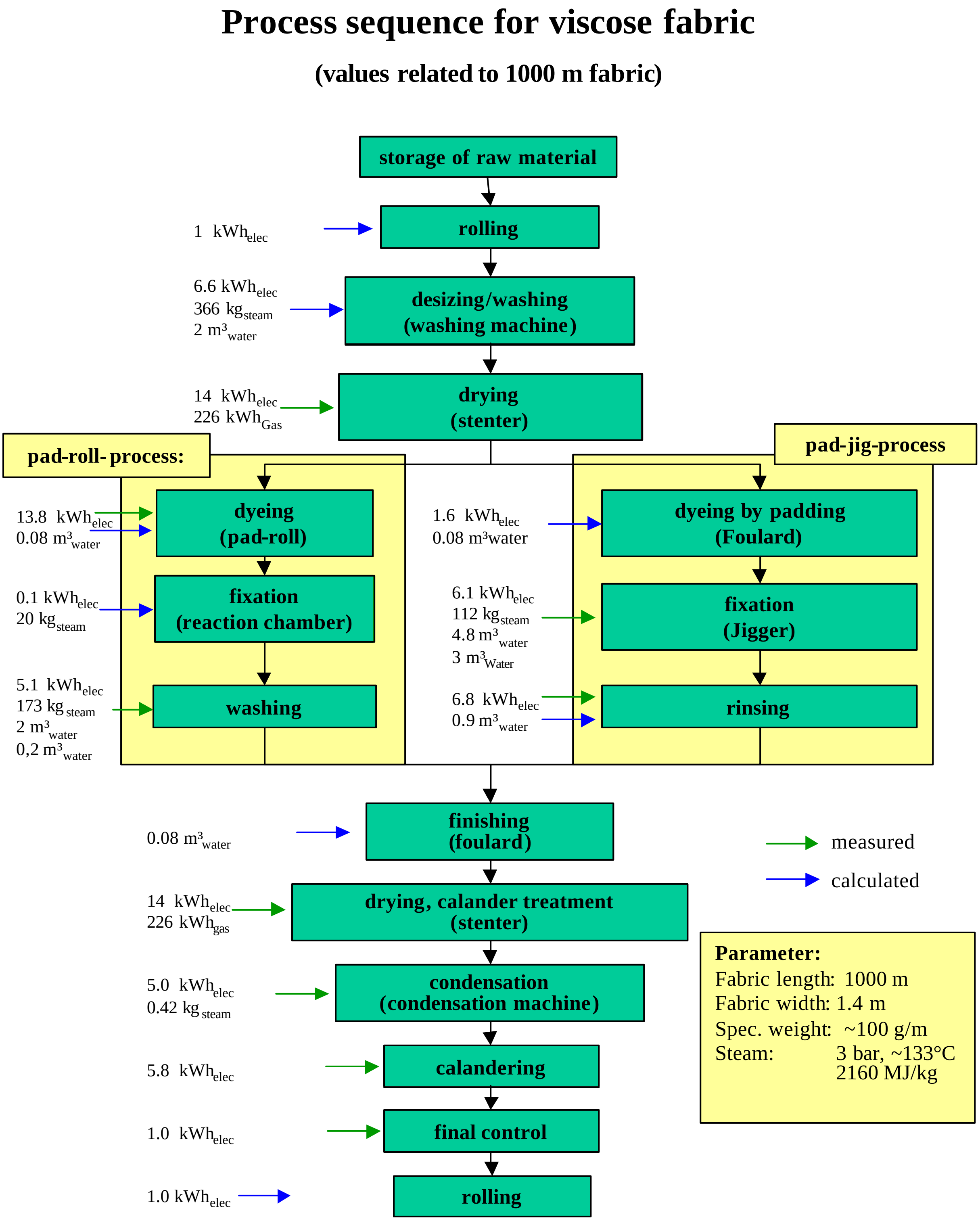


Figure 3.9: Distribution of thermal and electric energy consumption for the finishing of viscose fabric- [Eutech/ITA/LTT, 2000]

In case, there is a high temperature process for dyeing also, energy consumption is relevant also for such a process. indicates this fact for the example of finishing woven fabric consisting of viscose/polyester blend. The polyester fibres are dyed at high temperatures which requires significant quantities of thermal energy. However, also electric energy is higher compared to other processes.

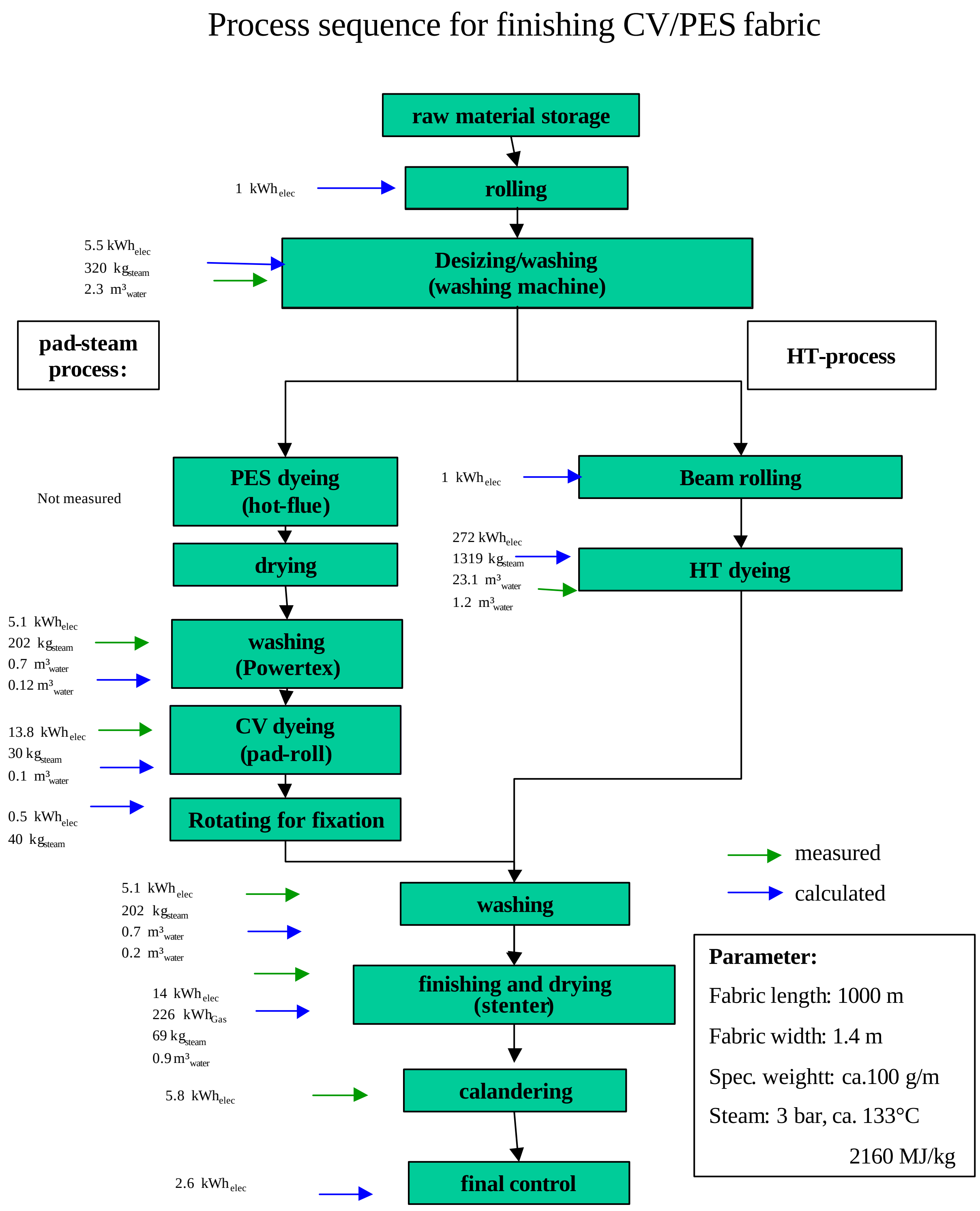


Figure 3.10: Distribution of thermal and electric energy consumption for the finishing of viscose/poyester fabric- [Eutech/ITA/LTT, 2000]

It has to be stressed that the Figure 3.9 and Figure 3.10 are examples which are very rare. However, the basic drawn conclusions may be transferable to the textile sector. Regarding these examples, it is obvious, that only such detailed analysis may allow the identification of the processes, most relevant for minimising energy consumption.

3.3.1.2 TFI finishing woven fabric mainly consisting of cotton and viscose having a relevant printing section

In Table 3.24, the values of six TFI with a relevant printing section (more than 30% of the textile substrates are printed) are compiled. TFI 4 does not carry out pre-treatment but is finishing already pretreated fabric. In all the six TFI, pigment printing is negligible; reactive printing and etch printing is dominating. Thus, these TFI have a maximum of processes (all processes indicated in Figure 3.5) which has the effect of relatively high specific water consumption and wastewater flow respectively. Also COD emission factors are high, because, in addition to sizing agents, high COD load from printing section (washing of printing equipment and printing after-washing) contribute. The specific wastewater flow of the six industries varies from 155-283 l/kg which is highest in comparison to all other kinds of TFI. TFI 4 is nor directly comparable because it only carries out printing and finishing. The values clearly indicate that textile finishing industries with a relevant printing section have highest wastewater emissions. The high values for specific wastewater flow are confirmed by [FhG-ISI, 1997]; in this document, values for further seven TFI are presented: 282, 288, 327, 450, 261, 189 and 302 l/kg – entirely higher values compared to all other kinds of TFI.

As already mentioned, the COD emission factors are on a high level. Also higher AOX values occur which is mainly due to vat dyes containing halogens. Ammonia concentrations and emission factors are also much higher because of the application of urea, especially for printing pastes (up to 150 g urea/kg printing paste). In wastewater, urea hydrolyse to ammonia. Furthermore, concentrations and emission factors for copper are significantly higher compared to other categories of TFI because of low fixation rates of copper-phthalocyanine-complex reactive dyestuffs.

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. The values from a typical example are:

- dyestuffs:	88	[g/kg textile substrate]
- textile auxiliaries:	180	[g/kg textile substrate]
- basic chemicals:	807	[g/kg textile substrate]

Depending on individual conditions, values for other finishers of woven fabric mainly consisting of coton and viscose having a relevant printing section may differ.

The high specific consumption of dyestuffs has two major reasons. First, colouration is performed two times: for plaine dyeing the fabric and for printing. Second, many liquid dyestuff formulations are in use and the water content is included for calculating the factors.
The high specific consumption of basic chemicals is due to the high consumption for pre-treatment and for printing.

Concerning energy consumption, there is information available for one TFI only. The total consumption of it is 18.8 kWh/kg (2.3 kWh/kg for electricity, 13.5 kWh/kg for natural gas and 3 kWh/kg for oil).

	spec.	COD		BOD_5		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	264	1167	308	272	72			18.1	4.8		1.4	26.0					0.61	161	0.1	26			0.22	58
TFI 2	155	1265	196	605	94	0.4	0.06			9	2.8	19.0					0.06	9	0.02	2	0.03	5	0.15	23
TFI 3	229	859	197	267	61	1.3	0.3			9.1	2.8	33.7	98	22	24	5	0.4	92	0.08	18				
TFI 4*[1]	139	819	114	215	30	2.4	0.3				2.5		146	20										
TFI 5	255	570	145	169	43					9.3			13.5	3.4	156	39.7								
TFI 6	283	760	216	215	61	1.7	0.5			9.6	1.3		170	45			0.1	28			0.01	2.8	0.15	43

*[1] textile substrate is already pre-treated

Table 3.24: Concentration values and textile substrate specific emission factors for wastewater from six TFI mainly finishing woven fabric mainly consisting of CO or CV, having a relevant printing section
Cells without number mean that concerned information is not available

3.3.1.3 TFI finishing woven fabric mainly consisting of wool

In Table 3.25, the values for wastewater emissions from two TFI finishing fabric mainly consisting of wool are compiled. The specific wastewater flow is high, usually higher than for TFI finishing cellulosic fibres. The two mentioned values (141 l/kg and 296 l/kg) are confirmed by five values, reported by [FhG-ISI, 1997] which are 133, 156. 253, 142 and 243 l/kg). It is not possible to draw conclusions by hand of two values which additionally have a big difference. However, compared to the other kinds of TFI, the high emission factors for chromium are noticeable (54 and 71 mg/kg). The reason why is the application of chromium containing dyestuffs.

3.3.1.4 TFI finishing woven fabric consisting of polyamide

Concerning finishing of woven fabric consisting of polyamide, there data from one TFI which are compiled in Table 3.26. The value for specific wastewater flow is very low (7 l/kg) because this TFI only practise pre-treatment of PA fabric which is just continuous washing for removal of preparation agents and sizing agents. For continuous washing with modern machines, the specific water consumption and wastewater flow respectively is low. Thus, COD concentration is relatively high. Compared to COD, BOD_5 is relatively low. The ratio of these parameters is about 6:1 indicating low biodegradability.

Figure 3.11 shows the evaluation of the composition of the COD load of wastewater from a TFI finishing woven fabric consisting mainly of polyamide. It is another TFI than the one mentioned in Table 3.26. It is obvious that preparation agents contribute to COD load to a significant extend. Their removal require relatively high amounts of washing and sequestring agents which finds expression in high percentage of pre-treatment auxiliaries of COD load. The comparatively high percentage of dyestuffs is not due to the dyestuffs themselves but due to dispersing and levelling agents present in the dyestuff formulations.

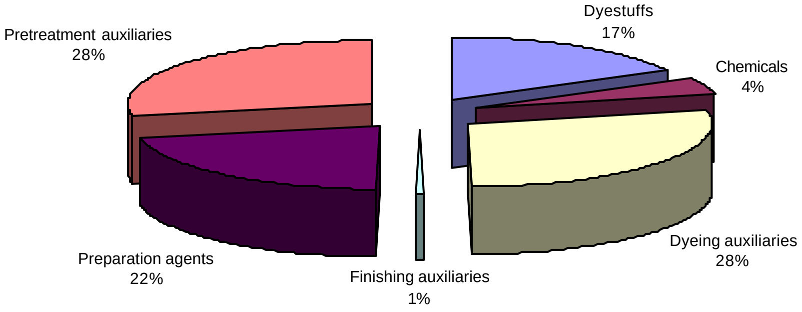


Figure 3.11: Composition of the COD load of a TFI finishing woven fabric mainly consisting of polyamide

	spec.	COD		BOD$_5$		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	141	659	93	227	32			8.5	1.2		1	26.7					0.08	11	0.38	54			1.3	183
TFI 2	296	814	241	308	91	0.31	0.09			7.1	1.9	29.7			22.7	6.7	<0.05	<15	0.24	71	<0.05	<15	0.61	181

Table 3.25: Concentration values and textile substrate specific emission factors for wastewater from two TFI mainly finishing woven fabric mainly consisting of wool
Cells without number mean that concerned information is not available

	spec.	COD		BOD$_5$		AOX		H_xC_y		pH	L	T	NH_4		org.N		Cu		Cr		Ni		Zn	
	Q_{WW}	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/kg]	[mg O2/l]	[g/kg]	[mg O2/l]	[g/kg]	[mg Cl/l]	[g/kg]	[mg/l]	[g/kg]		[mS/cm]	[°C]	[mg/l]	[g/kg]	[mg/l]	[g/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]	[mg/l]	[mg/kg]
TFI 1	7	1950	14	317	2	0.13	0.001			11	0.6	31.9												

Table 3.26: Concentration values and textile substrate specific emission factors for wastewater from one TFI mainly finishing woven fabric consisting of PA
Cells without number mean that concerned information is not available

3.3.2 Process-specific input/output of TFI finishing woven fabric

Process-specific information is submitted on

- continuous pre-treatment of woven fabric
- continuous and semi-continuous dyeing
- rotary screen printing
- finishing of cellulosic fibres

As already mentioned at the beginning of Chapter 3, information on emissions to air are submitted in a separate chapter (Chapter 3.5) in order to submit a compact compilation of data.

3.3.2.1 Continuous pre-treatment of woven fabric

3.3.2.1.1 Pre-treatment of cellulosic woven fabric

For cotton, the most common processes are desizing, scouring and bleaching. In addition, after scouring, mercerisation could take place. Today, these processes are often combined. Figure 3.12 shows the process of desizing in case of water-soluble sizing agents which can be removed just with water. The desizing bath contribute to organic load to a high extend. The COD concentration and load can be calculated from the load of sizing agents on the fabric and the specific COD value, contained in Annex I. According to Figure 3.12, water consumption for desizing is 4 l/kg. Suppose the load of sizing agent on the fabric is 6 weight-% and the specific COD is 1600 g/kg (in case of polyvinyl alcohol), the resulting COD concentration is about 24000 mg O_2/l and the resulting COD emission factor 96 g O_2/kg fabric. The mentioned water consumption (4 l/kg) is very low and can be considered as best achievable value. Older washing machines have higher water consumption, which can be five times. As a consequence, COD concentration is five times lower.

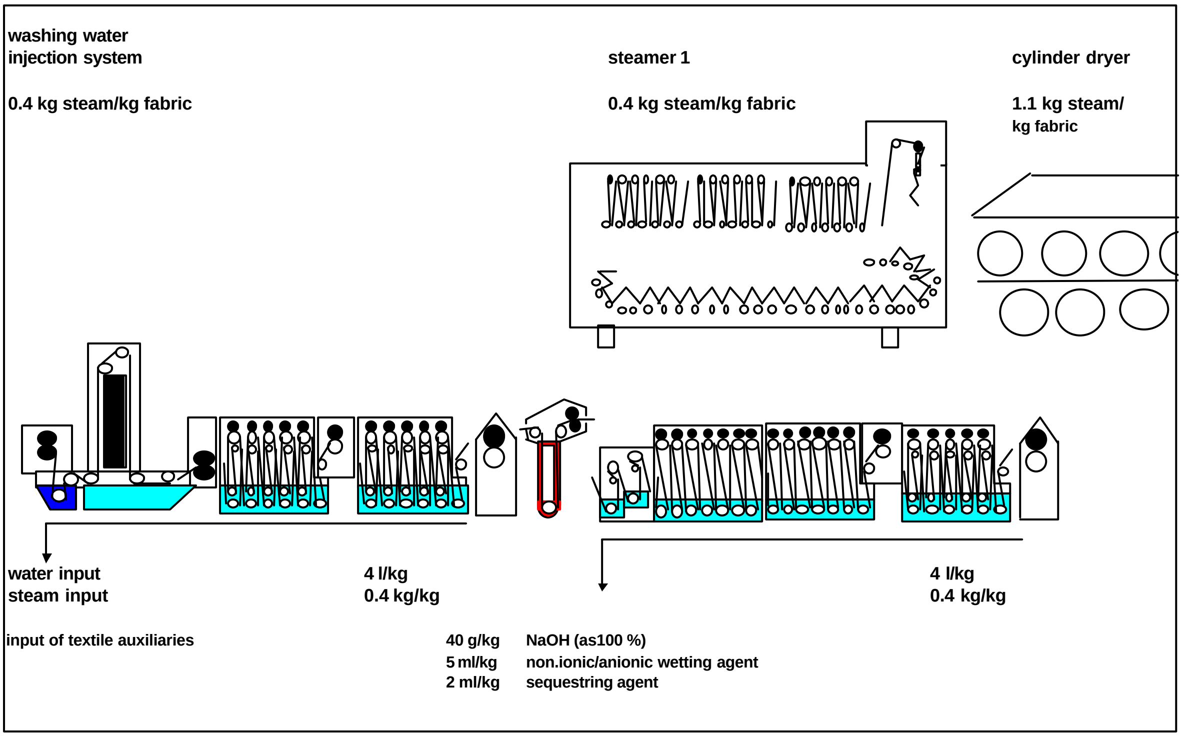


Figure 3.12: Typical continuous process for desizing (first two compartments) and scouring (with the process sequence: padding of scouring liquor, steam treatment, washing, drying)

In case of starch and modified starch, usually enzymatic desizing or oxidative desizing (cold bleaching) is applied with subsequent washing. In Annex II, typical recipes for enzymatic desizing (2.1.1.1 in Annex II), for cold oxidative desizing (2.1.1.2 in Annex II) and for desizing of water-soluble sizing agents (2.1.1.3 in Annex II) are given.

Subsequent bleaching is carried out continuously also (Figure 3.13).

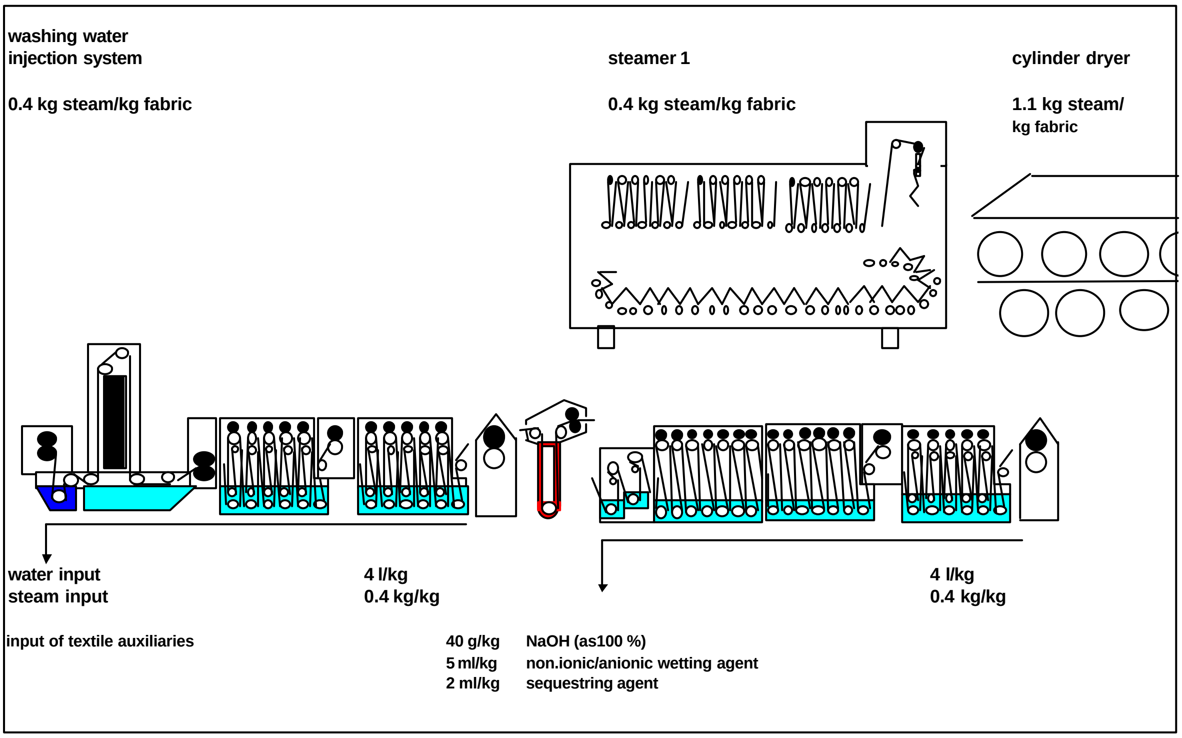


Figure 3.13: Typical continuous bleaching with the process sequence: padding of the bleaching liquor, steaming, washing and drying.

Regarding water consumption for pre-treatment processes of cotton fabric, following values are achieved for modern equipment (Table 3.27). However, older equipment may have significantly higher consumption. Table 3.27 also contains the values for steam consumption.

Pre-treatment process	Total water consumption [l/kg]	Hot water consumption [l/kg]	Steam consumption without heat exchanger [kg/kg]	Steam consumption with heat exchanger [kg/kg]
Desizing	3 - 4	3 - 4	0.6 - 0.8	0.3 - 0.4
Washing after scouring	4 - 5	4 - 5	0.8 - 1	0.4 - 0.5
Washing after bleaching	4 - 5	4 - 5	0.8 - 1	0.4 - 0.5
Washing after cold bleaching	4 - 6	4 - 6	0.8 - 1.2	0.4 - 0.6

Table 3.27: Specific water consumption and steam consumption for the pre-treatment processes of cotton fabric

3.3.2.1.2 Pre-treatment of synthetic woven fabric

Synthetic woven fabric is pretreated both discontinuously and continuously. The main purpose is to remove preparation agents. Typical recipes are submitted in Annex II.

In case of continuous pre-treatment, very high concentrations of hydrocarbons may result. E.g. with a load of hydrocarbons of 1.5 weight-% and a specific water consumption of 5 l/kg, a concentration of hydrocarbons of 3000 mg/l result. As this single wastewater stream is high in hydrocarbon concentration but low in flow, it is considered as a concentrated stream.

In case of fabric with a certain percentage of elastane, silicon oil is also present (Annex I). The complete removal of silicone oil can be very difficult. In some cases, still tetrachloroethene is applied; however, totally closed systems are applied to this purpose today having very low losses of tetrachloroethene

3.3.2.1.3 Pre-treatment of woolen woven fabric

The availability of detailed information on the pre-treatment of woolen fabric is limited. Thus, reference is given to the standard recipes for pre-treatment in Annex I is given only.

3.3.2.2 Continuous and semi-continuous dyeing

Exhaust dyeing of woven fabric is not described because it is very similar to exhaust dyeing of knit fabric. In principle, the sequence of baths is the same. Thus, semi-continuous and continuous dyeing is described only. Thereby, the application of dyestuffs by padding is the same but fixation is different. The latter can take place at room temperature (in case of cold pad batch dyeing; here after padding, for fixation, the textile is remained by slow rotation for 8-24 h) or at about 100°C by steaming or at up to 220°C by hot air etc. There are various combinations. However, the preparation of the padding liquor is required for all processes. Very often, the whole quantity of padding liquor is prepared in advance. In order to avoid a stop of the process, a surplus of liquor is prepared. Nowadays, still the residual padding liquor in the padder and the residual liquor in the preparation tank is discharged to wastewater. Compared to the overall wastewater flow, the quantity of these concentrated dyestuff liquors is very low. However, they contribute to the overall dyestuff load in wastewater to a high extend. The quantity of liquor in the padder mainly depends on width, weight of dyed fabric and type of construction. The range is about 10-15 l for very modern designs and 100 l for old designs and heavy woven fabric (>200 g/m^2). The residues in the preparation tanks depends on applied dosage and control technology and can be a few litres under optimised conditions and up to 150-200 l. The latter is not too exceptional. The quantity of residual padding liquors can be estimated with the number of batches per day (e.g. 40,000 m/d and average batch of 800 m result in 50 batches per day). The number of batches multiplied by the average volume of residual padding liquor per batch results in the daily overall quantity of residual padding liquor.

Provided a realistic pick-up of 100% (representing the magnitude) and a typical range of dyeings from 0.2 - 10%, the dyestuff concentration in the padding liquor varies between 2 - 100 g/l. Concerning the dyestuffs themselves and not considering dyestuff finishing agents (also present in the commercially applied dyestuff products), specific COD of the dyestuffs is in the order of 1 g O_2/g. Thus, COD contribution of the dyestuffs in the padding liquors varies between 2000 - 100,000 mg O_2/l.

In the following, typical recipes for the most important kind of dyestuffs and padding liquors respectively are mentioned (Table 3.28-Table 3.31). Thereby, the concentration of dyestuffs is given with "x", but the range for their concentration is mentioned above.

	[ml/l]	comment
Reactive dyestuffs	x [g/l]	
NaOH 38°Bé	20 - 40	
Water glass 37/40° Bé	30 - 50	Today, there are recipes available without water glass, with alkali only
Wetting agent	1 - 2	
Complexing and sequestring agents	1 - 3	Mainly phosphonates and polyacrylates in order to minimise silicate deposits
Urea (45%)	about 200 g/l	Applied in case of reactive dyestuffs with comparatively low water solubility

Table 3.28: Typical recipe for padding liquors for cold pad batch dyeing of cellulosics (CO and CV) with reactive dyestuffs

	[g/l]
Sulphur dyestuffs	x
NaOH 38°Bé	20 - 30
Anti-foaming agent	1 - 2
Wetting agent	1.5 - 3
Reducing agent (liquid)	20 - 30

Table 3.29: Typical recipe for padding liquors for the application of sulphur dyestuffs (for dyeing of cellulosics (CO and CV))

	[g/l]
Vat dyestuffs	x
Wetting agent	1 - 2
Complexing and sequestring agents	1 - 3
Antimigration agent	10 - 15
For reduction	
NaOH 38°Bé	60 - 120
Na-dithionite	60 - 100
Wetting agent	1 - 2

Table 3.30: Typical recipe for padding liquors for the application of vat dyestuffs (for dyeing of cellulosics (CO and CV))

	[g/l]
Vat and disperse dyestuffs	x
Wetting agent	1 - 2
Complexing and sequestring agents	1 - 3
Antimigration agent	10 - 15
Acetic acid (60%)	0.5 - 1

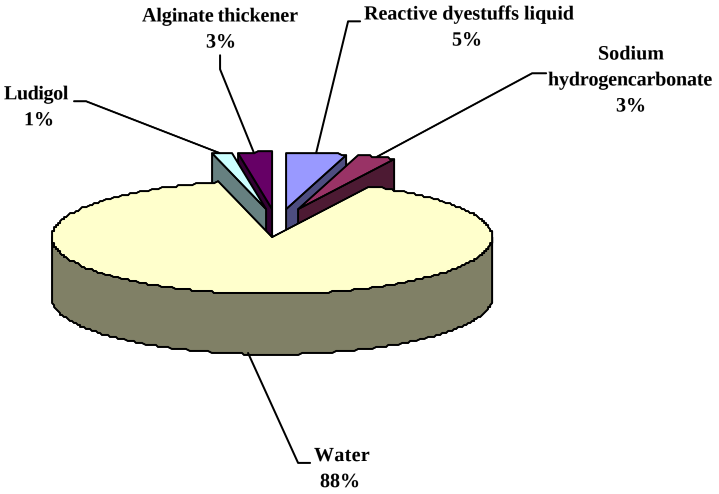
Table 3.31: Typical recipe for padding liquors for the application of vat and disperse dyestuffs (for dyeing of cellulosics/PES blends with one padding liquor)

3.3.2.3 Rotary screen printing

Concerning rotary screen printing, it is well-known that losses of printing pastes are considerable and therefore of high environmental relevance. In addition, in printing, fixation rates of dyestuffs is significantly lower compared to exhaust dyeing; compared to semi-continuous and continuous dyeing, the difference is even bigger. Also for printing, the fixation rates for copper or nickel phthalocyanine complex dyestuffs is lowest and may be less than 50%.

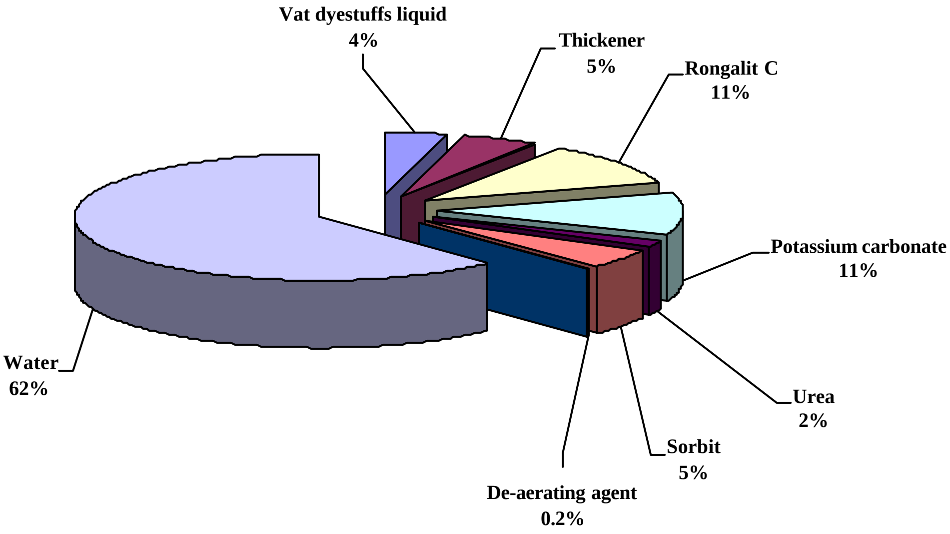
Depending on diameter and length, the volume of conventional squeegees is 2.5 - 4 l (resp. 2.5-4 kg printing paste). The pipes and the pump also contains about 2.5 kg printing pastes. Also the screens contain residual printing pastes (1-2 kg). Thus, for conventional printing paste supplying systems, volumes (= losses) of 6.5 - 8 kg result. Depending of the quantity and pattern of textile substrate to be printed, the losses of printing paste can be higher than the one printed on the textile substrate. E.g. for a quantity of 250 m with 200 g/m and a coverage of printing paste of 80% (ratio of total textile area to the printed area), 40 kg printing paste is required. In case of 7 colours and 6.5 kg per supplying system, the loss is 45.5 kg and therefore higher than the quantity printed on the textile substrate. This calculation has not taken into account the residues in the printing paste buckets.

Printing pastes are concentrated mixtures of different chemicals. Concerning organic compounds, pigment printing pastes are the most concentrated ones whereas reactive printing pastes have the lowest content of organic compounds. In Figure 3.14-Figure 3.17, typical recipes for reactive, vat, disperse and pigment printing pastes are submitted.



Total- COD: ca. 55.000 g/kg

Figure 3.14: Typical composition of printing pastes with reactive dyestuffs



Total-COD: ca. 160,000 g/kg

Figure 3.15: Typical composition of printing pastes with vat dyestuffs

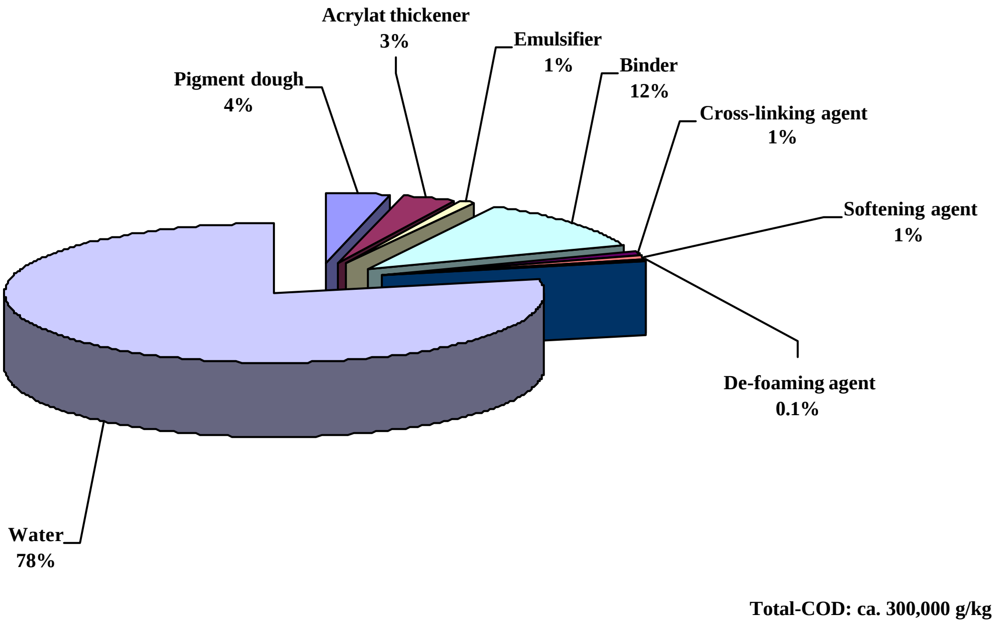


Figure 3.16: Typical composition of pigment printing pastes

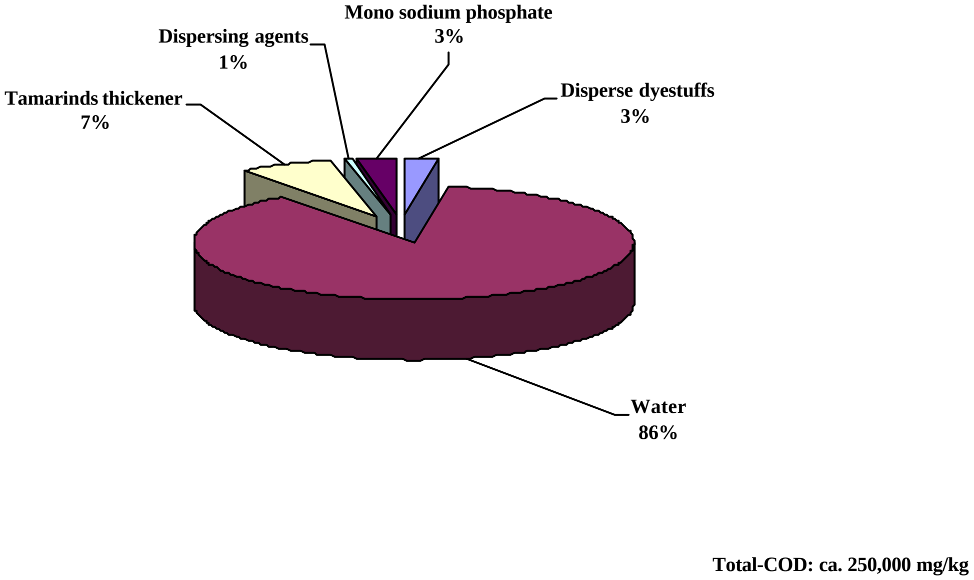


Figure 3.17: Typical composition of printing pastes with disperse dyestuffs

After having finished a certain dessin, the printing utilities, such as squegees, pipes, pumps and screens are cleaned in special equipment. Typical values for water consumption are as follows:

- 350 l per pump and pipes for one printing paste supplying system
- 35 l per squegee (modern washing equipment)
- 90 l per screen (modern washing equipment)

In addition, water is consumed for printing blanket washing, which is about 1200 l/h. Normally, the washing facility is coupled with printing blanket movement which is only about 25% of time. Further, the blanket of the dryer, subsequent to the printing process is also washed. A typical consumption is about 400 l/h; also here the washing facility is coupled with printing blanket movement.

3.3.2.4 Finishing of cellulosic fibres

There is a big number of different chemicals and even more recipes available in order to finish textile substrates with certain using properties. For woven fabric, these chemicals are applied in a continuous process by padding the finishing liquor with subsequent reaction and fixation in a stenter. In most cases, there is no after-washing. In some cases, after-washing is required. Then, wastewater problems may occur. Outstanding examples are the finishing with reactive flame retardants (organo phophorous compounds) and with reactive easy-care (for non-ironing effects) compounds. For the latter, a typical recipe is presented in Table 3.32.

	[g/l]	
Dimethyloldihydroxy ethylene urea as cross-linking agent	130 - 200	The reaction is carried out at acidic conditions (pH 2-3), reaction time is 20 - 40 h at 25-30°C
Sulfuric acid (48%)	15 - 30	
Washing agents	2	Fatty acid ethoxilates

Table 3.32: Standard recipe for the finishing of cotton woven fabric with reactive easy-care (for non-ironing effects) compounds; COD of the padding liquor is about 130,000 mg O_2/l

The chemicals, applied both for flame retardancy and non-iron finishing are non-biodegradable and pass biological treatment almost unchanged. Also adsorption to activated sludge is very low.

Regarding cotton woven fabric, agents for the improvement of crease and shrink resistance are widely applied. In this case, no after-washing is carried out. One example is presented in Table 3.33.

Specific weight: 250 g/m^2
Fabric width: 1.6 m

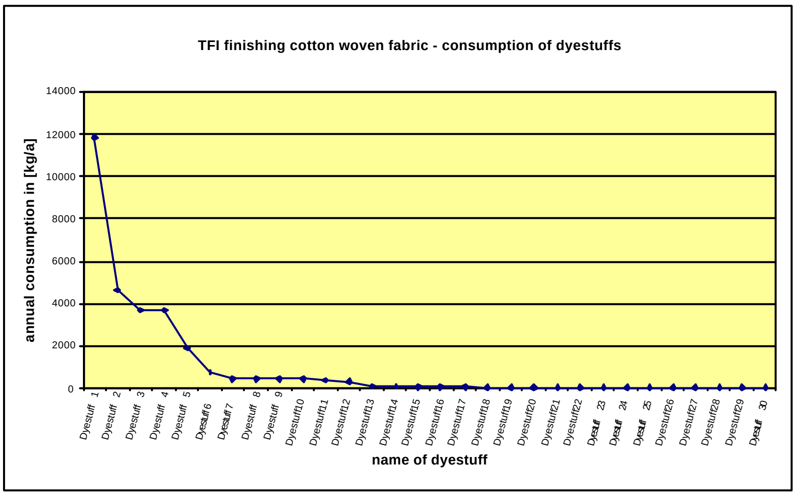
Component	Quantity [l/1000m]	0.91 x 0.91 because of dilution	spez. COD [g O_2/kg]	COD [mg/l]
Levelling and dispersing agent	5	4.55	645	2934.75
Methyloldihydroxiethylene urea	40	36.40	790	28756
$MgCl_2$	10	9.10		
Sodium F-borate	0.15	0.14		
Optical brightener	2	1.82	360	655.2
Additive for cross-linking agents	20	18.20	628	11429.6
Smoothness agent	40	36.40	340	12376
Softening agent 1	30	27.30	530	14469
Softening agent 2	30	27.30	440	12012
	177.15			
	total 195 l liquor/1000m		total	**82632.55**

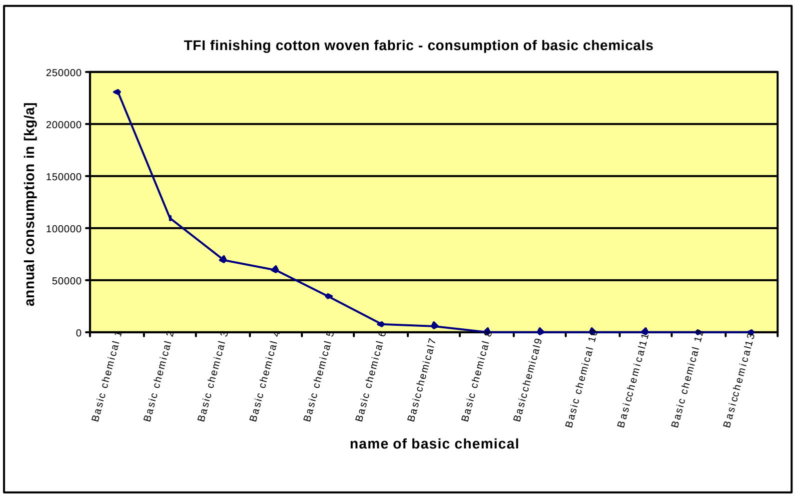
Table 3.33: Typical recipes for the improvement of crease and shrink resistance

In this case, there is no after-washing. Thus, the residual finishing liquor in the padder and the preparation tank is discharged. The reactive component (methyloldihydroxiethylene urea) , the optical brightener and the softening agents are not biodegradable and contribute to residual COD in the treated effluent of biological wastewater treatment plants.

3.3.2.5 Consumption of chemical products

Like for finishers of yarns and knit fabric, for finishers of woven fabric, the consumption curve for applied dyestuffs, textile auxiliaries and basic chemicals is hyperbolic (Figure 3.18). The same is for TFI having a relevant printing section (Figure 3.19).





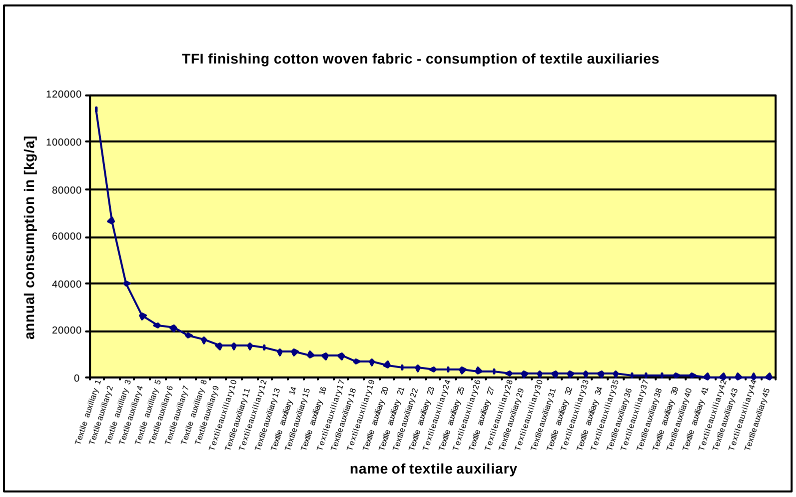


Figure 3.18: Typical hyperbolic curve for the annual consumption of dyestuffs, textile auxiliaries and basic chemicals of a TFI finishing cotton woven fabric - according to [UBA, 2001]

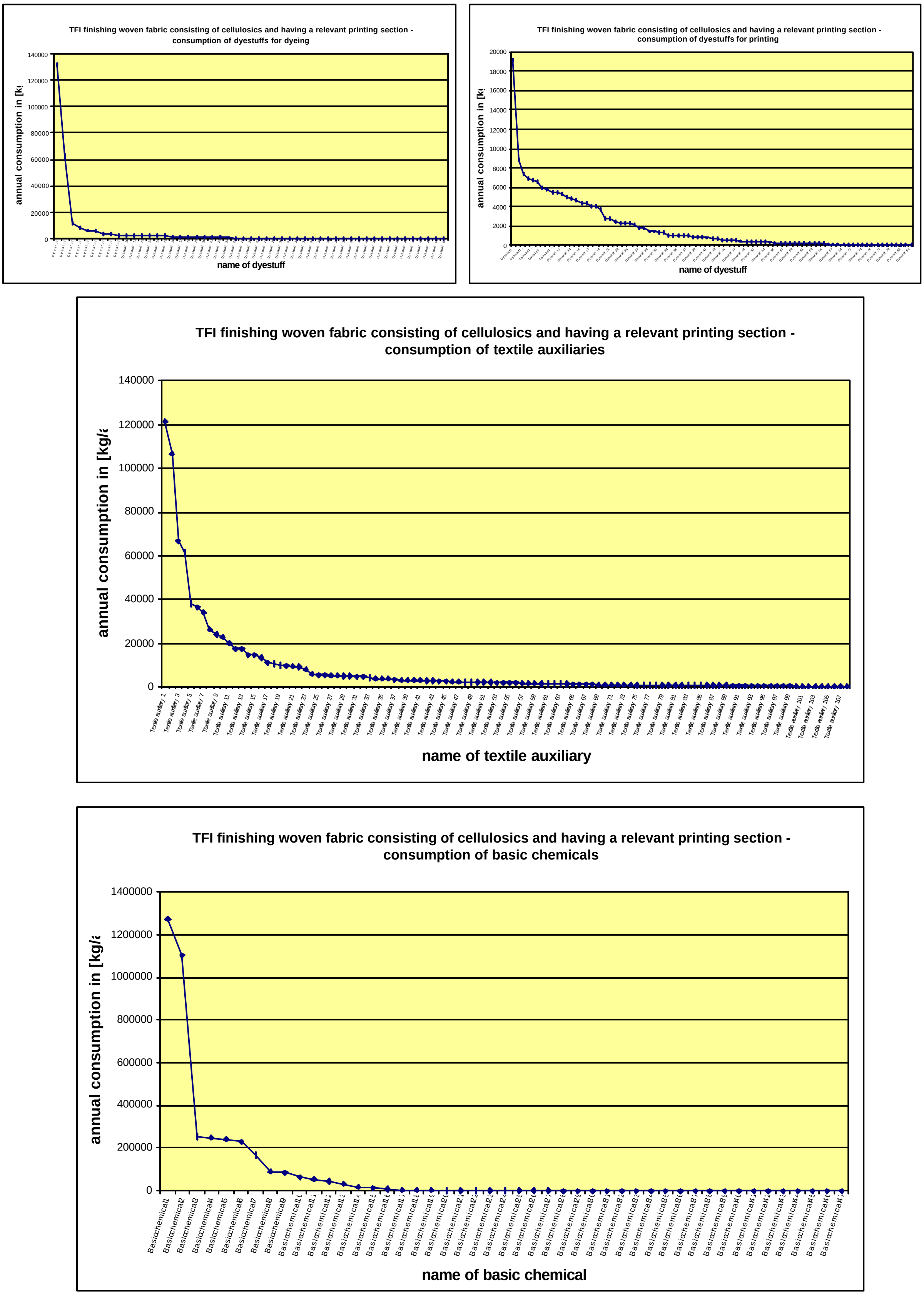


Figure 3.19: **Typical hyperbolic curve for the annual consumption of dyestuffs, textile auxiliaries and basic chemicals of a TFI finishing cellulosic woven fabric and having a relevant printing section; the consumption of dyestuffs for dyeing and for printing are illustrated separately- according to [UBA, 2001]**

3.4 Finishing of carpets

3.4.1 Site specific input/output data

There is limited information available for the finishing of carpets. In principle, there are three main processes:

- Dyeing (usually, there is no special pre-treatment and removed preparation agents are dispersed in the dyeing bath)
- Printing
- Coating

Table 3.34 compiles data for wastewater emissions from two carpet finishing industries. Here, specific consumption is not related to kg but to m^2. Both TFI practise all above mentioned processes. Specific wastewater flow of TFI 1 is less than half of TFI 2. However, COD concentration is in the same range which results in double COD emission factor of TFI 2. All other values are not conspicuous.

Concerning wastewater flow, the exhaust dyeing section is most relevant (about 80%), followed by the printing section (18.5%). So-called latex wastewater is caused from cleaning the latex application equipment and has a percentage of about 1.5%. It is usually treated by flocculation/precipitation resulting in considerable amounts of sludge to be disposed off.

The applied chemicals are grouped in dyestuffs, textile auxiliaries and basic chemicals. The values of two TFI are following:

- dyestuffs:	2.1 / 3.4	[g/m^2 carpet]	
- textile auxiliaries:	21.6 /n.a.	[g/m^2 carpet]	For one of the two TFI, only the sum of textile auxiliaries and basic chemicals is available which is 55.2 g/m^2
- basic chemicals:	4.4 /n.a.	[g/m^2 carpet]	

n.a. = not available

Whereas one TFI is backing the carpet with latex, the other one is carrying out the backing with a textile substrate.

The specific consumption of electricity of the two TFI is 0.9 and 1.3 kWh/m^2. The consumption of oil or natural gas is not available.

3.4.2 Process-specific input/output for TFI finishing carpets

There is not detailed information available which can be provide a realistic and representative picture.

	spec.	COD		BOD5		AOX		HxCy		pH	L	T	NH4		org.N		Cu		Cr		Ni		Zn	
	QWW	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac				Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac	Conc.	E-Fac
	[l/m^2]	[mg O$_2$/l]	[g/m^2]	[mg O$_2$/l]	[g/m^2]	[mg Cl/l]	[g/m^2]	[mg/l]	[g/m^2]		[mS/cm]	[°C]	[mg/l]	[g/m^2]	[mg/l]	[g/m^2]	[mg/l]	[mg/m^2]	[mg/l]	[mg/m^2]	[mg/l]	[mg/m^2]	[mg/l]	[mg/m^2]
TFI 1	14.7	1980	29							7	0.73	29					0.3	4.4	0.11	16.2			0.23	3.4
TFI 2	35.6	1670	59	490	17	0.28	0.01			6.8		37												

Table 3.34: Concentration values and textile substrate specific emission factors for wastewater from TFI finishing carpets mainly consisting of PA
Cells without number means that concerned information is not available

3.5 Emissions to air

3.5.1 Main sources of off-gases (waste gases) in textile finishing

Emissions to air from textile finishing includes both, captured emissions released from stacks and uncaptured, fugitive emissions. The latter are important concerning working place 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
- Energy generation (boiler houses)

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.

During aqueous pre-treatment steps and dyeing mainly fugitive emissions are relevant (esp. if highly volatile substances resp. substances with a high water vapour volatily 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.

It is important to know that emissions to air are caused by

- the textile materials
- the auxiliaries/chemicals
- the machines (esp. if direct heated stenters or drying apparatus are used).

In the following at first a closer look on the emission potential of textile raw materials and a detailed catalogue of the main substances to be detected in the off-gas in textile finishing is given (Chapters 3.5.2 and 3.5.3). In Chapters 3.5.4 - 3.5.9, information on the consumption of chemicals and auxiliaries as well as on emissions to air is presented on process level. Finishing, singeing, printing, coating and energy generation are mentioned. Chapter 3.5.10 focuses on smell intensive processes and substances. The emission characteristic in textile finishing regarding examples from an on site level view is described in the Chapters 3.5.11.1 - 3.5.11.4. Chapter 3.11.5 shows an example for emission levels along a typical process sequence in textile finishing.

3.5.2 Textile raw material

Emissions from the textile raw materials are observed during

- thermal treatment of grey fabrics (esp. in heat setting),
- thermal treatment of fabrics which are pre-washed in an inefficient way (esp. in heat setting, drying and fixation),
- non-wovens production (thermo bonding processes).

Possible sources for off-gas loads caused by the textile raw materials are summarized in Table 3.35:

Fibre	**Impurities/by-products**	**Off-gas load**
Man-made fibres in general	Preparation agents	Mineral oils, fatty acid esters and their by-products resp. thermal decomposition compounds
Natural fibres in general	Preparation agents Natural impurities	Mineral oils, fatty acid esters and their by-products resp. thermal decomposition compounds Decomposition products (esp. aldehydes)
PU (elastane)	Residual fibre solvent Preparation agents	N,N-Dimethylacetamide Silicones
Meta-aramides	Residual fibre solvent	N,N-Dimethylacetamide, N-Methylpyrrolidone
PAC	Residual fibre solvent	N,N-Dimethylformamide, N,N-Dimethylacetamide
PA 6	Residual monomer	Epsilon-Caprolactam

Table 3.35: Possible sources for off-gas loads caused by textile raw materials

3.5.3 Typical substances in the off-gas

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 following tables give an overview on the most important substances to be detected in finishing, printing, and coating processes. The classification concerning less respectively more dangerous properties follows German and European legislation.

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

Substance	Possible source
Acetaldehyde	Polyvinyl acetate, acetic acid
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
Chloromethane (methylchloride)	Quaternary ammonium compounds
Chlorinated aromatic hydrocarbons	Carriers
Chloroethanol	Decomposition of flameretardants (chlorinated P-ester)
Chloroparaffines	Flameretardants
Dichloroethene	Polyvinylidenechloride
Dichloromethane	Solvent cleaning
Diethylenetriamine	Softeners
Di(ethylhexyl)phtalate	Dyeing auxiliaries/polymer dispersions
Diglycidylether	Epoxide resins
Diisocyanatetoluene, 2,4-	Fluorocarbonresin (extender), polyurethane
Diisocyanatetoluene, 2,6-	Fluorocarbonresin (extender), polyurethane
N,N-Dimethylacetamide	Fibre solvent (m-aramide)
Dioxane, 1,4-	Surfactants (ethoxilated products)
Diphenylmethane-2,4 diisocyanate	Extender, polyurethane
Diphenylmethane-4,4' diisocyanate	Extender, polyurethane
Dipropylenetriamine	Softeners
Acetic acid-(2-ethoxiethyl)-ester	Softeners/fluorocarbonresins
Ethoxyethanol	Softeners/fluorocarbonresins
Ethanedialdehyde (glyoxal)	Crosslinkers

Substance	Possible source
Ethylenediamine	Softeners
Fluoroorganics, lowmolecular	Fluorocarbon resins
Formaldehyde	Crosslinkers, conservation agent, stenter off-gas
Formic acid	Various textile auxiliaries
Hexamethylendiamine	Polycondensationproducts
Hexamethylenediisocyanate	Fluorocarbon resins, polyurethane
Hexanone, 2-	Fluorocarbon resins
Hydrogen chloride	Catalyst
Isocyanatomethyl-3,5,5-trimethylcyclohexyl-Isocyanate,3	Fluorocarbon resins, polyurethane
N-Methylpyrrolidon	Fibre solvent (m-aramides), machine cleaning
N-alkylmorpholine	Non wovens coating
Oxalic acid	Bleaching auxiliary
Tetrachloroethene	Dry cleaning
Thiourea	Dyeing auxiliary
Triethylamine	Special crosslinkers
Tricresylphosphate	Flameretardants
Trimethylphosphate	Flameretardants
Tin derivatives, organic, inorganic	Fluorocarbon resins, Hydrophobing agents, biocides
Vinylacetate	Polyvinyl acetate

Table 3.37: Substances with more dangerous properties which may be present in waste gas

Substance	Possible source
Arsenic trioxide/antimonytrioxide	Flameretardants
Dimethylsulfate	Quaternary ammonium compounds
Ethylenimine	Flameretardants
Acrylonitrile	Polymer dispersions
1,3-Butadiene	Polymer dispersions
2-Vinylcyclohexen	Polymer dispersions
Epichlorohydrine	Polycondensation products
1,2-Epoxypropane (propyleneoxide)	Surfactants (propoxilated products)
2,3-Epoxy-1-propanol	Some antistatics
Ethyleneoxide	Surfactants (ethoxilated products)
Vinylchloride	Polymer dispersions (PVC)
Acrylamide	Reactive polymers, flameretardants
Butanoneoxime	Fluorocarbon resins, polyurethanes
Pentachlorophenol	Pesticides
Propyleneimine	Flame retardants and polyurethane crosslinker
N-vinylpyrrolidon	Polyvinylpyrrolidone dispersions

Table 3.38: Substances with cancerogenic properties which may be present in waste gas

3.5.4 Finishing of fabric (knitted and woven fabric)

3.5.4.1 Consumption of chemicals and auxiliaries

Consumption of textile auxiliaries in textile finishing depends on

- type of textile effect to be achieved,
- type of substrate to be finished
- recipe resp. kind and quantity of products used,
- liquor pick-up of the textiles in the application device (usually 60-120% depending on the substrate and the textile construction),
- amount of residual liquors.

Due to unavoidable rests of finishing liquors in the application devices (padding mangles), preparing vessels and pipings relatively small, but normally high concentrated, residual liquors are to be accepted in finishing.

The amount of residual liquors in textile finishing is in a range from approx. 0.5 to approx. 35% (concerning the total amount of finishing liquors prepared) [EnviroTex, 2001]. The lower value is for an integrated mill finishing only one substrate; the higher value is from a commission finisher, finishing small lots and different substrates.

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, amount of residual liquors is much higher)

3.5.4.1.1 Typical recipes in textile finishing

Recipes for padding liquors in textile finishing are compiled in Table 3.39. Recipes are collected from 22 textile finishing plants. Different substrates (CO, WO, CV, PA, PES, PAC and blends) and the main finishing agents (softening agents, repellents, non-slip agents, easy-care agents, antifelting agents, antistatic agents, optical brighteners, stiffening agents, and flame retardants) are regarded. It is clearly to be seen that in most cases the padding liquor has to fulfill a multifunctional task (e.g. softening agents and crosslinking agents are combined). The amount of auxiliaries in padding liquors is in most cases in a range between 5-50 g/l per auxiliary. In some cases a higher concentration of auxiliaries is applied.

Effect	**Substrate**	**Process temperature [°C]**	**Recipe**
Softening	PES/CV/CO	150	Softening agent: 130 g/l Foaming agent: 15 g/l
Softening	PES	170	Softening agent: 40 g/l
Softening	CO	150	Softening agent: 10 g/l
Softening	PES/WO	130	Softening agent: 5 g/l
Softening	PAC	160	Softening agent 1: 10 g/l Softening agent 2: 10 g/l
Softening, optical brightening, antielectrostatic	PES	185	Softening agent: 5 g/l Optical brightener: 19 g/l Antielectrostatic agent: 6 g/l Wetting agent: 2 g/l Levelling agent; 2 g/l

Effect	**Substrate**	**Process temperature [°C]**	**Recipe**
Softening, stiffening	CO	120	Starch: 50 g/l Softening agent 1: 30 g/l Softening agent 2: 15 g/l Wetting agent: 2 g/l
Softening, stiffening	PES/PAC	130-170	Softening agent: 160 g/l Stiffening agent: 20 g/l Wetting agent: 2 g/l
Softening Antielectrostatic	PA (wet in wet process)	150	Softening agent: 10 g/l Antielectrostatic agent: 10 g/l
Hydrophobic, conditioning	PES	160-190	Hydrophobic agent: 52 g/l Conditioning agent: 27 g/l
Hydrophobic, conditioning, softening	PES	175	Hydrophobic agent: 25 g/l Conditioning agent: 20 g/l Softening agent: 6 g/l
Hydrophobic	PAC/PES	180	Hydrophobic agent: 40 g/l Acetic acid: 2 g/l
Hydrophobic	WO	150-190	Hydrophobic agent: 60 g/l Wetting agent: 0,3 g/l Acetic acid: 1 g/l
Hydrophobic, oleophobic	PES/CV	160	Repellent 1: 30 g/l Repellent 2: 45 g/l Repellent 3: 30 g/l Catalyst: 12 g/l Crosslinking agent: 55 g/l Wetting agent: 10 g/l Acetic acid: 2 g/l
Oleohobic	CV/CO/PES	165	Oleophobic agent: 155 g/l Additive: 4 g/l
Non-slip	CO/PES/CV	180	Non-slip agent: 15 g/l
Non-slip	PES/WO	130	Non-slip agent: 30 g/l
Easy-care, softening, optical brightening	CO/PES	150-180	Crosslinking agent: 25 g/l Catalyst: 8 g/l Wetting agent: 5 g/l Softening agent:15 g/l Optical brightener: 4 g/l Dyestuff: 0,01 g/l Acid: 0,5 g/l
Easy-care	PES	155	Non creasing agent (formaldehyde-free): 25 g/l Additive for easy-care: 10 g/l Dispersing agent: 1 g/l Stabilizer: 1 g/l Levelling agent: 5 g/l
Easy-care, softening	CV (wet in wet)	170	Crosslinking agent: 150 g/l Catalyst 1: 50 g/l Catalyst 2: 18 g/l Softening agent: 90 g/l Acetic acid: 1 g/l

Effect	**Substrate**	**Process temperature [°C]**	**Recipe**
Easy-care, softening	CV	190	Crosslinking agent: 50 g/l Catalyst 1: 20 g/l Catalyst 2: 0,5 g/l Softening agent 1: 10 g/l Softening agent 2: 40 g/l Acetic acid: 0,5 g/l
Easy-care, softening, optical brightening	CO	100-150	Crosslinking agent: 50 g/l Softening agent 1: 35 g/l Softening agent 2: 10 g/l Optical brightener: 25 g/l
Easy-care, softening, dyeing aftertreatment	CO/EL	170	Crosslinking agent: 20 g/l Catalyst: 8 g/l Softening agent: 30 g/l Dyeing aftertreatment: 10 g/l Acetic acid: 1 g/l
Easy-care, softening, optical brightening	CO	150	Crosslinking agent: 40 g/l Catalyst 1: 12 g/l Softening agent 1: 25 g/l Softening agent 2: 20 g/l Optical brightener: 2 g/l
Easy-care, softening	CV/PA 6	180	Crosslinking agent: 65 g/l Catalyst 1: 20 g/l Catalyst 2: 0,2 g/l Softening agent 1: 50 g/l Softening agent 2: 15 g/l
Easy-care, softening	CV/PES	170	Crosslinking agent: 50 g/l Softening agent 1: 50 g/l Softening agent 2: 30 g/l Catalyst 1: 20 g/l Acetic acid: 1 g/l
Easy-care, softening, non-slip	LI/CO	180	Crosslinking agent: 70 g/l Catalyst: 40 g/l Non-slip agent: 35 g/l Softening agent 1: 10 g/l Softening agent 2: 40 g/l Deaeration agent: 2 g/l
Antielectrostatic, non-slip	PES	100	Non-slip agent: 90 g/l Antielectrostatic agent: 5 g/l
Antielectrostatic, optical brigthening	PES	190	Optical brightener: 9 g/l Antielectrostatic agent: 7 g/l
Antifelting	WO	140-160	Antifelting agent 1: 35 g/l Antifelting agent 2: 35 g/l Deaeration agent: 5 g/l
Antifelting	PES/WO/EL	160-190	Antifelting agent: 30 g/l Coating: 30 g/l Wetting agent: 0,3 g/l Sodium carbonate: 2 g/l
Flame retardant	CO	145	Flame retarder: 160 g/l

Table 3.39: Typical recipes in textile finishing [EnviroTex, 2001]

The emission potential of each finishing recipe can be calculated on the basis of the individual substance emissions factors of the input auxiliaries, the concentration of the auxiliaries in the recipe and the liquor pick-up (see formula below and Table 3.40).

The substance based emission factor is defined as the amount of substances (organic or inorganic) in grammes that can be released at defined process parameters (curing time, curing temperature and type of substrate) from one kg of auxiliary. There are two sorts of substance emission factors: fc giving the total emissions of organic substances expressed as total content of Carbon; and fs giving the emission of a specific substance in case of more toxic or carcinogenic organic substances or in the case of particular inorganic substances like ammonia, hydrogen chloride.

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):

WF [g Y/kg throughput textile] =Ó(Subst. emissionsfactor [g Y/kg aux.] x liquor conc. [g aux./kg liquor] x liquor pick-up [kg liquor/kg textile substrate]/1000)

Y = Organic-C (sum parameter used in the case of non- or low-toxic substances) or
Y = specific emitted substance (in the case of more toxic organic substances or in the case of particular inorganic substances).

WF is called textile substrate-based emission factor and gives the amount of emissions in grammes, that can be released by the finishing process referred to one kg of input textile good under the defined process parameters (curing time, curing temperature, type of substrate).
With this procedure the emissions of a finishing process can be predicted offering the opportunity to optimize the process emissions.

Information on substance based emission facors – a prerequisite for the above mentioned calculation of textile substrate based emission factors is given by the textile chemical industry [TEGEWA, 1994; LAI, 1997]

Recipe	**Auxiliaries**	**FK [g/kg]**	**FA [kg/kg]**	**Substrate**	**T [°C]**	**fs [g/g]**	**fc [g/g]**	**FK*FA *fs**	**FK*FA *fc**	**WFs [g/kg]**	**WFc [g/kg]**
Recipe 1	Fatty acid ester	20	0.65	CO	170	-	0.0152		0.2	-	-
	Polysiloxane	20	0.65	CO	170	-	0.0052	-	0.07	-	-
	Reactant cross-linking agent/Cat	100	0.65	CO	170	0.0041 FO	0.0009	0.27 FO	0.06	-	-
	Stearylurea-Derivative/Cat	20	0.65	CO	170	0.0165 FO	0.0162	0,21 FO	0.21	-	-
Total 1		-	-	-	-	-	-	-	-	**0.48 FO**	**0.54**
Recipe 2	Softening agent	50	1	CO	150	-	0.005		0.25	**-**	**-**
	Easy-care crosslinking agent (formaldehyde-free)	12	1	CO	150	-	0.010	-	0.6	**-**	
	Easy-care catalyst	12	1	CO	150	-	0.008	-	0.1	**-**	**-**
Total 2										**-**	**0.95**

FK: Liquor concentration in g auxiliary/kg liquor
FA: Liquor pick-up in kg liquor/kg textile substrate
Substrate: textile good to be finished
T: Finishing temperature in °C
fs: Substance emission factor of a auxiliary in g emission/g auxiliary
fc: Total carbon substance emission factor of a auxiliary in g emission/g auxiliary
WFs: Textile substrate-based emission factor of a recipe in g emission/kg textile substrate = Ó(FK*FA*fs)
WFc: Textile substrate-based total carbon emission factor of a recipe in g emission/kg textile substrate = Ó(FK*FA*fc)
FO: Formaldehyd

Table 3.40: Two examples for the calculation of textile specific emission factors

3.5.4.2 Emission levels

3.5.4.2.1 Typical substance specific emission factors of textile auxiliaries

Volatility of textile auxiliaries can be characterised by hand of substance emission factors (see 3.5.4.1).

The tables below give an overview on the main textile auxiliary classes and their emission factor resp. their potential to release Organic-C or specific substances like formaldehyde during thermal processes in finishing. Only auxiliaries listed in the „Textile Auxiliaries Buyers' Guide“ [THK, 2000] are mentioned [EnviroTex, 2001]. All emission factors mentioned in the tables below are measured according to German regulation on air emission [LAI, 1997].

Due to the different chemical composition and different content (concerning kind and quantity) of active ingredients, by-products and impurities considerable differences in the emission behaviour of auxiliaries which belong to the same class of auxiliaries are observed.
However it is evident that especially

- conventional preparation agents based on mineral oils and fatty acid esters
- some antifoaming agents
- some wetting agents
- some conditioning agents
- carriers
- some flame retardants
- and some antimicrobiotics

are auxiliaries with a high emission potential concerning Organic-C. However exceptions have to be regarded carefully.

Formaldehyde is released mainly from auxiliaries based on cross-linking compounds (esp. crosslinking agents and reactive flame retardants). Regarding easy-care finishing formaldehyde emission potential of melamine derivatives is in most cases higher compared to auxiliaries based on Dimethyloldihydroxyethen urea derivatives (Table 3.42, Table 3.43 and Table 3.48)

Antifoaming agents which contains highly volatile hydrocarbons as main active compound have a very high emission potential compared to silicon based types (Table 3.44)

For wetting agents on the basis of tributylphoshate, which is characterized by a high vapour pressure substance specific emission factors up to approx. 340 g Organic-C/kg are observed. Due to the fact that various additives/by-products which are not specified in the Material Safety Data Sheets are used and the amount of active ingredients can differ in a great range the emission factors of the other wetting agents mentioned in Table 3.45 vary in a great range.

Softening agents based on fatty acid derivatives are characterized by emission factors between 1 and 5 g Organic-C/kg. Polysiloxane based types show higher values. The highest mentioned value in Table 3.46 is caused by a fatty acid type with an additive of a high volatile wax.

Carriers are highly volatile substances; emission factors above 300 g Organic-C/kg are observed (Table 3.47 and Chapter 3.5.5.1).

Levelling agents used in dyeing can – like carriers - be transfered to heating steps and cause considerable amounts of off-gas loads. However, due to missing data they are not mentioned here.

Differences in the emission potential of flame retardants are mainly caused by the different types of active substances and various amounts of by-products/additives (alcohols (esp. methanol in case of reactive types), glycols, glycol ethers) (Table 3.48).

Regarding repellents (Table 3.49) also a wide range of emission factors is observed. This is mainly caused by a different kind and quantity of solvents used for fluorocarbon resins (e.g.buthyl/ethyl acetate, methylethyl/isobutylketone, ethandiol, propanediol) and different amounts of active ingredients if paraffine based types are regarded.

In the case of conditioning agents it is clearly to be seen that products based on paraffines (which have a relatively high volatility) have a higher emission potential than fatty acid derivatives (Table 3.50).

For optical brighteners and antielectrostatic agents emission potential vary due to different active ingredients and differences in the formulations of the auxiliaries (Table 3.51 and Table 3.52).

Filling and stiffening agents based on natural or synthetic polymers have a low emission potential (Table 3.53).

Emission levels for aftertreatment agents are low (Table 3.54).

Biocides can contain aromatic hydrocarbons; this leads to increased emission factors (Table 3.55).

Emission potential of silicic acid based non-slip agents is very low (Table 3.56).

Active ingredients	Organic-C [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
Mineral oils	500-800	190; 2 (PES)
Conventional fatty acid esters	100-250	190; 2 (PES)
Steric hindered fatty acid esters	50-100	190; 2 (PES)
Polyolesters	20-200	190; 2 (PES)
Polyester-/polyethercarbonates	10-50	190; 2 (PES)

Table 3.41: Substance specific emission factors: Preparation agents

	Organic-C [g/kg]	Formaldehyde [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
A	14	4	170; 4 (CO)
B	15	5	170; 3 (CO/PES)
C	2	6	180; 1.5 (CO)
D	15	4	170; 3 (CO/PES)
E	20	4	170; 3 (CO)
F	23	3	150; 2 (CO)
G	5	3	170; 3 (CO)

Table 3.42: Substance specific emission factors (organic carbon and formaldehyde): Easy-care finishing agents based on dimethyloldihydroxyethen urea derivatives

	Organic-C [g/kg]	Formaldehyde [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
A	13	6	160; 1 (PES)
B	33	19	190; 1.5 (PES)
C	24	31	170; 1.5 (CO)
D	21	51	170; 3 (CO)
E	7	5	150; 3 (CO)
F	11	4	170; 3 (CO)

Table 3.43: Substance specific emission factors (organic carbon and formaldehyde): Easy-care finishing agents based on melamine derivatives

	Active ingredients	Organic-C [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
A	Fatty acid ethoxilate, hydrocarbons	112	190; 1.5 (PES)
B	Silicone	22	160; 2 (PES)
C	Hydrocarbons (80%)	573	170; 4 (CO)
D	Hydrocarbons	737	190; 1.5 (PES)

Table 3.44: Substance specific emission factors: Antifoaming agents

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Fatty alcohol ethoxilate	64	150; 2 (WO)
B	Fatty alcohol derivative	31	190; 1.5 (PES)
C	Tributylphosphate	239	170; 4 (CO)
D	Tributylphosphate	228	170; 4 (CO)
E	Tributylphosphate	335	190; 1.5 (PES)
F	Phosphoric acid esters	45	170; 4 (BW)
G	Fatty alcohol ethoxilate	81	190; 1.5 (PES)
H	Fatty alcohol ethoxilate	294	190; 1.5 (PES)
I	Alkylsulfonates	142	150; 1.5 (PES)

Table 3.45: Substance specific emission factors: Wetting agents

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Polysiloxane	19	170; 4 (CO)
B	Polysiloxane	10	170; 4 (CO)
C	Polysiloxane	3	170; 3 (CO)
D	Polysiloxane	17	160; 0.5 (CO)
E	Polysiloxane, polyethylene	0,6	170; 4 (CO)
F	Polysiloxan	17	170; 4 (CO)
G	Fatty acid derivative	1,9	170; 3 (CO)
H	Fatty acid derivative	4	170; 4 (CO)
I	Fatty acid derivative	5	170; 2 (CO)
K	Fatty acid derivative	2	170; 3 (CO)
L	Fatty acid derivative	1	170; 4 (CO)
M	Fatty acid derivative, waxes	38	180; 1.5 (PES)

Table 3.46: Substance specific emission factors: Softening agents

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Aromatic carboxylic acid derivative	357	150; 4 (PES)
B	Aromatic esters	219	190; 1 (PES)
C	Alkylphthalimide derivative	125	150; 4 (PES)
D	Biphenyl	220	150; 4 (PES)
E	o-phenylphenol	354	190; 1.5 (PES)

Table 3.47: Substance specific emission factors: Carriers

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Phosphonic acid derivative	124	190; 1.5 (PES)
B	Phosphonic acid derivative	37	100; 1 (PES)
C	Inorganic salts	2	170; 3 (CO)
D	Organic-P-compound	19; formaldehyde: 30 g/kg	160; 3.5(CO)
E	Organic P-compound	0,2; formaldehyde: 3,6 g/kg	120; 2 (CO)
F	Alkylphosphate	109	150; 2 (PES)
G	Inorganic/organic salts salts	12	110; 2 (PES)
H	Organic P-compound	24	175; 1 (PES)
I	N-and P-containing compound	0,2	150; 3 (CO)
K	Inorganic/organic salts	3	110; 2 (PES)
L	N-and P-containíng compound	30	190; 1.5 (PES)

Table 3.48: Substance specific emission factors: Flame retardants

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Fluorocarbon resin	43	190; 1.5 (PES)
B	Fluorocarbon resin	47 42	190; 1.5 (PES) 170; 4 (CO)
C	Fluorocarbon resin	23	150; 4 (CO)
D	Fluorocarbon resin	19 9	150; 3 (CO) 170; 3 (PES)
E	Fluorocarbon resin	22	150; 3 (PES)
F	Various fluorocarbon resins (same producer)	13; 15; 5; 7 22; 8; 13; 37	170; 4 (CO) 190; 1.5 (PES)
G	Paraffine, inorganic salt	43	120; 2 (CO)
H	Paraffine, Zr-salt	15	150; 4 (CO)
I	Paraffine	29	170; 3 (CO)
K	Polysiloxane	37	150; 3 (CO)
L	Polyurethane derivative	25	170; 3 (CO)
M	Melamine derivative	19; formaldehyde: 2 g/kg	140; 4 (CO)

Table 3.49: Substance specific emission factors: Repellents

	Active ingredients	Organic-C [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
A	Paraffine, polyethylene	75	190; 1.5 (PES)
B	Fatty acid ester	13	170; 4 (CO)
C	Wax	67	190; 1.5 (PS)
D	Paraffine	79	190; 1.5 (PES)
E	Wax	172	190; 1.5 (PES)
F	Fatty acid derivative	5	170; 1.5 (CO
G	Fatty acid derivative	2	140; 2 (CO)
H	Fatty acid derivative	3	190; 1.5 (PES)

Table 3.50: Substance specific emission factors: Conditioning agents

	Active ingredients	Organic-C [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
A	Diaminostilbene disulfonic acid	2	170: 3 (BW)
B	Pyrazoline derivative	32	190; 1.5 (PES)
C	Diaminostilbene disulfonic acid	3	170; 3 (BW)
D	Benzoxazol derivative	2	190; 1.5 (PES)
E	Distyrylbenzene derivative	18	190; 1.5 (PES)
F	Pyren and oxazol derivatives	22	190; 1.5 (PES)
G	Benzoxazol derivative	11	190; 1.5 (PES)

Table 3.51: Substance specific emission factors: Optical brighteners

	Active ingredients	Organic-C [g/kg]	Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate
A	Org. salt	72	150; 3 (PES)
B	Alkylphosphate	27	190; 1.5 (PES)
C	Polyglykolether	7	150; 3 (PES)
D	Org. P-compound	14	170; 1 (PES)
E	Quaternary ammonium compound	4	190; 1.5 (PES)
F	Alkylphosphate	5	190; 1.5 (PES)
G	Quaternary ammonium compound	24	190; 1.5 (PES)

Table 3.52: Substance specific emission factors: Anti-electrostatic agents

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Polyvinyl alcohol	3	170; 1.5 (CO)
B	Starch derivative	1	160; 4 (CO)
C	Polyacrylate	2	170; 1.5 (CO)

Table 3.53: Substance specific emission factors: Filling and stiffening agents

	Active ingredients	**Organic-C [g/kg]**	**Testing conditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Quaternary ammonia compound	3	170; 1.5 (CO)
B	Quaternary ammonia compound	3	170; 4(CO)
C	Quaternary ammonia compound	< 1	180; 1 (CO)

Table 3.54: Substance specific emission factors to air: Aftertreatment agents for fastness improvement

	Active ingredients	**Organic-C [g/kg]**	**Testconditions (Curing temperature [°C]; Curing time [min]); Substrate**
A	Heterocyclic ompounds	5	170; 4 (CO)
B	Aromatic compounds	47 241	170; 4 (CO) 190; 1.5 (PES)
C	Isothiazolinone	55	190; 1.5 (PES)
D	Isothiazolinone	46 302	170; 4 (CO) 190;1 (PES)

Table 3.55: Substance specific emission factors: Antimicrobiotics

	Active ingredients	Organic-C [g/kg]	Testconditions (Curing temperature [°C]; Curing time [min]); Substrate
A	Silicic acid	0.6 3.7	100; 0.5 (CO) 170; 3 (PES)
B	Silicic acid	1.3 2.8	170; 3 (CO) 170; 1.5 (PES)

Table 3.56: Substance specific emission factors to air: Non-slip, ladder-proof agents

3.5.4.2.2 Captured emissions to air

Emission data from 15 textile finishing mills measured by official order according to German regulations on exhaust air are compiled. Thereby, from each finishing mill different processes are considered.

3.5.4.2.2.1 Typical off-gas volumes, off-gas temperatures and air-textile ratios

Off-gas volumes and off-gas temperatures as well as air-textile ratios (specific air consumption for the treatment of 1 kg fabric) for stenter processes are summarised in Table 3.57. If an emission abatement system is installed the values for the clean-gas are given [EnviroTex, 2001].

Regarding the data in Table 3.57, an average air/textile of approx. 30 Nm^3/kg textile (extreme values > 100 Nm^3/kg textile and < 10 Nm^3/kg textile are not taken into consideration) can be assessed.

The off-gas has an average temperature of

- 373 °K (approx. 100 °C) (in cases where an emission abatement is not installed)
- 318 °K (approx. 45 °C) (in cases where an emission abatement is installed).

Textile company Process	**Stenter technology, emission abatement**	**Process**	**Textile Production [kg/h]**	**Off-gas volume [Nm³/h]**	**Off-gas temperature [°K]**	**Air/textile ratio [Nm³/kg]**
1.1	Direct heated	Heat setting	30 (very low specific weight)	4400	430	147
1.3	Direct heated	Finishing	222	4550	391	21
2.1	Indirect heated Thermo oil	Finishing	569	9780	411	17
2.4	Indirect heated Thermo oil	Finishing	583	11200	439	19
3.4	Direct heated Heat recovery	Heat setting prewashed textiles	1146	11800	351	24
3.5	Direct heated Heat recovery, electrostatic filtration	Heat setting	1146	13700	322	12
4.3	Direct heated	Finishing	588	9280	358	16
4.4	Indirect heated	Finishing	658	9280	358	14
5.1	Indirect heated	Finishing	337	15200	348	45
5.4	Indirect heated	Finishing	308	15200	348	49
6.1	Indirect heated Heat recovery	Finishing	1166	10200	314	9
6.2	Indirect heated Heat recovery	Finishing	451	4440	348	10
7.1	Direct heated Aqueous scrubber	Coating	408	8560	313	21
8.1	Direct heated Aqueous scrubber	Finishing	513	11800	313	23
8.2	Direct heated Aqueous scrubber	Finishing	628	12000	314	19

Textile company Process	**Stenter technology, emission abatement**	**Process**	**Textile Production [kg/h]**	**Off-gas volume [Nm³/h]**	**Off-gas temperature [°K]**	**Air/textile ratio [Nm³/kg]**
8.3	Direct heated Aqueous scrubber	Coating	586	11800	311	20
9.2	Indirect heated	Finishing	199	1370	346	7
9.3	Indirect heated	Finishing	322	5930	320	18
10.2	Direct heated Aqueous scrubber	Heat setting	289	11200	310	39
10.4	Direct heated Aqueous scrubber	Heat setting	412	14900	310	36
11.4	Direct heated Aqueous scrubber electrofiltration	Heat setting	546	20800	319	38
11.5	Direct heated Aqueous scrubber electrofiltration	Finishing	312	20800	319	67
12.1	Direct heated	Finishing	422	9030	393	21
12.2	Direct heated	Finishing	397	9030	393	23
13.1	Direct heated Condensation, electrofiltration	Heat setting	259	23000	290	89
13.3	Direct heated Condensation Electrofiltration	Heat setting	213	23000	290	108
14.2	Direct heated	Finishing	505	13200	370	26
14.4	Direct heated	Finishing	352	12900	370	37

Textile company Process	**Stenter technology, emission abatement**	**Process**	**Textile Production [kg/h]**	**Off-gas volume [Nm³/h]**	**Off-gas temperature [°K]**	**Air/textile ratio [Nm³/kg]**
15.1 (data from raw gas are regarded)	Direct heated Aqueous scrubber	Heat setting	907	10600	311	12

Table 3.57: Off-gas volume, off-gas temperature and air/textile ratio (measured values)

3.5.4.2.2.2 Typical emission values (mass concentrations and emission factors)

Process specific emission values (off-gas mass concentrations, emission factors, and mass flows) for the 15 above mentioned textile finishing plants (Table 3.57) are compiled in Table 3.58 [EnviroTex, 2001]. If emission abatement systems are installed, all values shown in Table 3.58 concern clean-gas. In case of direct heated stenters, Organic-C contribution of fuel (methane, propane, butane; Chapter 3.5.4.2.2.3) is mentioned separately and is not considered in the data concerning the Organic-C values (emission factor, mass-flow, and concentration).

The following processes resp. recipes are considered (in some cases, a combination of finishing effects is achieved in one single process using a combination of different auxiliaries):

- Heat setting of grey and pre-washed textiles
- Softening
- Easy-care finishing
- Antistatic finishing
- Optical brightening
- Hydrophobic finishing
- Stiffening
- Coating
- Non-slip finishing

It is to be seen that

- Heat setting of grey textiles causes a considerable off-gas load. If heat setting of PA 6 is carried out considerable amounts of caprolactam are emitted (processes 1.1 and 13.3).
- In case of textiles which contains low-emission preparation agents significant lower emissions can be regarded (textile finishing plant 15).
- Thermal treatment of textiles on stenters can be influenced from upstream finishing processes (dyeing carriers in process 4.4 and perchlorethylene treatment in process 12.1 and 12.2).
- With exception to heat setting processes (if conventional preparation agents are considered) an emission factor of 0.8 g Organic-C per kg textile can be achieved in nearly all processes in textile finishing (but it has to be kept in mind that in Table 3.58 in cases where emission abatement systems are installed emission values for the clean-gas are given).
- Organic-C emissions caused by unburned fuel are in a range of 0.1 g/kg textile to > 5 g/kg textile in case of poorly maintained burners
- Formaldehyde emissions are caused by the auxiliaries resp. their reaction products and by machine based emissions (see also Chapter 3.5.4.2.2.3).

Textile company, Process	**Stenter technology Emission abatement**	**Recipe**	**Substrate**	**Process temperature [°C]**	**Emission factor [g Org.C/kg textile]**	**Concentration [mg Org.-C/Nm³]**	**Mass-flow [g Org-C/h]**	**Machine based emission [g Org.-C/kg textile]**	**Remarks**
1.1	Direct heated	Heat setting grey fabric	PA 6	185	12	82	359	5.4	4.3 g/kg Caprolactam
1.2	Direct heated	Crosslinking agents), deaeration, non-slip)	PA 6	150	3.5	21	101	7.7	1.5 g/kg formaldehyde
1.3	Direct heated	Antistatic, softening	PA 6.6	150	0.7	33	148	0.1	
2.1	Indirect heated	Easy-care, softening, acetic acid	CO/EL	170	0.9	52	506	-	0.02 g/kg formaldehyde
3.1	Direct heated Heat recovery	Flame retardant	CO	145	0.3	19	155	0.2	0.01 g/kg formaldehyde
3.2	Direct heated Heat recovery	Optical brightener, antistatic	PES	190	0.6	24	277	0.5	
3.3	Direct heated Heat recovery, electrofiltration	Heat setting grey textiles	PES/PAC	180	0.7	92	1260	0.1	
3.4	Direct heated Heat recovery, electrofiltration	Heat setting pre-washed textiles	PES/PAC	180	0.9	77	1055	0.2	
4.1	Indirect heated	Softening	PES/WO	130	0.6	187	529	-	0.05 g/kg formaldehyde
4.2	Indirect heated	Non-slip	PES/WO	130	0.3	15	188	-	0.01 g/kg formaldehyde
4.3	Direct heated	Heat setting	PES/WO/EL	165	0.2	14	130	1.6	0.08 g/kg formaldehyde
4.4	Direct heated	Heat setting (carrier dyed fabric)	PES/WO/EL	165	6.5	460	4269	1.4	0.08 g/kg formaldehyde
5.1	Direct heated	Stiffening, softening	PES	170	0.4	9	123	0.2	0.03 g/kg formaldehyde
5.2	Direct heated	Softening	PES	170	0.5	10	149	0.2	0.04 g/kg formaldehyde
6.1	Direct heated Heat recovery	Coating (polyvinyl acetate)	CV/PP	110	0.6	68	689	1.4	0.06 g/kg formaldehyde

Textile company, Process	**Stenter technology Emission abatement**	**Recipe**	**Substrate**	**Process temperature [°C]**	**Emission factor** [g Org.C/kg textile]	**Concentration** [mg Org.-C/Nm^3]	**Mass-flow** [g Org-C/h]	**Machine based emission** [g Org.-C/kg textile]	**Remarks**
6.2	Indirect heated Heat recovery	Coating (polyvinyl acetate), softening, thickener, acetic acid	CV/CO	120	0.08	8	36	-	
7.1	Direct heated Aqueous scrubber	Coating /acrylate, crosslinking agent,foaming agent	CV	150	0.35	16	142	0.1	0.14 g/kg formaldehyde
8.1	Direct heated Aqueous scrubber	Wetting agent, stain release	CV/CO/ PES/WO	165	0.5	22	255	0.4	
8.2	Direct heated Aqueous scrubber	Softening, foaming agent	PES/CV/ CO	150	0.3	17	200	0.3	
8.3	Direct heated Aqueous scrubber	PU-coating	PES/CO	130	0.2	10	121	0.1	
9.1	Indirect heated	Easy-care, softening, wetting agent, acetic acid	CO/EL	150	0.2	43	56	-	0.03 g/kg formaldehyde
9.2	Indirect heated	Easy-care, softening, wetting agent, acetic acid, stiffening, hydrophobic	CO/CV/ EL	150	0.3	53	69	-	0.05 g/kg formaldehyde
10.1	Direct heated Aqueous scrubber	Drying after dyeing	PA/EL	135	0.4	12	138	0.1	
10.2	Direct heated Aqueous scrubber	Heat setting	PA 6.6/EL	190	1.5	38	427	0.1	
10.3	Direct heated Aqueous scrubber	Heat setting pre-washed textiles	PA 6/EL	190	2.2	84	945	0.2	
10.4	Direct heated Aqueous scrubber	Heat setting	PA/EL	190	2.6	71	1052	1.4	
11.1	Direct heated Aqueous scrubber, electrofiltration	Heat setting	PES	150	1.2	24	507	0.5	

Textile company, Process	Stenter technology Emission abatement	Recipe	Substrate	Process temperature [°C]	Emission factor [g Org.C/kg textile]	Concentration [mg Org.-C/Nm^3]	Mass-flow [g Org-C/h]	Machine based emission [g Org.-C/kg textile]	Remarks
11.2	Direct heated Aqueous scrubber, electrofiltration	Heat setting pre-washed textile	PES	150	0.8	19	394	0.4	
12.1	Direct heated	Wool protecting (polyurethane, polyacrylate) wetting agent	PES/WO/EL	190	1.3	60	542	0.3	0.7 g/kg perchlorethylene
12.2	Direct heated	Hydrophobic, wetting agent, acetic acid	PES/WO/EL	190	0.9	41	370	0.4	0.8 g/kg perchlorethylene
13.1	Direct heated Condensation, electrofiltration	Heat setting	PES	205	3.2	36	820	1.2	
13.2	Direct heated Condensation, electrofiltration	Heat setting	PES/PAC	180	2.2	59	1350	0.5	
13.3	Direct heated Condensation, elctrofiltration	Heat setting	PA 6	185	1.9	18	410	0.5	0.7 g/kg Caprolactam
14.1	Direct heated	Heat setting	CO/PES	200	1.1	95	697	0.1	
14.2	Direct heated	Hydrophobic	PAC/PES	180	0.5	18	238	1.3	
14.3	Direct heated	Softening	CO/PES	160	0.5	34	439	0.7	
14.4	Direct heated	Anti-slip	PAC	160	0.7	19	245	1.8	
14.5	Direct heated-	Easy-care	CO/PS	170	1,5	50	764	0,6	0.06 g/kg formaldehyde
15.1	Direct heated, aqueous scrubber	Heat setting	PES	190	0.8	65	689	0.2	Raw-gas data considered
15.2	Direct heated Aqueous scrubber	Heat setting	PES/CO	90	0.6	39	421	0..2	Raw-gas data considered

Table 3.58: Process specific emission data (measured values)

3.5.4.2.2.3 Stenters; Machine based emissions

Direct heated stenters themselves produce relevant emissions. The emissions are caused by a more or less partially burning out of the gas (methane, propane, butane). Besides components of combustion gases, such as carbon monoxide and nitrogen oxides, considerable amounts of Organic-C and formaldehyde can be observed (Table 3.59) [EnviroTex, 1998a]. Data from 28 textile finishing mills (at each plant one or more processes (in total: 100 processes) are collected.

Substance/parameter	Concentration [mg/Nm³]
Methane (as Organic-C)	5-500
Propane/butane (as Organic-C)	5-600
Formaldehyde	0.1-60
Carbon monoxide	5-400
NO_x	2-10

Table 3.59: Typical ranges for machine based emissions

Especially in case of formaldehyde-free recipes machine based formaldehyde emissions can be of crucial interest if compliance to limit values concerning consumer safety is essential.

3.5.5 Carry over of emissions from up-stream processes to drying and fixation

Textile auxiliaries and chemicals (resp. their by-products and impurities) with a certain affinity to the fibres can be fixed temporarily on the textile esp. if washing/rinsing is carried out in an insufficient way. In down-stream drying and heatsetting/finishing these substances can be released from the textiles and load the off-gas. Typical substance classes to be regarded from this point of view are:

- Carriers
- Levelling agents
- Aftertreatment agents
- Wetting agents
- Hydrocarbons ex printing pastes
- Acetic acid
- Perchlorethylene (if dry-cleaning is carried out)
- Conditioning agents.

Data on emission potential of carrier-dyed fabrics and dry-cleaned fabrics are given below.

3.5.5.1 Emission potential of carrier- dyed fabrics

Carriers are mainly used for dyeing of PES and PES blends. As mentioned above drying and fixation of carrier-dyed fabrics can lead to considerable air-emissions, due to the fact that part of the carrier (in some cases to 50% and more) is absorbed on the fabric and emit during downstream heat treatment.
The degree of carrier exhaustion mainly depends on

- liquor ratio
- absolute quantity of carrier used
- dyeing process (esp. time/temperature characteristic)
- textile substrate
- processing conditions during rinsing.

Emission potential of carrier-dyed fabrics are summarised in Table 3.60.

Data are based on carrier-dyed but not dried fabrics (industrial scale); drying of the fabrics (150 °C) and air-emission measurement was carried out on a laboratory stenter.

Carrier active components	**Emission factor [g C/kg textile]**
Benzyl benzoate; Phthalic acid ester	9
Biphenyl; Dimethyl phthalate	8
Alkylphthalimide	6

Table 3.60: Characteristic data on air-emission of carrier dyed textiles - [EnviroTex, 2000a]

Table 3.61 shows a representative selection of air-emission values of 4 textile mills during drying/fixation of carrier dyed fabrics.

Textile company	**Emission abatement efficiency [%]**	**Carrier chemistry**	**Emission factor** **[g Org.-C/kg textile]**	**Concentration** **[mg Org.-C/Nm³]**	**Mass-flow** **[kg Organic-C/h]**
1 Fabric A	15	Aromatic solvents	24	2000-4500	28
Fabric B	25	Aromatic solvents	7.6	200-1000	8
2 Fabric A	Not installed	Phthalimide Dimethyl phthalate	0.77	66	0.4
Fabric B	Not installed	Biphenyl, Dimethyl phthalate	1.2	84	1.1
3 Fabric A	30-40	Benzoate, Phthalate	0.8-0.9	22-25	0.2
Fabric B	10-25	Benzoate Phthalate	2.0-2.2	50-60	0.6
4	Not installed	Benzoic acid ester, Aromatic compounds	6.5	400	4.3

Table 3.61: Air emission values during drying/fixation of carrier dyed fabrics - [EnviroTex, 2000a]

It is clearly to be seen that - especially if carriers based on aromatic solvents are used – the active compounds of carrier formulations can lead to a considerable off-gas load during drying and heat setting. Efficiency of emission abatement systems can be insufficient (10 to 40% (comparison of Organic-C-concentration in raw- and clean-gas) in case of cleaning carrier loaded off-gas streams.

3.5.5.2 Emission potential of dry-cleaned fabrics

The retentivity of perchloroethylene (mainly used solvent in dry-cleaning) on textiles is high; in downstream thermal processes (esp. drying) perchloroethylene can be released to the off-gas.

Due to a potential risk of PCDD/PCDF formation by drying/fixation of perchloroethylene-cleaned fabrics there exists a processing ban for treating perchloroethylene-cleaned fabrics on direct heated stenters in Germany.

Dry-cleaning is used in Germany for the following purpose:

- cleaning of grey textiles (esp. elastane blends (conventional washing processes are insufficient in case of silicone preparations mainly used for elastane fibres))

- aftertreatment for wool/elastane or wool/PES fabrics to achieve improved colour fastness esp. for dark shades
- quality corrections (removal of spots).

Besides the intentional use of perchlorethylene a considerable amount of dry-cleaned fabrics is finished in Germany due to the fact that imported goods are often dry-cleaned.
Dry-cleaning is normally carried out by the textile finisher itself, in some cases (esp. for quality corrections of small lots) external dry-cleaning companies doe the job.

Table 3.62 summarizes emission measurements of different perchloroethylene-cleaned fabrics. For each textile finishing mill (5 finishing mills have been regarded) several textiles are investigated. Emission potential of the fabrics have been investigated on a laboratory stenter (process temp. 150 °C) [EnviroTex, 1998b].

Ranges of air-emission values for perchloroethylene-cleaned fabrics during drying/fixation are

0.1 – 0.8 g perchloroethylene/kg textile	dry-cleaning on-site at finishing plant
0.3 – 1.7 g perchloroethylene/kg textile	external dry-cleaning.

Textile company,	**Emission factor [g Org. C/kg textile]**	**Concentration [mg Org. C/Nm^3]**	**Mass flow [g Org. C/h]**	**Emission factor [g PER/kg textile]**
1.1*	0.11	28.1	3.77	0.27
1.2*	0.23	32.6	4.28	1.17
2.1*	0.19	16.1	1.88	0.95
2.2*	0.26	21.7	2.71	0.66
2.3*	0.14	11.7	1.68	0.63
2.4*	0.13	6.1	0.82	0.47
2.5*	0.85	70.8	9.27	1.65
2.6**	0.29	21.1	2.59	0.67
2.7**	0.11	8.0	0.99	0.51
3.1**	0.27	19.3	2.37	0.09
3.2**	0.18	12.9	1.58	0.19
3.3**	0.30	20.1	2.47	0.13
4.1**	1.23	94.9	11.95	0.79
4.2**	0.86	65.9	8.11	0.65
4.3**	0.80	53.1	6.53	0.54
5.1**	0.09	6.6	0.80	0.46
5.2**	0.12	4.0	0.50	0.67
5.3**	0.15	6.4	0.81	0.82

Table 3.62: Emission values for perchloroethylene-cleaned fabrics
*** External dry-cleaning**
**** On-site dry-cleaning at finishing plant**

3.5.6 Singeing

In singeing the fabrics passes normally directly over a flame. Protruding fibres are burned off.
The simplified principle of singeing machines is shown in Figure 3.20.

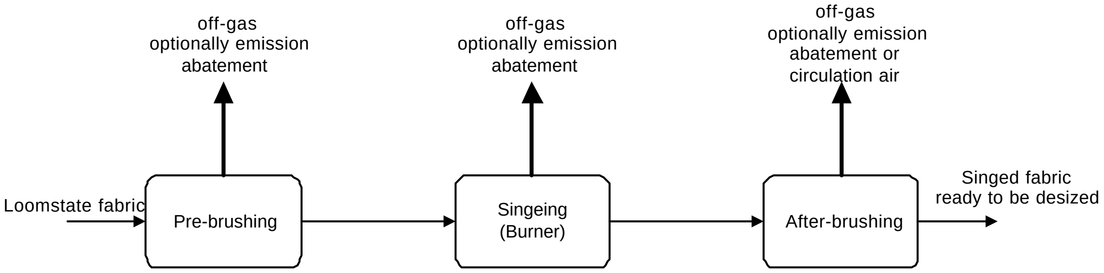


Figure 3.20: Simplified principle of singeing equipment

Quality and quantity of air emissions in singeing depend strongly on the

- kind of substrate to be treated
- position of burners (angle and distance to the textile; one-sided or double-sided singeing)
- kind of emission abatement installed

Main air emissions are

- dust from the fibres burned-off
- Organic-C from volatile substances on the substrate and/or crack-products and methane ex incompletely combustion of burner gases
- Formaldehyde ex burner gases.

The emission levels are summarised in Table 3.63. Five textile finishing industries are regarded [EnviroTex, 2001; Bautzen, 2001].

If an aqueous scrubber is used for emission abatement in the after-brushing compartment dust emissions < 0.1 mg/m³ can be achieved, however concentrations up to 6 mg/Nm³ can also be detected. Organic-C concentrations caused by the process itself (methane emission not considered) diverge in a wide range (from 1 to 26 mg C/Nm³). Formaldehyde emission is in a range of 1 to 3 mg substance/Nm³ (burner compartments).

It is to be mentioned that singeing can be a very odour intensive process. An odour value of 6000 OU/kg textile could be measured for an installation singeing cotton without emission abatement [EnviroTex, 1998c].

Textile company	Sampling point	Installed emission abatement	Substrate	Concentration Organic-C [mg C/Nm³]	Concentration Organic-C methane not considered [mg C/Nm³]	Concentration formaldehyde [mg HCHO/Nm³]	Dust [mg/Nm³]	Air flow [Nm³/h]	Off-gas temp. [°C]	Process velocity [m/min]
A	Pre-brushing + burner compartment	Pre-brushing + burner: aqueous scrubber; after-brushing: circulating air, fabric filter	CO	99	22	not measured	1.8-3.7	5900	28	60-100
B	Pre-brushing + burner compartment	Pre-brushing + burner: Aqueous scrubber after-brushing: aqueous scrubber	PES/CO	82	< 1	not measured	0.3-0.4	3800	34	120
B	After-brushing compartment	Pre-brushing + burner: Aqueous scrubber after-brushing: aqueous scrubber	PES/CO	not measured	not measured	not measured	0.1	5670	24	120
C	Pre-brushing + burner compartment	Pre-brushing + burner: Aqueous scrubber; after-brushing: circulating air, fabric filter	CO	74	not measured	not measured	6.2	8200	32	100-120
D (process 1)	Burner compartment	After-brushing: aqueous scrubber	CO	not measured	not measured	0.9	< 0.1	4410	83	2160 kg textile/h
D (process 2)	Burner compartment	After-brushing: aqeous scrubber	PES/CO	not measured	not measured	1.9	< 0.1	4410	83	1620 kg textile/h
D (process 2)	After-brushing compartment	After-brushing: aqeous scrubber	PES/CO	not measured	not measured	not measured	< 0.1	1090	27	1620 kg textile/h
E	Burner compartment	After-Brushing: aqueous scrubber	PES/EL	42.4	26.3	3.2	not measured	3190	118	60 1746 kg/h
E	After-brushing compartment	After-Brushing: aqueous scrubber	PES/EL	not measured	not measured-	not measured	6.6	2760	27	60 1746 kg/h

Table 3.63: Data on emission to air from singeing facilities of five different TFI

3.5.7 Printing

Data on typical compositions of printing pastes and consumption data in printing are mentioned above (Chapter 3.3.2.3).

Drying and fixation in printing are not subject of regulations concerning exhaust air in Germany. But it is well-known that printing pastes contain substances with a high emission potential Especially the following substances are of interest when a heat treatment is carried out on printed goods [EnviroTex, 2000b]:

- Ammonia (ex urea)
- Methanol (ex fixation agents)
- formaldehyde (ex fixation agents)
- aliphatic hydrocarbons (C_{10}-C_{20}) (ex binders)
- alcohols, glycoles (ex emulsifiers)
- N-Methylpyrrolidon (ex emulsifiers)
- monomers as acrylates, acrylonitrile, acrylamide, 1,3-butadiene, vinylcyclohexene, phenylcyclohexene (ex thickener, binder).

Emission of the volatile compounds of printing pastes can occur during drying (printing mansardes) and fixation of the printed textiles. Additionally a carry-over of these substances to downstream finishing processes is possible. White spirit pigment printing with its very high emissions to air due to hydrocarbons used as solvent is not carried out in Germany.

Due to the fact, that emission measurements at printing installations are not regulated by the German authorities, only a few data exist.

However in a study made for Austrian authorities it could be clearly demonstrated that emissions caused by drying and fixation of printed goods exceeds emissions for the top-finishing [EnviroTex, 1997]:

- emissions caused by pigment printing in Austria:	approx. 90 t organics/year
- emissions caued by top-finishing processes in Austria:	approx. 55 t organics/year.

Also by emission measurements in Germany, significant excess of limit values in those cases where printed fabrics are finished and heat treated could be observed. [UMEG,1997]. In Table 3.64, emission data are compiled. For textile finishing mill A emission measurement was carried out on-site. In case of company B printing, drying and fixation was carried out at the finishing mill. Carry-over of emission relevant products to downstream finishing was measured at a laboratory stenter. It is clearly to be seen that heat treatment of printed goods is related to considerable off-gas loads. Carry-over of volatile substances into downstream processes (often a finishing step is carried out after printing) has to be taken into consideration.

Company	Printing process	Processing step	Substrate	Process temperature [°C]; Curing time [min]	Emission factor [g C/kg textile]
A	Vat-discharge printing on direct dyed grounds	Drying	CV		0.3
		Steaming	CV	102; 13	1.0
	Vat two phase printing	Drying			0.6
		Fixation		135; 1	1.3
	Disperse printing	Drying	PES		1.3
		Fixation	PES	175; 5	0.01
	Pigment printing	Drying	CO	150	0.2
		Condensation	CO	160; 5	0.1
B	Pigment printing, simulation pilot stenter	Finishing	CO	175; 1.5	0.6

Table 3.64: Emission measurements from printing processes - [EnviroTex, 1998; EnviroTex, 2001]

3.5.8 Coating

Coating agents and auxiliaries used in coating of textiles with a closer look on their emission potential are described in Chapter 3.5.8.1. Examples for emission values caused by coating processes are given in Chapter 3.5.8.2.

Backcoating in carpet industry is decribed elsewhere in a special BREF [TFI, 2001]. Therefore only emission data compiled at three companies are given in chapter 3.5.8.2.

3.5.8.1 Coating compounds and auxiliaries

Coating agents are chemically characterized as

- **coating powders** as polyolefines (esp. polyethylene), polyamide 6, polyamide 6.6, copolyamides, polyester, polyurethane, polyvinyl chloride, polytetrafluoroethene.

- **coating pastes** on the above mentioned chemical basis with additives: as dispersing agents (surfactants (often: alkylphenolethoxylates), solubilizing agents (glycols, N-methylpyrrolidone, hydrocarbons), foaming agents (mineral oils, fatty acids, fatty acid ammonia salts), softeners (esp. phthalates, sulfon amides), thickeners (polyacrylates), ammonia.

- **polymer dispersions** (approx. 50% in water) on basis of poly-
  - (meth)acrylate (butyl, ethyl, methyl etc.)
  - acrylic acid
  - acrylonitrile
  - acryloamide
  - 1,3-butadien
  - styrene
  - urethane
  - vinylchloride
  - vinylacetate
  - and copolymers of the above mentioned compounds
  - and additives like in coating pastes.

- formulations of melamin resins in water (50 - 70%).
- solvent containing polymer formulations on basis of polyurethane and silicones.

Coating powders

Emission potential of the coating powders are in most cases negligible (with exception to polyamide 6 and copolymers of polyamide 6 (epsilon-caprolactam is released at usual process temperatures). In some cases softeners (often phthalates) can be released.

Coating pastes

The emissions from the coating pastes result dominantly (except PA 6; see above) from the additives. These are mainly

- fatty alcohols, fatty acids, fatty amines ex surfactants
- glycoles, oligooles ex emulsifiers
- alkylphenoles ex dispersants
- glycoles, aliphatic hydrocarbons, N-methylpyrrolidone ex hydrotropic agents
- aliphatic hydrocarbons, fatty acids/salts, ammonia ex foaming agents
- phthalates, sulfonamides/esters ex softeners/plasticisers
- acrylic acid, acrylates, ammonia, aliphatic hydrocarbons ex thickeners

Polymer dispersions

The emission potential of polymer dispersions is quite lower than for the coating pastes. Especially the dispersing agents have to be regarded concerning emissions to air. Additionally there are residual components from the polymerisation (esp. t-butanol ex catatalyst in radically initialized polymerisation reactions) to be taken into account.

However emission of monomers, which arise from the uncomplete reaction during polymerisation have to be taken into account especially concerning working place atmosphere and odour nuisances:

- acrylic acid, butylacrylate, ethylacrylate, methylacrylate, ethylhexylacrylate and vinylacetate.
- cancerogenic monomers like acrylonitrile, vinylchloride, acrylamide, 1,3-butadien and vinylcyclohexene.

It is to be mentioned that often vinylcyclohexene is not identified. However it is always existing if 1,3-butadien is used (2 + 2 cycloaddition-product).

Acrylamide emissions are often related to formaldehyde emissions (reaction products of methylolacrylamide).

Melamin resins

Melamin resins are widely spread. Melamin resins are produced by reaction of melamin and formaldehyde and following etherification with (mostly) methanole in aqueous medium. The products can contain considerable amounts of free formaldehyde and methanol. During the application the crosslinking reaction of the resin with itself or with the fabric (e.g. cotton) is initiated by acid catalysts and/or temperature. Hereby stoichiometric amounts of methanol and formaldehyde are released.

Polymers in solvents

Solvent coating is not wide-spread in textile finishing industry. This technique involves automatically an exhaust air cleaning equipment based on thermal incineration or adsorption on active carbon.

3.5.8.2 Emissions to air

Process specific emissions values for coating processes (including one laminating processes) collected at 4 textile finishing plants are compiled in Table 3.65 [EnviroTex, 2001]. However it has to be taken into account that due to the fact that in coating processes unique recipes are applied in most cases the emission situation regarding kind and amount of emitted substances can vary in a great range. Therefore, the examples in Table 3.65 can give only a first insight on the topic. In Table 3.66 emission data from carpet backcoating collected at three plants are compiled [LfU, 2002].

Textile company	**Drying apparatus technology Emission abatement**	**Recipe**	**Substrate**	**Process temperature [°C]**	**Emission factor [g Org.C/kg textile]**	**Concen-tration [mg Org.-C/Nm^3]**	**Mass-flow [g Org-C/h]**	**Machine based emission [g Org.-C/kg textile]**	**Remarks**
1	Direct heated Aqueous scrubber	Coating agent (acrylate dispersion) Fixation agent (melamine) Foaming agent Thickener (acrylate based)	CV (non-woven)	150	0.4	20	173	0.1	Formaldehyde 0.14 g/kg
2	Indirect heated	Laminating PVC adhesive (PVC-powder, softener, stabiliator, primer, emulsifier)	PVC-foil on knitted goods	105	-	82	144	23 g C/h	Phthalates 6 mg/Nm^3; Vinylacetate 12 mg/Nm^3
3	Direct heated	Flame laminating	PU-foam on PA substrate	-	-	74	232	798 g C/h	HCN 3.6 mg/Nm^3 TDI 0.5 mg/Nm^3
4	Direct heated	Acrylate dispersion with additives (thickener, ammonia, catalyst)	CO	150	0.4	-	138	1.9	Ammonia 0.02 g/kg

Table 3.65: Process-specific emission data in coating processes

Textile company	**Stenter technology**	**Recipe**	**Substrate**	**Process temperature [°C]**	**Emission factor WFc [g C/kg textile]**[1]	**Massflow [kg C/h]**	**WFs [g/kg textile]**	**Massflow m [g/h]**
1[2]	Indirect heated main stenter; direct heated pre-stenter	Coating with a latex	WO/PP	130	0.55	0.6	FO: 0.005 BU: 0.001 VCH: 0.001 ST: 0.005 ET: 0.0002	FO: 4.8 BU: 1.3 VCH: 1.1 ST: 5.7 ET: 0.2
	Indirect heated main stenter; direct heated pre-stenter	Coating with a latex	WO/PP	130	0.3	0.3		
2	-	Coating with polypropylene	PP		0.09	0.06	BU: <0.01	BU : <1
	-	Coating with polypropylene	PA 6.6/PES		0.03	0.05	VA : <0.01	VA : < 1
3[2]	Direct heated main stenter and prestenter	Coating with a latex	PA 6 (PA 6.6)/PP	120	0.74	1.3	FO: 0.06 NH_3: 0.05 – 0.23	FO: 32 NH_3: 31 - 132
	Direct heated main stenter and prestenter	Coating with a latex	PA 6	130	0.86	0.46	FO: 0.06 CL: 0.001 NH_3: 0.07 – 0.49	FO: 32 CL: 0.99 NH_3: 36 - 247

1) emission values relating to the process;contribution of unburnt fuel is not considered

2) total emissions of pre- and main stenter

2) FO = Formaldehyde; BU = 1,3-Butadiene; VCH = 4-Vinyl-1-Cyclohexene; ST = Styrene; EA = Ethyl acrylate; VA = Vinylacetat; CL = Caprolactam

Table 3.66: Process-specific emission data from carpet backcoating

3.5.9 Boiler houses

Emissions of boiler houses are not scope of the Textile BREF. Nevertheless to rank process specific emissions it is of great interest to have data on energy generating in textile industry. Therefore, characteristic emission values, collected at eight textile finishing plants each with one or more boilers are summarized in Table 3.67 [EnviroTex, 2001].

Mainly used primary energy source in boiler houses in German textile finishing industry is methane. Often the burners work with natural gas and (due to a high general demand on natural gas in winter time) partially with fuel oil.

Besides natural gas and fuel oil the following primary energy sources are used:

- Hard coal
- Lignite
- Heavy fuel oil
- Recycling oil.

Boiler-House	**Fuel**	**Max. capacity [MW]**	**Capacity during measurement [MW]**	**Fuel consumption** **Natural gas [m^3/h]** **Fuel oil [kg/h]**	**Off-gas temperature [°K]**	**Off-gas volume stream [Nm^3/h]**	**CO [mg/Nm^3]**	**NOx [mg/Nm^3]**	**Dust [mg/Nm^3]**	**SO_2 [mg/Nm^3]**
1 A	Natural gas	3.8	1.9	187	502	2547	25	100	-	-
1 B	Fuel oil	3.8	1.9	155	441	2177	36	187	-	-
2 A	Natural gas	7.1	3.4	324	495	5519	43	127	-	-
2 B	Fuel oil	6.2	3.2	273	483	4512	30	173	-	-
3 A	Natural gas	2.4	1.6	156	473	2263	30	135	-	-
3 B	Fuel oil	5.4	3.5	296	500	3902	37	127	-	-
4 A	Natural gas	16.4	10.8	1045	405	16739	49	69	-	-
4 B	Fuel oil	17.5	13.2	1109	415	16827	44	129	-	-
5	Natural gas	5.8	4.8	459	409	5611	31	79	-	-
6	Natural gas	5.5	1.9	96	415	2453	28	67	-	-
7	Hard coal (off-gas cleaning: electrostatic filtration)	21.3	21.3	2500 kg/h	441	22500	30	328	8.8	399
8	Heavy fuel oil (off-gas cleaning: selective non catalytic reduction)	6.3	6.3	450	402	7860	28	428	84	-

Table 3.67: Typical emission values for boiler houses installed in German textile finishing industries; concentration data are based on a standardized O_2 content of 3 vol% Mentioned fuel consumption and concentrations refer to the capacity during measurement

3.5.10 Odour nuisances in textile industry

Textile finishing processes are often accompanied by odour emissions. Smell intensive substances are summarised in Table 3.68.

Data on odour concentrations collected at 16 finishing plants which have all problems concerning complaints on odour nuisances are summarized in Table 3.69 [EnviroTex, 2001]:

Substance	**Possible source**
Epsilon-caprolactam	Heat setting of polyamide 6 and polyamide 6 blends; Paste and powder coating with PA 6 and PA 6-copolymers
Paraffines, fatty alcohols, fatty acids, fatty acid esters (less odour intensive substances, but high concentrations)	Heat setting of grey textiles and inefficiently pre-washed textiles
Hydrocarbons	Printing, wetting agents, machine cleaner
Aromatic compounds	Carriers
Acetic acid, formic acid	Various processes
Hydrogen sulfide, mercapantes	Sulfur dyeing
Sulfur derivatives	Reducing agents
Ammonia	Printing (ex urea), coating, non-woven processing
Acrylates	Printing (ex thickening agents), coating, non-woven processing
Formaldehyde	Easy-care finishing , finishing of non-wovens, permanent flame retardants
Terpene (d-limonene)	Solvents, machine cleaners
Styrol	Styrol polymers and copolymers
Vinylcyclohexene	Butadiene polymers and coploymers
Aldehydes	Singeing
Acroleine	Decomposition of glycerol
Phosphoric acid esters (esp. tributylphosphate)	Wetting agents, deaeration agents
Phthalates	Levelling and dispersing agents
Amines (low molecular)	Various processes
Alcohols (octanol, butanol)	Wetting agents, antifoaming agents

Table 3.68: Smell intensive substances in textile finishing

Substrate/Process	**Range of odour concentration [OU/m³]**	**Average odour concentration [OU/m³]**
PA 6 Heat setting grey fabric	2000-4500	2500
PA 6 Finishing of heatsetted and pre-washed fabrics	500-2000	1100
PES Heat setting grey fabric	1500-2500	2000
PES Finishing of heatsetted and pre-washed fabrics	500-1500	800
CO Finishing	300-1000	500

Substrate/Process	Range of odour concentration [OU/m³]	Average odour concentration [OU/m³]
Fibre blends Heat setting	1000-2500	1500
Fibre blends Finishing of heat setted and pre-washed fabrics	500-2000	1200
Sulfur dyeing		Up to 10000
Singeing		Up to 2500
Non-wovens (monomer containing binders)		Up to 10000
Printing (mansardes) Pigment (CO) Vat-2-phase (CV) Disperse (PES) Vat discharge (CO)	Data collected at one finishing mill [EnviroTex, 1998c]	 300 600 50 300
Printing (steamer) Pigment (CO) Disperse (PES Vat 2-phase (CO)	Data collected at one finishing mill [EnviroTex, 1998c]	 700 600 6003

Table 3.69: Typical examples for odour concentrations in textile finishing
(OU: odour unit)

Odour mass flows can be estimated on the basis of the data compiled in Table 3.69 assuming an average air flow in the stenters of 10000 m³/h.

3.5.11 Characteristic of waste gas emissions (on site level)

As mentioned above, organic-C-loads in textile finishing is caused by the textile raw materials, the auxiliaries and chemicals used but also by machine based emissions in case of direct heated stenters. Process specific emission data are shown previously. Emission data from an on-site point of view considering the total emissions from textile finishing plants with exception to boiler houses are given in the following examples [EnviroTex 2001].

It is to be noted that emissions due to textile raw materials are calculated on basis of data from yarn and fabric manufacturers (if available) or estimated. Emissions from auxiliaries/chemicals are calculated by hand of consumption data and emission factors. Emission of stenters is calculated if data from emission measurements had been available or estimated.

3.5.11.1 Example 1

The TFI as example 1 can be characterised as follows:

- Mainly man-made fibres (esp. PA 6) are produced
- To a considerable amount heat setting of grey textiles is carried out.

The off-gas situation is shown in Figure 3.21.

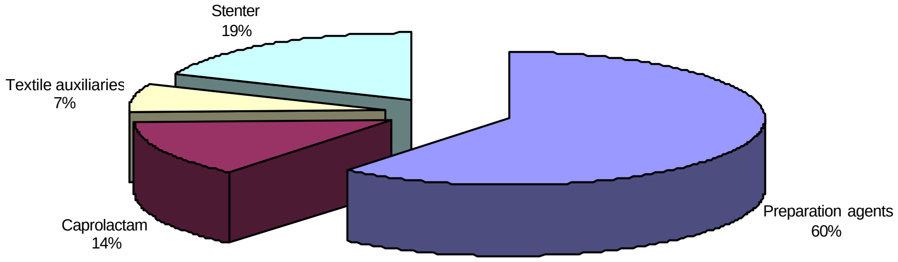


Figure 3.21: Textile finishing company 1. Organic-C-load in off-gas

It is evident, that main Organic-C-load results from the ecological loads carried of from up-stream processes (preparation agents and epsilon-caprolactam ex PA 6). Textile auxiliaries contribute only with 7% to the total Organic-C-load of the company.

3.5.11.2 Example 2

The TFI as example 2 mainly finishes PES and PES blends (Figure 3.22). To a considerable amount heatsetting of grey textiles is carried out.

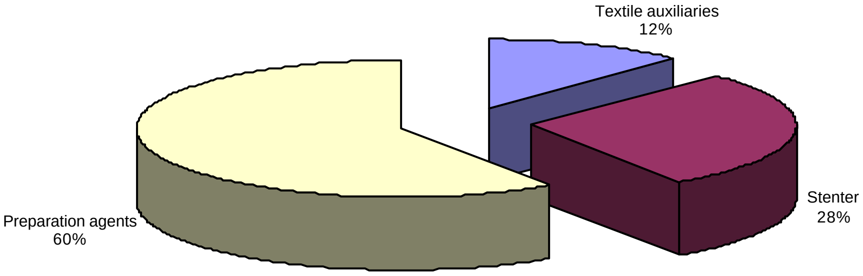


Figure 3.22: Textile finishing company 2. Organic-C-load in off-gas

This example emphasises also that main off-gas-load in textile finishing can be caused by the textile raw materials if heatsetting of grey textiles is carried out.

3.5.11.3 Example 3

The TFI as example 3 mainly finishes man-made fibres. The composition of organic carbon load in waste gas is illustrated in Figure 3.23.

- The grey textiles are washed before thermal processes.
- Coating is carried out.
- Carriers are used in dyeing.

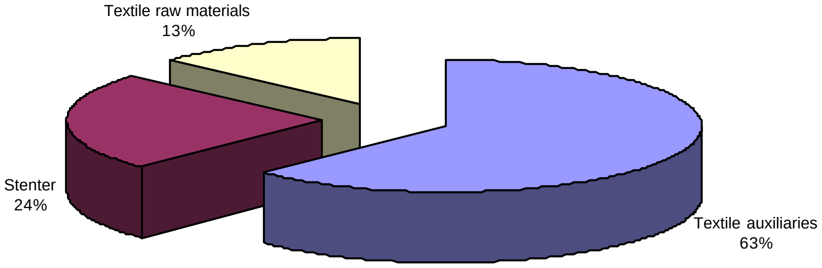


Figure 3.23: Textile finishing company 3. Organic-C-load in off-gas

In comparison to the examples above contribution of textile raw materials to the Organic-C-load is reduced due to pre-washing steps. Textile auxiliaries are dominant in this case. It is to be noted that in this case approx. 40% of the Organic-C load emitted by the textile auxiliaries is caused by textile auxiliaries used in dyeing (mainly carriers).

3.5.11.4 Example 4

The TFI as example 4 finishes
- non-wovens, woven and knitted textiles (mainly PES, PES/PA and CV blends)
- heatsetting on grey textiles is not carried out

The Organic-C-load is dominated by emissions of coating agents and stenter emissions.
The composition of organic carbon load in waste gas is illustrated in Figure 3.24.

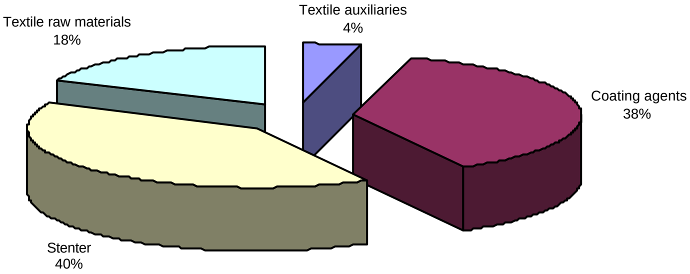


Figure 3.24: Textile finishing company 4. Organic-C-load in off-gas

3.5.11.5 Emission factors for a typical process sequence in textile finishing

Off-gas emissions for a typical process sequence in finishing cotton including pre-treatment, printing and finishing and intermediate drying steps is given in Table 3.70. Data from emission measurements carried out at one finishing mill with a great printing compartment are presented. [EnviroTex, 1998c].
In all the processes mentioned below captured emissions are regarded. Pre-treatment steps with exception to singeing are of relatively low relevance considering Organic-C-load. Odour nuisance in singeing, caustisizing and drying of the printing paste has to be taken into consideration. Dust occurs only in singeing. Ammonia emission results from decomposition of urea used in printing pastes.

Process	Organic-C [g/kg textile]	Dust [g/kg textile]	Odour [OU/kg textile]	Formaldehyde [g/kg textile]	Ammonia [g/kg textile]
Singeing	0.2	0.3	6000	< 0.01	-
Caustisizing	0.1	-	2300	-	-
Peroxide bleaching	< 0.1	-	900	-	-
Drying (stenter)	< 0.1	-	300	-	-
Pigment printing (drying)	0.2	-	3500	0.02	0.7
Pigment printing (condensation)	0.1	-	2000	0.03	0.4
Finishing (softening, easy-care) Drying	0.3	-	1400	0.04	-
Finishing Condensation	0.4	-	1000	0.09	-

Table 3.70: Emissions for a typical process sequence

3.6 Solid wastes

In textile finishing industries, many different solid and liquid wastes are caused and have to be disposed of. Some of them can be recycled or reused, others are incinerated or put to secured landfill; there are also some wastes which (in a few cases) are treated in anaerobic digesters. Many of these wastes are not specific for the textile finishing industry. Therefore, in the following, the distinction is made between wastes which are specific and non-specific for this sector (Table 3.71).

Wastes, non-specific for TFI	Wastes, specific for TFI
Waste, not in need of control ▪ Waste glass ▪ Paper, paper board (including cones) ▪ Wood ▪ Iron scrap (pipes, old machines etc.) ▪ Electric cables ▪ Plastic drums (clean) ▪ Metal drums (clean) ▪ Non-contaminated plastic wrap ▪ Rubble from building sites	Waste, not in need of control ▪ Waste yarn ▪ Waste fabric (knit and woven fabric) (bad works, trails, selvedge cutting) ▪ Wastes from shearing and raising
Waste, in need of control ▪ Waste oil ▪ Oil contaminated cloth ▪ Non-halogenated waste solvents ▪ Soot from oil incinerators ▪ Glue and adhesive agents ▪ Contaminated packing material ▪ Dyestuffs and pigments ▪ Electronic scrap	Waste, in need of control ▪ Residual padding dyeing liquors ▪ Residual printing pastes ▪ Residual padding finishing liquors ▪ Oil-containing condensates from off-gas Treatment (waste gas from stenters) ▪ Sludge from textile wastewater treatment
Waste, highly in need of control ▪ Waste from oil/water separators ▪ Halogenated waste solvents ▪ PCB-containing condensers	

Table 3.71: Solid and liquid wastes from textile finishing industries (TFI); not every kind of waste will be relevant for every TFI and most of the wastes are not specific for the textile sector

Information on the quantities is available for twelve textile finishing industries. The available data show a big range of the textile substrate specific quantities. In Table 3.72, for textile waste (waste yarn, waste fabric), available information is compiled. Usually, most of the textile waste is recycled.

Today, there are only a few TFI, which segregate high loaded wastewater streams, such as residual padding dyeing liquors and residual padding finishing liquors. In case of exceeding limits for COD, nitrogen or colour, such measures are applied. It is more common to dispose off residual printing pastes separately. These pastes are disposed in incineration plants or, in case of reactive and vat printing pastes in anaerobic digesters.

There are TFI treating their wastewater by flocculation/precipitation. The volume specific sludge quantity after de-watering (usually in chamber filter presses) including the water content (which is usually 60-65%) is normally within the range 1 - 5 kg/m^3 treated wastewater. Taking into account a specific wastewater flow of 100-150 l/kg, the textile substrate specific sludge quantity is 100-750 g/kg finished textiles.

Number of TFI	Specific quantity for textile waste [kg waste/t textile product]	Comment
TFI 1	39	PA sock manufacturing company; most of the waste is caused during confection of the socks
TFI 2	37	Woven fabric manufacturing industry
TFI 3	20	Woven fabric finishing industry; half of the quantity is fibre dust and the other half waste fabric
TFI 4	32	Woven fabric manufacturing industry
TFI 5	6	Yarn finishing industry
TFI 6	88	Commission finisher for knitted fabrics); high percentage from shearing and raising
TFI 7	52	Finishing plant with weaving and finishing compartment
TFI 8	14	Commission finisher (mainly wool); shearing and raising waste
TFI 9	160	Finishing mill with fabric manufacturing. Raising and shearing waste
TFI 10	7	Finishing mill mainly finishing PES knitted goods
TFI 11	84	Tufting and finishing carpets
TFI 12	43	Finishing plant with coating compartment (selvedge cutting waste) Total waste (textile and non textile waste): 273 kg/t (174 kg/t waste to be recycled 85 kg/t to be incinerated)

Table 3.72: Quantity of textile waste from nine different TFI

3.7 References

[Bautzen, 2001]
Staatliches Umweltfachamt Bautzen, D-Bautzen
Personal information

[EnviroTex, 1997]
EnviroTex GmbH, D-Augsburg
Substitution und Minimierung von Problemstoffen in der Textilindustrie
Bundesministerium für Umwelt, Jugend und Familie, A-Wien (1997)

[EnviroTex, 1998a]
EnviroTex GmbH, D-Augsburg
Emissionen aus der Direktbefeuerung von Textilveredlungsanlagen
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, D-München (1998)

[EnviroTex, 1998b]
EnviroTex GmbH; D-Augsburg
Emissionen aus der Direktbefeuerung von Textilveredlungsanlagen. Teilbericht 1: Die Verarbeitung von mit Perchlorethylen vorgereinigter Ware
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, D-München (1998)

[EnviroTex, 1998c]
Envirotex GmbH, D-Augsburg
Erstellung eines Leitfadens für ein Umwelt-Qualitätsmanagement in der Textilveredlungsindustrie und seine Umsetzung in die betriebliche Praxis
Deutsche Bundesstiftung Umwelt (Aktenzeichen 06762), D-Osnabrück (1998)

[EnviroTex, 2000a]
EnviroTex GmbH; D-Augsburg
Erweiterte, wichtige immissionsschutzrechtliche Fragestellungen beim Betrieb von Textilveredlungsanlagen. Teilbericht 3: Trocknen und Fixieren carriergefärbter Ware
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, D-München (1998)

[EnviroTex, 2000b]
EnviroTex GmbH, D-Augsburg
Erweiterte, wichtige immissionsschutzrechtliche Fragestellungen beim Betrieb von Textilveredlungsanlagen
Teilbericht 2: Pigmentdruck
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, München (2000)

[EnviroTex, 2001]
EnviroTex GmbH, D-Augsburg
Emission measurements according to German law and audits in German textile finishing industry (1994-2001)
Not published

[Eutech/ITA/LTT, 2000]
Eutech Energie- und Umweltberatung (Eutech), Institut für Textiltechnik der RWTH Aachen (ITA), Lehrstuhl für Technische Thermodynamik der RWTH Aachen (LTT)
Branchen-Energiekonzept für die Textilindustrie in Nordrhein-Westfalen (kruska@ltt.rwth-aachen.de)
to be published

[FhG-ISI, 1997]
Böhm, E.; Hillenbrand, T.; Landwehr, M.; Marscheider-Weidemann, F.
Fraunhofer-Institut für Systemtechnik und Innovationsforschung (FhG-ISI)
Untersuchung zur Abwassereinleitung: Statistik wichtiger industrieller und gewerblicher Branchen zur Bewertung der Umweltgefährlichkeit von Stoffen (1997)

[ITV, 1992]
Institut für Textil- und Verfahrenstechnik Denkendorf (ITV)
Die Ermittlung der Quellen von adsorbierbaren organisch gebundenen Halogenen (AOX) in Abwässern der Textilindustrie und Maßnahmen zu ihrer Vermeidung
Abschlußbericht (1992)

[LAI, 1997]
Bausteine für Regelungen bei Textilveredlungsanlagen
ed.: Länderausschuss für Immissionsschutz, Erich Schmidt Verlag, LAI-Schriftenreihe 17 (1997)

[LfU, 2002]
Bayerisches Landesamt für Umweltschutz, D-Augsburg
Personal information

[TEGEWA, 1994]
TEGEWA
Leitfaden zur Berechnung von Emissionsfaktoren, D-Frankfurt/Main (1994)

[TfI, 2001]
Teppichforschungsinstitut (TFI), D-Aachen
Draft of IPPC-BREF Carpet Industry (2001)

[THK, 2000]
Textilhilfsmittelkatalog 2000
Deutscher Fachverlag, D-Frankfurt/Main (1999)

[UBA, 2001]
Schönberger, H.
Die gegenwärtige Verbrauchs- und Emissionssituation der deutschen Textilveredlungsindustrie
UBA-Texte (submitted to be published)

[UMEG, 1996]
UMEG – Ges. für Umweltmessungen und –erhebungen mbH, D-Karlsruhe
„Abschlußbericht über die Durchführung von Emissionsmessungen in Betrieben der Textilveredelnden Industrie, Jahresaktion der Gewerbeaufsicht 1996, Aktion B 8“
Bericht Nr.: 33-01/97 (1997)

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

4.1 General best management practice

4.1.1 System measures and good housekeeping for the minimisation of emissions

Description
As a first approach to improve environmental performance in textile finishing system measures and good housekeeping should be considered. In the following a brief overview on the main items is given:

Education/training of employees
- education to increase the level of environmental awareness. Training should be process and machinery specific.
- appropriate education of workers concerning handling of chemicals and auxiliaries (esp. in case of hazardous substances)

Maintenance of technical equipment (machines in production as well as abatement and recovery devices)
- machinery checking (esp. pumps, valves, level switches, stenters (general maintenance by specialised companies at regular intervals; at regular intervals checking of the burner air inlet concerning blocking by fluffs or oil; cleaning of off-gas pipes; adjusting of the burners by specialists))
- leaks control (esp. water piping, oil heat transfer, compressed air)
- filter maintenance (periodically cleaning and controlling)
- calibration of measuring equipment (chemicals measuring and dispensing devices, thermometers, pressure and flow regulators etc.)

Chemicals storage, handling, dosing, and dispensing
- proper storage according to the instruction of the Material Safety Data Sheet; special compartments for toxic and explosive chemicals
- dosing and dispensing without spilling
- automated colour kitchens
- automated dosing systems (see 4.1.3)
- use of vapour balancing lines that transfer the displaced vapour from the container being filled to the one being emptied (for larger tanks)

Improved knowledge of the raw materials used
- Dyestuffs, textile auxiliaries and basic chemicals: information from the supplier concerning proper storage and handling; environmental characteristics (COD, BOD_5, aquatic toxicity, degree of biodegradation/bioelimination, content of nitrogen, phosphorous, sulfur, AOX-relevant compounds, kind and amount of volatile compounds, emission factor, health and safety aspects)
- textile raw material: information from the supplier concerning kind and amount of preparation agents and sizing agents, amount of residual monomer and solvent content of the fibres

Minimisation/optimisation of chemicals used
- regular revising of the recipes (auxiliaries and chemicals with a high degree of biodegradation/bioelimination, low human and ecological toxicity, low volatility and low smell intensity should be preferred)
- avoiding any kind of surplus of applied chemicals and auxiliaries

- optimising scheduling in production (e.g. in dyeing: dyeing dark shades after pale shades reduces water and chemicals consumption for machine cleaning; e.g. in finishing: proper scheduling minimises machine stops and heating-up/cooling down steps)
- low add-on devices (spraying, foam application, special padding devices)
- minimisation of printing paste residues (see 4.2.1.4.3 and 4.2.1.4.4)

Water management

- avoidance of leaks and spills
- substitution of overflow rinsing or minimisation of water consumption in overflow rinsing by means of optimised process control
- optimisation of scheduling of processes
- adjustment of processes in pre-treatment to quality affords in downstream processes (e.g. bleaching is often not necessary if dark shades are produced)
- reuse of rinsing bathes (esp. final rinsing bathes)
- reverse current flows in continuous washing
- segregation and reuse of cooling water as process water
- cleaning and recycling of process water in selected low charged wastewater streams
- operational safety in preparing of fresh water avoids bad-works and re-works

Off-gas management

- use of low emission preparation agents through the total textile chain where possible (see 4.2.1.1.3)
- use of low emission auxiliaries, implementation of an emission factor concept (see 4.2.1.1.2)
- proper adjusting of drying/curing temperature and drying/curing time and minimizing of the air flow ratio
- proper pre-treatment and washing/rinsing after dyeing prevents carry over of volatile auxiliaries to upstream heat treatment. Special care should be taken to select the appropriate detergent, to have an efficient long dwell time and the right temperature in pre-treatment (washing) of textile raw materials

Solid waste management

- prevention of solid waste takes priority
- separate collection of unavoidable solid waste
- reduction of packaging
- use of returnable containers
- reuse, recycling of textile wastes

Main achieved environmental benefits

Savings in the consumption of chemicals, auxiliaries, dyestuffs, fresh water and energy and minimising the amount of solid waste as well as ecological loads in wastewater and off-gas are the main ecological advantages achieved with management methods. Also an improved working place situation can be achieved.

Applicability

For most of the described methods only staff costs have to be considered. Well trained employees are a prerequisite for implementing system measures. If existing equipment has to be rebuilt or a new equipment has to be installed (automated dosing systems etc.) the applicability can be limited due to the fact that the measures may be too cost-intensive or there is a technological/logistic, or a space problem.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants
Various textile finishing mills in Germany as well as throughout the world have implemented system measures to improve the environmental performance and are working according to a good housekeeping concept.

Operational data
System methods and good housekeeping depend on a high organised management. Tools like EN ISO 9000 ff, EN ISO 14001, and EMAS will sustainably support this approach. Material and energy flow management are also necessary (see 4.1.2). Information, communication on companies level as well as with the whole supply chain are demanded.

Economics
The described measures enable improved operational reliability. Thus, economical advantages are achieved. Savings in the consumption of energy, fresh water, chemicals, dyestuffs and auxiliaries as well as savings in costs for wastewater and off-gas cleaning and discharge of solid waste are the main economical benefits.

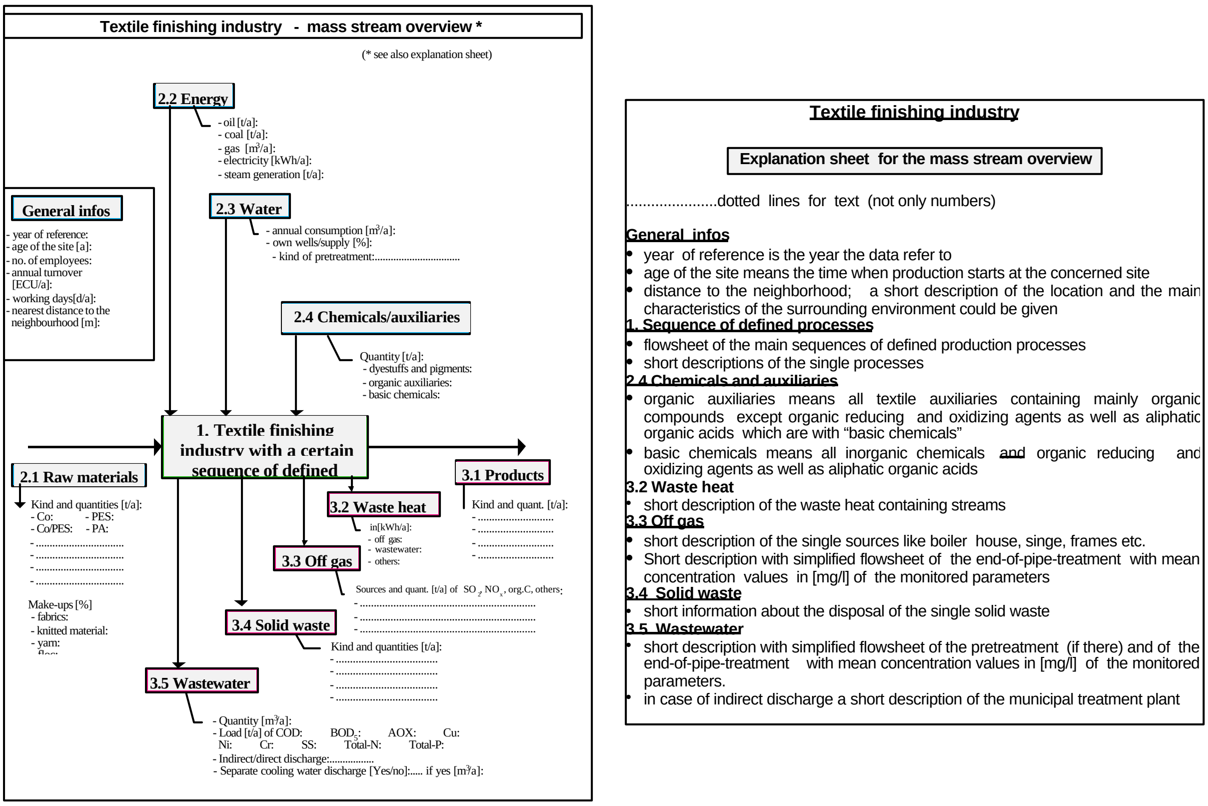
Driving force for implementation
Cost savings, improvement of operational reliability, improved environmental performance and legal requirements are the main reasons for implementing system measures and good housekeeping.

Reference literature
[--]

4.1.2 Input/output mass streams evaluation/inventory

Description

All environmental problems are directly linked with mass streams. Therefore, it is of fundamental relevance to know as much as possible about quality and quantity of input and output mass streams. Detailed knowledge about these mass streams is fundamental and both the basis and prerequisite for the identification of optimisation potentials and their priorities. This is not with respect to environmental pollution prevention and control only, but also to economic optimisation. Input/output mass streams inventories can be carried out on different levels. The most general level, providing the first overview is the site specific level on an annual basis. Figure 4.1 indicates the relevant input/output mass streams. With the annual quantities, textile substrate specific input and output factors can be calculated (e.g. litre water consumption/kg processed textiles or g COD in wastewater/kg processed textiles etc.). These factors can be compared with factors from similar textile finishing industries (TFI). Regarding wastewater emissions, available data for different categories are presented in Chapter 3.



Textile finishing industry

Explanation sheet for the mass stream overview

......................dotted lines for text (not only numbers)

General infos
- year of reference is the year the data refer to
- age of the site means the time when production starts at the concerned site
- distance to the neighborhood; a short description of the location and the main characteristics of the surrounding environment could be given

1. Sequence of defined processes
- flowsheet of the main sequences of defined production processes
- short descriptions of the single processes

2.4 Chemicals and auxiliaries
- organic auxiliaries means all textile auxiliaries containing mainly organic compounds except organic reducing and oxidizing agents as well as aliphatic organic acids which are with "basic chemicals"
- basic chemicals means all inorganic chemicals and organic reducing and oxidizing agents as well as aliphatic organic acids

3.2 Waste heat
- short description of the waste heat containing streams

3.3 Off gas
- short description of the single sources like boiler house, singe, frames etc.
- Short description with simplified flowsheet of the end-of-pipe-treatment with mean concentration values in [mg/l] of the monitored parameters

3.4 Solid waste
- short information about the disposal of the single solid waste

3.5 Wastewater
- short description with simplified flowsheet of the pretreatment (if there) and of the end-of-pipe-treatment with mean concentration values in [mg/l] of the monitored parameters.
- in case of indirect discharge a short description of the municipal treatment plant

Figure 4.1: Annual mass stream overview for a textile finishing industry

The systematic listing and evaluation of applied chemicals (dyestuffs and pigments, textile auxiliaries and basic chemicals) is very important in view of identifying critical compounds. Therefore, it is recommended to use nine forms for following classes (example in Table 4.1):

- Auxiliaries and finishing agents for fibres and yarns
- Pre-treatment agents
- Textile auxiliaries for dyeing and printing
- Finishing assistants
- Technical auxiliaries for multipurpose use in the textile industry
- Textile auxiliaries, not mentioned in the Textile Auxiliaries Buyer's Guide [Melliand/TEGEWA, 2000]
- Basic chemicals (all inorganic compounds, all aliphatic organic acids, all organic reducing and oxidising agents, urea)
- Dyestuffs and pigments

Form 3 **TFI:** **Year:**

3. Textile auxiliaries for dyeing and printing

3.1 Dyestuff solubilizing and hydrophobic agents
3.2 Dispersing agents and protective colloids
3.3 Dyeing wetting agents, deaeration agents
3.4 Levelling agents
3.5 Carriers
3.6 Crease-preventing agents
3.7 Dyestuff protecting agents, boildown protecting agents
3.8 Padding auxiliaries
3.9 Fixing accelerators for continuous dyeing and printing
3.10 Aftertreatment agents for fastness improvement
3.11 Bonding agents for pigment dyeing and printing
3.12 Printing thickeners
3.13 Emulsifiers for gasoline printing
3.14 Agents to remove printing thickeners
3.15 Printing and edge adhesives
3.16 Oxidizing agents
3.17 Reducing agents
3.18 Discharging agents and discharging assistants
3.19 Resist agents
3.20 Mordants
3.21 Brightening and stripping agents
3.22 Fibre-protective agents
3.23 pH-regulators, acid and alkali dispensers

No.	Commercial name	Chemical characterisation	Process, application	Danger symbol	Annual consumption [kg/a]	Biological degradation resp. elimination [%] and testing method	spec. COD-value [mg O_2/g]	spec. BOD_5-value [mg O_2/g]	Heavy metal content [mg/g]	Org. halogen content [mg/g]	COD-load [kg O_2/a]
3.16	Revatol S Gran.	Nitobenzene sulfonic acid, Na-salt	dyeing	Xi	5.400	>90; OECD 302 B	0,990				5346
3.04	Alviron OG-BM fl.	Formulation of surfactants and high-boiling alcohols	dyeing	---	3.800	>80; after adaptation	0,760				2888
3.17	Cyclanon ARC Plv.	Sulfinic acid derivative and dispersing agent	dyeing	Xi	3.650	20-70; OECD Confirmatory	0,335				1223
3.02	Lamepon UV fl.	Polysaccharide	dyeing	---	2.500	>70; OECD 302 B	0,350				875
3.04	Drimagen E2R fl.	Aromatic polyether sulfonate	dyeing	Xi	1.300	46; OECD 302B	0,616				801
3.23	Sandacid PBD fl.	Aliphatic carbonic acid derivative	dyeing	---	1.250	80; OECD 302 B	0,309				386
3.04	Peregal P fl.	Polyamidoamine	dyeing	---	850	>70; OECD Confirmatory	0,430				366
3.23.	Egasol 910 Plv	Mixture of organic and inorganic salts	dyeing	Xi	620	---	---				
3.10	Indosol E-50 fl.	Aliphatic polyamine	dyeing	---	480	89; OECD 302 B	0,420				202

Table 4.1: **Form for the listing of textile auxiliaries for dyeing and printing; concerned forms are in use for the other 8 classes of chemicals mentioned above**

The first six categories are identical with Textile Auxiliaries Buyer's Guide. Textile auxiliaries are chemical formulations which mainly contain organic compounds. Basic chemicals comprise all inorganic compounds, all aliphatic organic acids, all organic reducing and oxidising agents and urea. The listing allows a first rough assessment of the applied chemicals and a COD input balance. The information on biological degradation/elimination is the basis for the selection of biological biodegradable products; however, it has to be pointed out, that only the assessment of all compounds of commercial products (which are usually formulations of various chemical compounds) serve the full real picture. In addition, in many cases the information on biological degradation/elimination has to be critically questioned with respect to the properties of chemicals and the testing methods.

The next level is the process or machine level. Here, Chapter 3 also contains examples for water consumption and wastewater flow respectively, for emissions to air and for energy consumption. In many cases, this level directly leads to the knowledge for improvements and optimisation. Figure 4.2 shows an example for energy consumption.

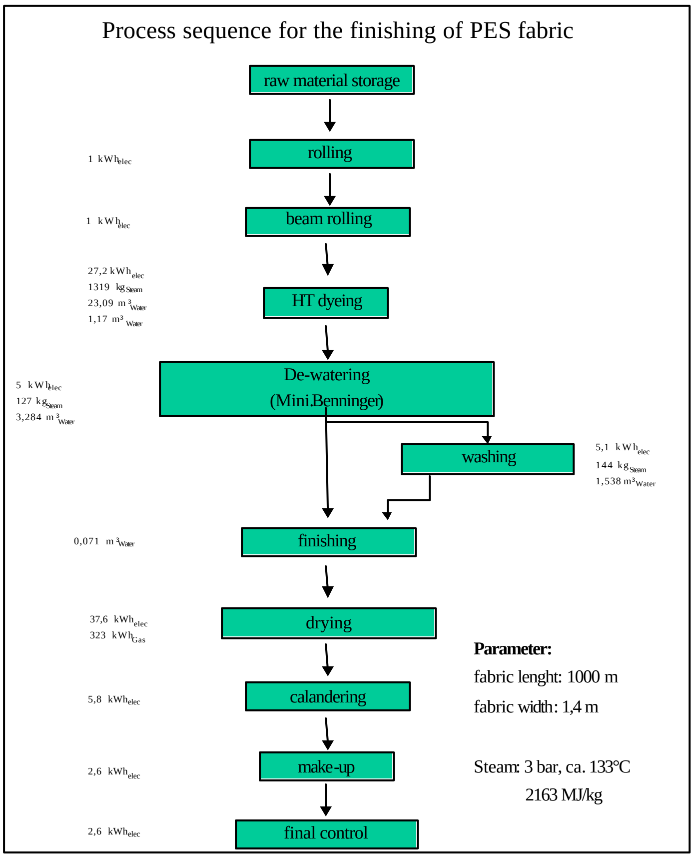


Figure 4.2: Example for input/output evaluation; the example is for energy consumption [Eutech/ITA/LTT, 2000] but the principle is same for e.g. water consumption, wastewater discharge or chemicals consumption

Main achieved environmental performance

The described evaluation and inventory of input/output mass streams is a management tool being a prerequisite for the identification of optimisation potentials both ecologically and economically. It is the essential part of a continual improvement process.

Applicability

The technique is applicable both to existing and new installations.

Cross-media effects

There are no cross-media effects to be mentioned. The input/output mass streams evaluation/inventory also is the basis for priority setting of reduction measures taking cross-media effects into consideration. This means the achievement of a high level of protection of the environment taken as a whole.

Reference plants

There are various textile finishing industries in Western Europe which have implemented input/output mass streams evaluation and documentation as inventories on site level. Only few are systematically applying this instrument on process level also.

Operational data

The application of such a management tool requires highly qualified staff. In many cases, the work of such experts pays back but this knowledge has no break through yet in the textile sector.

Economics

There is no specific information available on economical aspects but generally speaking, because of the big potential for improvements in the textile sector, the application of the described management tool pays back within short time in many cases.

Driving force for implementation

The knowledge of big improvement potentials and the target to make them accessible as well as the EMAS/ISO 14001 discussion have been the main driving forces.

References

[Melliand/TEGEWA, 2000]
Melliand/TEGEWA
Textile Auxiliaries Buyer's Guide 2000
Deutscher Fachverlag , Frankfurt (2000)

[Eutech/ITA/LTT, 2000]
Eutech Energie- und Umweltberatung (Eutech), Institut für Textiltechnik der RWTH Aachen (ITA), Lehrstuhl für Technische Thermodynamik der RWTH Aachen (LTT)
Branchen-Energiekonzept für die Textilindustrie in Nordrhein-Westfalen (kruska@ltt.rwth-aachen.de)
to be published

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduktion der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

4.1.3 Automated liquor bath preparation

Description

In textile finishing industry, the textiles are treated with different chemicals which are usually applied from aqueous solutions. In case of high concentrated padding liquors for pre-treatment, dyeing and finishing, it is of environmental relevance to prevent or to minimise excess of liquors. Today, there are automated systems available for just-in-time-preparations of liquors. In connection with on-line measurement of liquor pick-up and of quantity of processed fabric, the exact liquor quantity can be prepared and added. Thus, surplus of liquors is minimised and thus wastewater pollution. In modern systems, washing water of preparation vessel and supplying pipes is taken into account for the quantity of prepared liquor. Thus, in addition, wastewater flow and pollution is reduced.

Figure 4.3 and Figure 4.4 show examples for a principle scheme for automated dispensing of chemicals for the preparation of impregnation liquor for pre-treatment and finishing. Similar devices can be used in semi-continuous (cold pad batch - see the concerned described technique) and continuous dyeing

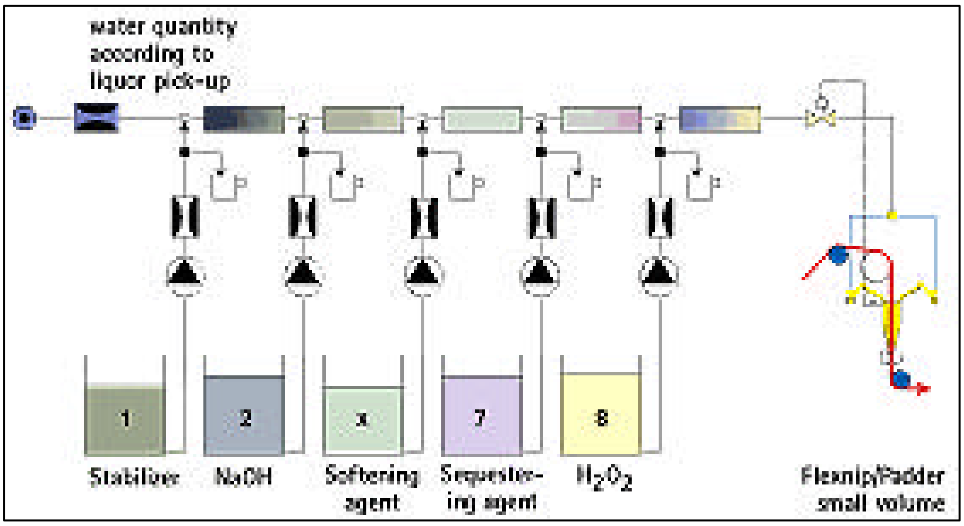


Figure 4.3: **Example for automated dispensing of chemicals according to measured pick-up and processed fabric for the padding of a bleaching liquor to cotton woven fabric (picture from Küsters GmbH, D-47805 Krefeld)**

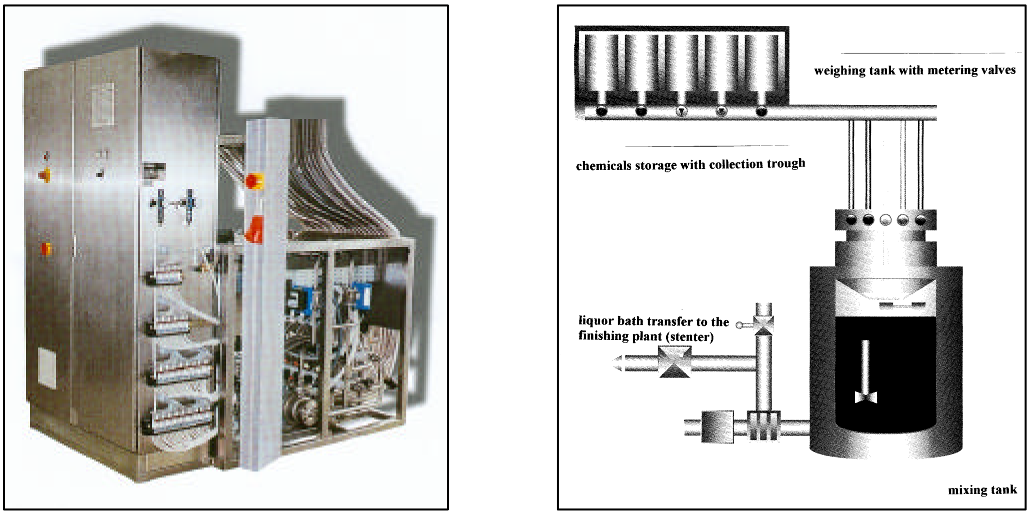


Figure 4.4: **Example for the on-line preparation equipment of padding liquor for the finishing of woven and knit fabric (pictures from Mutschink GmbH, D-47918 Tönisvorst)**

Main achieved environmental benefits

The common discharge of excess liquor is considerably minimised and thus wastewater pollution is significantly reduced. In addition, the quantity of wastewater flow for cleaning the preparation equipment and pipes is significantly reduced by using this water for preparing the liquors.

Applicability

Automated dispensing techniques are applicable, both to new and existing installations.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

There are various installations at textile finishing industries in Germany and Europe, e.g.:

- Brennet AG, D-79704 Bad Säckingen
- Schmitz Werke GmbH + Co., D-48282 Emsdetten
- Görlitz Fleece GmbH, D-02829 Ebersbach
- Weyermann GmbH & Co.KG, D-41751 Viersen
- Rheinische FutterstoffveredlungsGmbH, 42117 Wuppertal
- Irmen GmbH, D-41352 Korschenbroich
- Thorey Gera Textilveredelung GmbH, D-07551 Gera

Operational data

Automated dispensing systems require qualified operators. However, one person can easily operate the system. Cost savings (because of reduction of consumption of chemicals and water, increase of reproducibility) up to 30% are possible.

Economics

Depending on the number of machines, liquors to be prepared and on the number of used chemicals, investment cost usually vary between 70,000 - 250,000 EURO.

Driving force for implementation

The need to reduce wastewater pollution but also to increase reproducibility as well as economic aspects are the main driving forces for the implementation of such dispensing systems.

Reference literature

[--]

4.1.4 Minimisation of water consumption for different kind of textile finishing industries and for continuous open-width washing processes

Description

With respect to discontinuous textile finishing, water consumption mainly depends on liquor ratio, number of baths (which mainly depends on the substrate and applied pre-treatment/dyeing technique) and applied rinsing technique. Regarding minimisation of liquor ratio and optimised rinsing technique, a concerned technique is described (see 4.2.1.3.1); however, this technique is for fabric only but not for yarn or floc finishing. For the latter, liquor ratios of 1:6 - 1:8 are optimum.

Regarding water consumption, values are given in Chapter 3 in connection with expert judgement of the concerned TFI (assessment of processes, available machinery and applied rinsing techniques). Following water consumption values (for the annual water consumption in relation to the annual production) are commonly achievable:

- Finishing of yarn:	70 - 120 l/kg
- Finishing of knit fabric	70 - 120 l/kg
- Pigment printing of knit fabric	0.5 - 3 l/kg
- Finishing of woven fabric mainly consisting of cellulosic fibres	50 - 100 l/kg
- Finishing of woven fabric mainly consisting of cellulosic fibres including reactive and/or vat printing	< 200 l/kg
- Finishing of woven fabric mainly consisting of wool	< 200 l/kg
- in case of job finishers carrying out special processes which require high liquor ratios, the value can be	< 250 l/kg

For finishing open width fabric, modern machines with high efficient washing techniques are available. Following values are achieved (Table 4.2):

	Total water consumption [l/kg]	Hot water consumption [l/kg]
Pre-treatment processes		
Washing for desizing	3 - 4	3 - 4
Washing after scouring	4 - 5	4 - 5
Washing after bleaching	4 - 5	4 - 5
Washing after cold bleaching	4 - 6	4 - 6
Washing after mercerisation		
- Washing to remove NaOH	4 - 5 (hot)	
- Neutralisation without dryer	1 - 2 (cold)	
- Neutralisation with dryer	1 - 2 (warm)	
Washing after dyeing		
Reactive dyestuffs	10 - 15	4 - 8
Vat dyestuffs	8 - 12	3 - 7
Sulphur dyestuffs	18 - 20	8 - 10
Naphtol dyestuffs	12 - 16	4 - 8
Washing after printing		
Reactive dyestuffs	15 - 20	12 - 16
Vat dyestuffs	12 - 16	4 - 8
Naphtol dyestuffs	14 - 18	6 - 10
Disperse dyestuffs	12 - 16	4 - 8

Table 4.2: Achievable specific water consumption for continuous washing processes during finishing of open width woven fabric consisting of cotton or viscose or of concerned blends with synthetic fibres - the values for the different processes are additive and are submitted by machine suppliers which are confirmed by some TFI

Main achieved environmental benefits
Discontinuous processes: With optimised liquor ratio, rinsing techniques and minimisation of number of baths, considerable savings of water and energy respectively are achieved.
Continuous processes: Considerable savings of water and energy respectively are achieved.

Applicability
For discontinuous processes, in many cases, minimised liquor ratio is only possible by installation of new machines, whereas modern rinsing techniques and minimisation of number of baths can also be carried out very often in existing installations.
Continuous processes: The mentioned low values are only achievable in new installations; however most of existing installations can be optimised concerning water and energy consumption.

Cross-media effects
Highly intensive and efficient washing techniques with low water consumption require intensive mechanical washing conditions (spraying, sucking etc.) which may require some more electricity, however this is much less compared to savings of thermal energy for water heating.

Reference plants
There are many plants available and are successfully in operation throughout Germany, Europe and world-wide as well.

Operational data
Concerning continuous processes, it is important to mention, that many processes which have formerly been carried out discontinuously are nowadays performed continuously. This results in considerable savings of water and energy. In addition, very often processes are combined to one-stage-operation, such as scouring and bleaching. This also leads to considerable savings.

Economics
There is no specific information available.

Driving force for implementation
Increasing cost for water (in case of public process water supply) and wastewater (especially wastewater fees) and for energy as well, have been the main driving forces. In some regions, limited water availability/shortage is the major motivation for the minimisation of water consumption.

Reference literature
[--]

4.1.5 Measures for rational energy using

Description

Due to the fact that finishing processes are very energy intensive measures to reduce energy consumption are of great interest from an ecological as well as from an economical point of view. It has to be kept in mind that energy consumption is directly related to water and fresh air consumption (normally water and air in textile finishing is used to a great extent at elevated temperature) but also to running times of the processes.

The following list compiles various methods concerning energy saving in textile finishing:

- good housekeeping (adjusting and controlling of optimised temperatures in aqueous processes and drying/fixation, proper maintenance of burners, minimising off-gas flows and water consumption, monitoring energy usage, leaks control in compressed air pipes, etc. (4.1.1)
- controlling moisture content in circulating air and on textiles in drying and curing
- minimisation of water content of textiles to be dried by means of mechanical devices (squeezing vacuum suction)
- heat-insulating of pipes, valves, tanks, machines
- optimising boiler houses (reuse of condensed water, pre-heating of air supply, heat recovery in combustion gases)
- installing heat recovery systems (wastewater and off-gas)
- installation of frequency controlled electric motors
- use of co-generation after a well founded check of actual and future energy situation

Main achieved environmental benefits

Considerable minimisation of the CO_2 load and other flue-gases by reducing energy consumption is the main ecological benefit.

Applicability

The described methods are applicable for all new installations. If existing equipment have to be re-built the applicability in some cases can be limited due to the fact that re-construction is a technological/logistic or space problem.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

Techniques to reduce energy consumption especially heat recovery systems are installed nearly in all textile finishing plants in Germany and world-wide as well.

Operational data

It should be kept in mind that detailed knowledge on the energy situation at the textile plant is a prerequisite for installing the appropriate techniques. Integrated energy concepts should be preferred instead of stand alone solutions.

Maintenance of heat recovery systems is of great interest (esp. proper cleaning of the devices and monitoring of the effectiveness).

Economics

For the heat recovery from wastewater and the thermal isolation of HT-dyeing machines a calculation of pay-back periods is given below [EnviroTex, 2000]. Calculation of return on investment for heat recovery systems concerning off-gas is described in Chapter 4.2.1.5.1.

Heat recovery from wastewater

Two typical wastewater temperatures are inspected:

- 95 °C
- 68 °C

Calculation basis:

Fresh and wastewater quantity:	5 m³/h
Fresh water temperature:	15 °C
Efficiency of the heat exchanger:	88%
Gas costs:	0.25 EURO/m³
Maintenance:	500 EURO/a
Interest:	6%

		Temp. wastewater 95 °C		**Temp. wastewater 68 °C**	
		Cost savings [EURO]	**Pay-back period [a]**	**Cost savings [EURO]**	**Pay-back period [a]**
1 heat exchanger	1-shift	18950	1	12000	1.7
2 heat exchangers		22700	1.7	14450	2.8
1 heat exchanger	2-shift	37900	0.5	24000	0.8
2 heat exchangers		45400	0.8	29100	1.4
1 heat exchanger	3-shift	56850	0.3	36000	0.6
2 heat exchangers		68100	0.5	43650	0.9

Table 4.3: Pay-back periods for wastewater heat recovery

Heat isolation for HT dyeing aggregates

Calculation basis:

Thermal transm. coefficient stainless steel:	15.1 W/m²K
Thermal transm. coefficient insulation:	0.766 W/m²K
Dyeing temperature:	110 °C
Room temperature:	30 °C
HT-dyeing aggregate (av. temperature 110 °C):	10 h/d
Processing time:	230 d/a
Gas costs:	0.25 EURO/m³
Loss by energy transformation and -transport:	15%
Dyeing aggregate 1 – front:	17.5 m²
Dyeing aggregate 2 – front:	23.5 m²
Dyeing aggregate 3 – front:	31.6 m²

	Dyeing aggregate 1	**Dyeing aggregate 2**	**Dyeing aggregate 3**
Material costs insulation [EURO]	3838	5263	6500
Staff costs installation [EURO]	2000	2000	2000
Losses by thermal radiation/a [MWh]	45.4	60.9	81.9
Gas savings/a [EURO]	1434	1926	2590
Pay-back period [a]	4.9	4.6	3.8

Table 4.4: Pay-back periods for heat-insulation at dyeing aggregates

Driving force for implementation

Savings in energy costs are the main driving force for a strict reduction of energy consumption.

Reference literature

[EnviroTex, 2000]
EnviroTex GmbH, D-Augsburg
CO_2-Minderungspotenziale durch rationelle Energienutzung in der Textilveredelungsindustrie
Bayerisches Landesamt für Umweltschutz, D-Augsburg (2000)

4.1.6 Management tool to minimise odour nuisances

Description

Odour nuisances are widespread in the textile industry. A selection of main substances and their possible sources which may cause odour nuisances is compiled in Chapter 3.5.10 (Table 3.68)

To identify, estimate and minimise the smell potential, the following items have to be checked [EnviroTex, 1996; EnviroTex, 2000]:

a) Data registration:
Ascertainment of all data concerning auxiliary and dyestuff consumption; collecting and evaluation (with regard to odour potential of the substances) of all Material Safety Data Sheets and further product information. Registration of all textile materials concerning possible emissions of smell-intensive components (mainly preparation agents, but also fibre inherent loads (solvents, monomers). In some cases suppliers have to be asked for more complete information on the products.

Identifying of core processes and frequency of occurrence (running time) of the processes.

b) Estimation of odour concentrations and odour mass flows:
In this step the correlation of the product specific data with the process data is carried out (at best specific for every stenter). Heatsetting/heatsetting in loomstate, drying (carry over from upstream processes), finishing and machine based emissions in case of direct heated stenters should be considered. Organic- C-load which gives an overview on the main emission potential can be evaluated by means of emission factors given from suppliers (see 4.2.1.1.2). In most cases, due to lack of information, emissions from textile materials have to be estimated at first

On this basis and information on resp. estimation of product specific odour threshold values odour concentrations [OU/m³] and odour mass flows [OU/h] can be estimated. As a rough estimation an odour concentration of

- 2500 OU/m³ for heatsetting and
- 500 OU/m³ for finishing

can be assumed.

c) Assessment of odour situation
The assessment should include: kind and quantity and reasons for the odour nuisance. This should be done in a process specific as well as in a stenter resp. stack specific way. Consequences are

- discussions with suppliers
- substitution of smell intensive auxiliaries/chemicals or minimisation of consumption of these substances and
- processing parameter revision.

In cases where a estimation of the odour situation is not possible olfactometry is the best approach.

If odour nuisances can not be minimised with integrated pollution prevention methods off-gas cleaning or heighten of the stack is to be done.
The following Figure 4.5 and Figure 4.6 may be helpful if stack height have to be estimated considering different odour mass flows (it is to be taken into account that not only the stack height but also the number of stacks and local situation concerning stack positions determine the on site odour situation).

Stack height [m] Odour mass flow	5 m	10 m	15 m
10 x 10^6 OU/h	-	-	-
50 x 10^6 OU/h	**Probably**	-	-
100 x 10^6 OU/h	**Most probably**	**Probably**	-

Figure 4.5: **Estimation of odour situation (one-shift plant);**
Coloured segments: Frequency of odour awareness > 10% (OU: odour unit)

Stack height Odour mass flow	5 m	10 m	15 m
10 x 10^6/h	**Most probably**	**Probably**	-
50 x 10^6 OU/h	**Most probably**	**Probably**	**Probably**
100 x 10^6 OU/h	**Most probably**	**Most probably**	**Probably**

Figure 4.6: **Estimation of odour situation (three-shift plant);**
Coloured segments: Frequency of odour awareness > 10% (OU: odour unit)

Main achieved environmental benefits

Odour nuisances concerning working place atmosphere and neighbourhood can be minimised by identifying and substitution of smell intensive substances and/or modification of process steps.

Applicability

The method is applicable in all textile finishing mills. However sufficient data on input materials (textile raw materials, chemicals, auxiliaries) should exist. A detailed calculation of odour concentrations and odour mass flows based on odour threshold values for substances is limited due lack of data and the fact that often wide ranges concerning threshold values are given. However an estimation of the odour situation shows the dimension of the problem.

Cross-media effects

No cross-media effects have to be regarded.

Reference plants

In several textile finishing plants in Germany odour nuisances could be minimised using the above mentioned management tools without installation of off-gas abatement techniques.

Economics

Only staff costs are to be regarded. Savings in installation costs and running costs for off-gas cleaning equipment can be achieved.

Driving force for implementation

Odour nuisances concerning neighbourhood are especially in Germany where textile finishing plants are often located in town centres very often the reason for complaints. Therefore minimisation of smell intensive substances/processes is of great interest for textile finishing mills.

Reference literature

[EnviroTex, 1996]
EnviroTex GmbH, D-Augsburg
Projekt Mischgewebe
Umweltministerium Baden-Württemberg, D-Stuttgart (1996)

[EnviroTex 2000]
EnviroTex GmbH, D-Augsburg
Erweiterte, wichtige immissionsschutzrechtliche Fragestellungen beim Betreib von Textilveredlungsanlagen – Teilbericht 1: Geruchsintensive Inhaltsstoffe von Textilhilfsmitteln und deren Verschleppung.
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, D-München (2000)

4.2 Textile finishing (except floor covering)

4.2.1 Process- and production-integrated techniques

4.2.1.1 Raw material selection

4.2.1.1.1 Method for the classification of textile auxiliaries according to their wastewater relevance

Description

During the past 15 years, in the Netherlands (RIZA-Concept), in Denmark (SCORE-System) and in Switzerland (BEWAG-Concept) different schemes for the ecotoxicological assessment respectively classification have been developed [Lepper, 1996]. Taking these approaches into account, in Germany a more scientific new system for the classification of textile auxiliaries according to their wastewater relevance has been worked out [Lepper, 1996]. During the subsequent discussion, authorities and industry got across to a more simplified scheme. The main approach was to initiate a development which may be further developed in the future [TEGEWA, 1998].

The "Method of classification of textile auxiliaries according to their wastewater relevance" provides a logic system for the classification of textile auxiliaries in 3 classes of relevance:

Class I	Minor relevance to wastewater
Class II	Relevant to wastewater
Class III	High relevance to wastewater

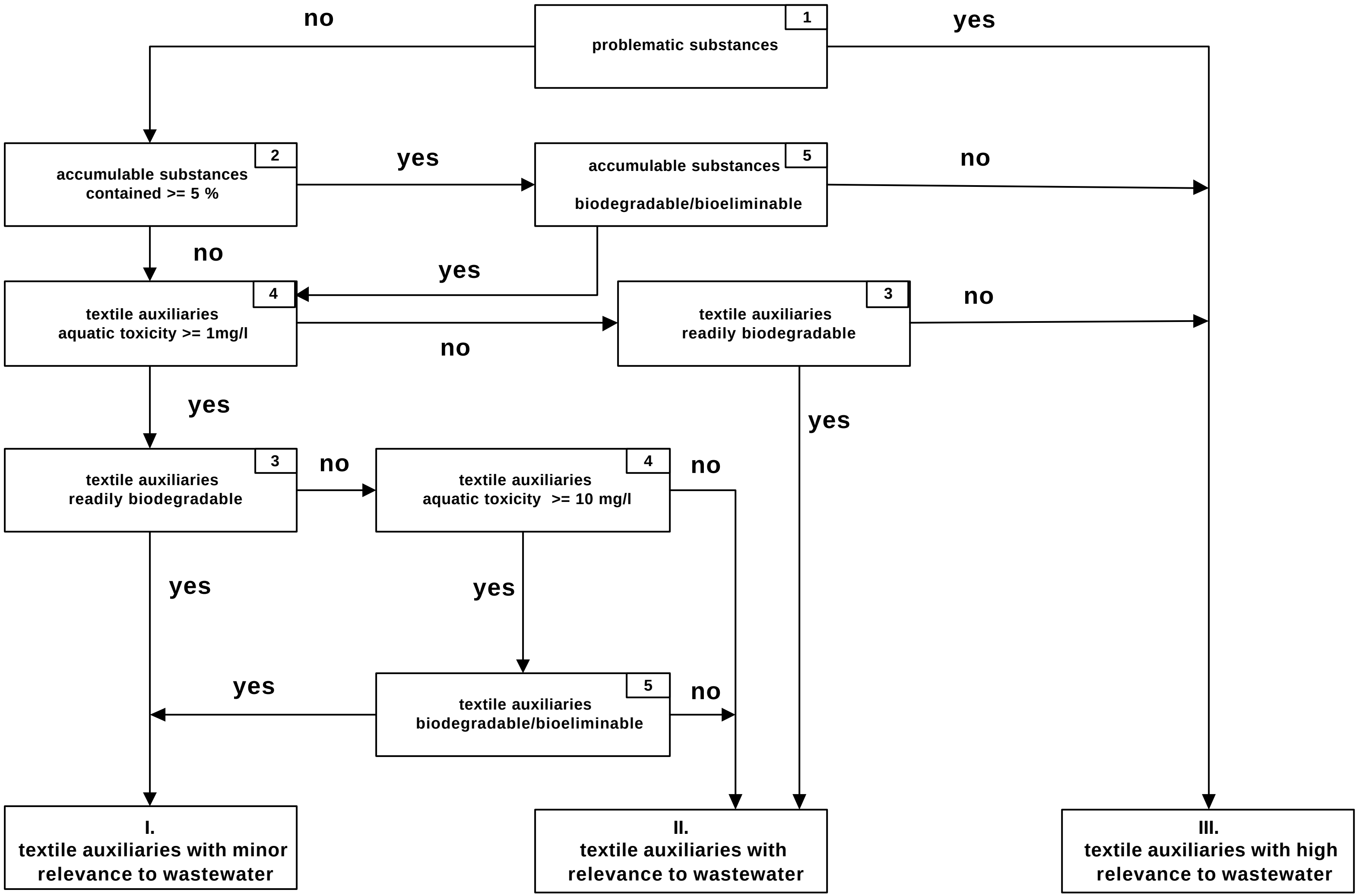
The main criteria for the classification are the content of certain harmful (including bioaccumulative) substances, biological degradation or elimination and aquatic toxicity of the sold products (scheme on next page).

The introduction of the classification concept rests essentially on the following pillars:

- Classification by producers on their own responsibility, guided by the association of textile auxiliaries suppliers, called TEGEWA (TEGEWA = Verband der TExtilhilfsmittel-, Lederhilfsmittel-, GErbstoff- und WAschrohstoff-Industrie e.V., D-60329 Frankfurt)
- Screening of correct classification of textile auxiliaries in the three classes by an expert.
- A monitoring report on the effectiveness of the voluntary commitment which will be communicated to the authorities. For this purpose numbers and quantities of textile auxiliaries classified in classes I, II and III and sold in Europe are collected by a neutral consultant from the manufacturers.
- The triggering of market mechanisms towards the development of environmentally sounder products.

It is not claimed that the classification concept allows a differentiated ecotoxicological evaluation of textile auxiliaries. The purpose of the classification concept is rather to allow users to select textile auxiliaries also from ecological aspects. Ecological competition is intended to trigger a trend towards the development of environmentally more compatible textile auxiliaries. The German Association of the Textile Finishing Industry (TVI-Verband, D-Eschborn) is officially supporting this concept and has signed and published a self-commitment to recommend the textile finishing industries to use classified products only and preferably such of classes I and II [TVI-Verband, 1997].

A classification of the textile auxiliary is possible both on the basis of data of the preparation and on the basis of data of the ingredients by calculating mean values for the ingredients. For data to be newly determined, it is recommended to determine those data on the basis of the ingredients.



Scheme for the classification of textile auxiliaries according to their wastewater relevance - [TEGEWA, 1998]

Footnotes mentioned in the classification scheme:

1. Problematic substances are
1.1 CMR substances which are - according to Annex I to Directive 67/548/EEC -
   - classified as "carcinogenic" cat. 1 or cat. 2 and labelled with R45 (May cause cancer) or R49 (May cause cancer by inhalation),
   - classified as "mutagenic" cat. 1 or cat. 2 and labelled with R46 (May cause heritable genetic damage) or R60 (May impair fertility),
   - classified as "toxic for reproduction" cat. 1 or cat. 2 and labelled with R61 (May cause harm to the unborn child).

1.2 Ingredients which have an aquatic toxicity (definition see footnote 4) of < 0.1 mg/l and are not readily biodegradable (definition see footnote 3),
1.3 Low-molecular halogen hydrocarbons (halogen share > 5%, chain length C_1 - C_{12}),
1.4 Arsenic and arsenic compounds,
1.5 Lead and lead compounds,
1.6 Cadmium and cadmium compounds,
1.7 Tri- and tetra-organotin compounds,
1.8 Mercury and mercury compounds,
1.9 APEO,
1.10 EDTA, DTPA.
2. In connection with classifications made within this voluntary commitment, substances shall be considered "accumulative" which are labelled either with R-phrase 53 "May cause long-term adverse effects in the aquatic environment" alone, or with R53 in combination with other R-phrases.
3. Readily biodegradable =
OECD tests 301 A-F with $\geq$ 60% BOD/COD or CO_2 formation, respectively, or $\geq$ 70% DOC reduction in 28 days.
4. Aquatic toxicity of textile auxiliaries =
LC 50 daphnia (if not available to be substituted by fish).
5. Biodegradable/eliminable =
OECD test 302 B: $\geq$ 70% DOC reduction in 28 days, or
OECD test 302 C: $\geq$ 60% O_2 consumption, or
Proof of a $\geq$ 70% reduction in precipitation typical of sewage treatment plants.

Note:
For textile auxiliaries the evaluation "readily biodegradable (3)", "aquatic toxicity (4)", and "biodegradable/bioeliminable (5)" can be made not only on the basis of test data of the ready-for-use preparation but also on the basis of valid data obtained by calculating mean values for the various ingredients.

Main achieved environmental benefits

The classification method is to allow users to select textile auxiliaries also from ecological aspects.
The introduction of the method in Germany in 1998 has brought a clear reduction of class III products (Table 4.5).

	Number				Quantity [t/a]				Quantity [%]			
	1997	1998	1999	2000	1997	1998	1999	2000	1997	1998	1999	2000
class I	2821	3020	3242	3164	98446	105983	102578	104406	63	67	75	77
class II	1499	1485	1358	1258	29972	29422	23321	22103	19	18	17	16
class III	460	417	358	297	27574	23830	10231	9206	18	15	8	7
total	**4780**	**4922**	**4958**	**4719**	**155992**	**159235**	**136130**	**135715**	**100**	**100**	**100**	**100**

Table 4.5: Textile auxiliaries sold in Germany from 1997 to 2000: number, quantity and percentage of textile auxiliaries in the classes I, II and III - according to TEGEWA

This is a result of
- Substitutions of critical ingredients
- Withdrawals of class III products from the market

Two further remarks to the development from 1998 to 2000:
- the number of class I-products has increased while the quantity (in tons) has decreased because many new developed products have still a small turnover. In addition there is a downward economic trend.
- There is a big decrease of the quantity (in tons) of class III-products while there is only a small decrease of the number of class III-products. The producers of textile auxiliaries started first to substitute problematic substances and to avoid a "high relevance" classification of such textile auxiliaries having a high turnover (priority setting). Besides this there is the downward economic trend.

Applicability

The method can be used without reservations at any time and anywhere in Europe for all textile auxiliaries.

Cross-media effects

There is no cross-media effect to be mentioned.

There are no adverse effects on the quality of textiles, because textile auxiliaries relevant to wastewater are only substituted by more favourable products if substitute products have the same properties where application technology is concerned.

Economics

Costs arise in the reformulation of textile auxiliaries and testing with regard to application technology. These costs vary depending on the product range and are difficult to estimate, but in Germany no major problems were encountered in this connection.

Reference literature

[Lepper, 1996]
Lepper, P.; Schönberger, H.
Konzipierung eines Verfahrens zur Erfassung und Klassifizierung von Textilhilfsmitteln
Abschlussbericht FKZ 10901210 zu einem Forschungsvorhaben im Auftrag des Umweltbundesamtes (1996) – not published

[TEGEWA, 1998]
Noll, L.; Reetz, H.
Gewässerökologisch orientierte Klassifizierung von Textilhilfsmitteln
Melliand Textilberichte 81 (2000) 633-635

[TVI-Verband, 1997]
Verband der deutschen Textilveredlungsindustrie, TVI-Verband, D-Eschborn
Official and published self-commitment concerning the classification of textile auxiliaries according to their wastewater relevance, dated 27.11.1997 (1997)

4.2.1.1.2 Emission factor concept

Description

In general, it is well known that the input of processes very often determine the output and emissions respectively. The cleaner production approach follows this basic recognition and promotes pollution prevention at source. According to this approach, in Germany, with respect to emissions to air, a so-called emission factor concept has been developed in co-operation between public authorities (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 concerns facilities for textile finishing (including drying devices) by heat setting, thermosol processes, coating, impregnation, and finishing. The aim of the concept is to minimise the air pollution potential of the applied textile auxiliaries and thus minimising emissions to air. A further aim of the concept is to receive clarity and transparency, knowledge and a better control on the emissions of the large amount of auxiliaries and recipes.

Normally, emissions are regulated by emission mass concentrations (mg substances/m^3 air) and emission mass flows (g substances/h). The emission factor-copncept defines substance emission factors and textile substrate-based emissions factors

Substance emission factors

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 chapter 3.5.4.2.1.

There is to differentiate between:

- fc giving the total emissions of organic substances expressed as total content of Carbon;
- and fs giving the emission of a specific substance in case of more toxic or carcinogenic organic substances or in the case of particular inorganic substances like ammonia, hydrogen chloride.

The substance emission factors has to be provided as product information (further to information in 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 (cancerogenic substances) exceeding 10 ppm is obligatory [TA-Luft, 1986]. They are either measured or calculated by a concept of the chemical industry [TEGEWA, 1994]. It is important to know, that in more than 90% of all cases the single components behave additionally.

Textile substrate-based emission factor

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 substances/kg textile substrate in case of more toxic or carcinogenic organic substances or in the case of particular inorganic substances like ammonia, hydrogen chloride.

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.

Examples for the calculation of textile substrate-based emission factors for typical recipes are given in Chapter 3.5.4.1.1.

Main achieved environmental benefits

The concept can be characterised as a self-learning integrated system to control and prevent air emission in textile finishing. Already during product and process design the system can be applied successfully.

In detail the main advantages are:

- Comparability of emission potential of auxiliaries (g emission/kg auxiliary)
- Comparability of emission potential of processes (g emission/kg textile)

- Information on and substitution of the recipes with a high emission potential
- Pre-calculation of emission potential of finishing recipes
- Identification of the main sources for process emission (proper priority setting!)
- Air/textile ratio (m^3/kg) can be reduced (energy saving!).

As a result of the concept, the following limit values can be met in textile finishing industry and are obligatory in Germany:

- 0.8 g organic C/kg textile (for substances categorised in class II and III item 3.1.7 TA-Luft), if the mass flow is equal to or higher than 0.8 kg C/h
- 0.4 g substance/kg textile (for substances categorised in class I item 3.1.7 TA-Luft (formaldeyde, acetic acid etc.)), if the mass flow is equal to or higher than 0.1 kg/h
- special limit values for carcinogenic and inorganic substances

Applicability
The concept is applied in Germany. It is suitable for facilities for textile finishing by heat setting, thermosol processes, impregnation, and finishing; for coating and technical textiles application is limited.

Cross media effects
There is no cross-media effect to be mentioned.

Reference plants
For nearly all textile auxiliaries on the common market the needed emission factors are available. About 10% are validated by measurements, 90% are calculated with respect to the acknowledged system of TEGEWA.

Operational data
In Germany the textile finishing mill has to check its recipes according to the emission factor concept at least one time a year.

Economics
Staff costs for calculating the finishing recipes according to the emission factor concept are negligible. There are no other costs for textile finishers. Cost savings due to substitution of auxiliaries are possible. In some cases installation of exhaust-air cleaning can be avoided.

Driving force for implementation
To pre-calculate emission potential of finishing recipes and to meet emission limit values are the main motivation for implementation of the emission factor concept.

Reference literature

[Bavaria, 1994]
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen
Anlage 1 zum UMS Nr. 8102-775-61749 vom 08.11.94

[LAI, 1997]
Bausteine für Regelungen bei Textilveredelungsanlagen, ed. Länderausschuss für Immissionsschutz, Erich-Schmidt Verlag, LAI-Schriftenreihe 17 (1997)

[Schmidt, 1995]
Schmidt, G.; Reinert, F.; Reichert, J.
Regulations on exhaust air emissions in textil finishing
Melliand Textilberichte - offprint 10/1995

[TA-Luft, 1986]
German Regulation based on the Air Act
Technical Instruction for maintaining clean air (1986)

[TEGEWA 1994]
N.N.
TEGEWA Leitfaden zur Berechnung von Emissionsfaktoren (1994)

4.2.1.1.3 Low emission preparation agents

Description

Man-made fibres cannot be produced and processed without auxiliaries. Preparation agents are applied on their way to yarns and fabrics (see also Annex I). In finishing esp. in pre-treatment (heat setting and washing) the preparation agents charge off-gas as well as wastewater. Conventional preparation agents are mainly based on mineral oils with their well known disadvantages concerning high add-on, low temperature stability, low biodegradability, and generation of non-sedimentable sludge in biological wastewater treatment.

Alternatives for the mineral oil containing conventional systems are low-emission preparation agents based on the following chemistry:

- polyester-/polyetherpolycarbonates
- special polyolesters or
- special steric hindered fatty acid esters.

(Low-emission preparation agents are defined as auxiliaries which under heat setting conditions (190 °C; curing time: 1.5 min; add-on adapted for the specific application) emit a maximum of 0.8 g C/kg textile (assumed air/textile ratio: 20 m³/kg) [Bavaria, 2001].)

Main achieved environmental benefits

A comparison of the emission behaviour between these new products and the conventional systems at heat setting of grey materials is given in Table 4.6.

Substance	Emission factor (app.) [g C/kg textile]	Concentration (app.) [mg C/m³]
Conventional products		
Mineral oils	10 - 16	500 – 800
Classic fatty acid esters	2 - 5	100 – 250
Optimised products		
Steric hindered fatty acid esters	1 – 2	50 – 100
Polyolesters	0.4 – 4	20 – 200
Polyester-/polyetherpolycarbonates	0.2 - 1	10 – 50

Table 4.6: Emission factors and corresponding Organic-C concentration in the off-gas
(Preparation add-on: 2%; air/textile ratio: 20 m³/kg; heat setting temperature: 190 °C; curing time 1.5 min)

In addition to the reduction of volatile compounds odour nuisance is minimised. The products are characterised by a better bioeliminiation/biodegradability compared to conventional preparation agents.

Applicability

Low emission preparation agents are applicable on PES, PA 6.6, PA 6, CV and cotton, wool and their blends with PES or CV. However, it should be noted that the applicability is fibre, yarn, fabric processing, and end-use specific. So normally, in all cases specific trials are essential.

Cross media effects

Emissions, which in former times charged the off-gas charge now the wastewater or remain on the product. But because of the lower quantities used and the good biodegradability of the new products the replacement will always bring benefits.

Reference plants
<u>Selection of suppliers:</u>

Agatex Feinchemie GmbH
A-4650 Lambach/Edt

BENJ^{N} Vickers & Sons LTD
GB-Leeds LS6 2EA

Chemische Fabrik Stockhausen GmbH
D-47705 Krefeld

Clariant GmbH
D-65926 Frankfurt am Main

Cognis Deutschland GmbH
D-40551 Düsseldorf

Dr. Th. Böhme KG
D-82538 Geretsried

GEMSAN
TR-34550 Halkali-Istanbul

Goulston Technologies, Inc.
USA-Monroe, NC 28110

Hansa Textilchemie GmbH
D-28872 Oyten

Schill & Seilacher GmbH & Co.
D-71009 Böblingen

Zschimmer & Schwarz GmbH & Co
D-56112 Lahnstein

<u>Selection of fibre/yarn producers:</u>

Inquitex S. A.
E-08006 Barcelona

Nurel S. A.
E-08007 Barcelona

Nylstar GmbH
D-24531 Neumünster

Nylstar CD Italy
I-20031 Cesano Maderno (MI)

Textilwerke Deggendorf GmbH
D-94459 Deggendorf

Trevira GmbH & Co KG
D-60528 Frankfurt am Main

Unifi Textured Yarns Europe LTD.
IRL-Letterkenny

Operational data

Yarn producer

- Some machine components have to be of refined steel.
- Esp. in case of polyester-/polyethercarbonate based agents compatibility problems with the conventional hydrophobic preparation systems require appropriate equipment cleaning.

Fabric producer

- Because of compatibility problems the equipment has to be cleaned carefully (esp. in case of polyester-/polyethercarbonate based auxiliaries).

Finishing mill

- Processes in pre-treatment have to be adjusted to the new preparation systems. Partly washing steps in pre-treatment can be simplified or omitted.

Economics

The following economic aspects affecting all members of the textile processing chain have to be taken into consideration:

Yarn producer

- Low-emission auxiliaries are high price products. However, this can be compensated by a lower add-on.

Finishing mill

- Saving of exhaust air cleaning equipment, simplified wastewater treatment and prevention of oil contaminated wastes will reduce investment, maintenance, and disposal costs.
- Cost savings due to the fact that partly washing steps can be simplified and that the operational reliability increases are to be expected.

Driving force for implementation

Minimising of off-gas loads caused by preparation agents and compliance to national regulations are the main reasons for the use of low emission preparation agents.

Reference literature:

[Bavaria, 2001]
Fischer, R.
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen
Written information to workshop “Textilveredlung” and TEGEWA (09.01.01)

[Dohrn, 1996]
Dohrn, W.; Winck, K.; Singendonk, O.; Ulmer, H.; Pölzl, W.
Neues Präparationssystem für PES-Filamente im Wirkwarenbereich
Melliand Textilberichte 77 (1996) 770

[Dohrn, 1998]
Dohrn, W.; Winck, K.
Neue emissionsarme, biologisch abbaubare Spinnpräparationen, Spulöle und Avivagen
Melliand Textilberichte 79 (1998) 130

[Dohrn, 1999]
Dohrn, W.
Praxiserfahrungen beim Einsatz umweltfreundlicher Präparationen
Melliand Textilberichte 80 (1999) 723

[EnviroTex, 1996a]
EnviroTex GmbH, D-Augsburg
Emissionsbeitrag von Präparationen
Bayerisches Staatsminsterium für Landesentwicklung und Umweltfragen, D-München (1996)

[EnviroTex, 1996b]
EnviroTex GmbH, D-Augsburg
Wirk/Maschenwarenprojekt
Bayerisches Staatsminsterium für Landesentwicklung und Umweltfragen, D-München (1996)

[EnviroTex, 1997]
EnviroTex GmbH, D-Augsburg
Einsatzmöglichkeiten thermostabiler Präparationen
Bayerisches Staatsminsterium für Landesentwicklung und Umweltfragen, D-München (1997)

[LfU, 2000]
Bayerisches Landesamt für Umweltschutz, D-Augsburg
Einsatz von thermostabilen Präparationen bei der Textilherstellung
Workshop, D-Augsburg (2000)

[Möbius, 2000]
Möbius, S.; Tiedemann, K.
Thermostabile Avivage für den Doppeldraht-Zwirnprozess
Melliand Textilberichte 81 (2000) 815

4.2.1.1.4 Application of biologically degradable/eliminable sizing agents

Description

In textile finishing industries finishing woven fabric, the COD-load in wastewater is caused to 30-70% by sizing agents. Sizing agents are applied to warp yarns before weaving in order to protect the yarns during the weaving process with its high mechanical stress. For the subsequent finishing processes, the sizing agents have to be removed practically completely. This removal is part of the textile pre-treatment and is called desizing. The amount of applied sizing agents can be minimised by applying prewetting of warp yarns (see 4.2.1.1.6). In addition, the add-on of sizing agents can be minimised by aimed selection of more efficient sizing agents which are usually synthetic polymers. In case of integrated mills, sizing agents may be recycled by ultrafiltration (see 4.2.1.2.2). However, in most cases, desizing liquors are discharged to wastewater which has to be treated. In most cases, treatment includes activated sludge. Thus, sizing agents should be biodegradable, or adsorbable to activated sludge at least. Developments in Switzerland have demonstrated that there are several combinations of different sizing agents available to cover all different kind of substrates, woven fabrics and weaving techniques. There are seven combinations that meet both application requirements and demands on biological degradation and elimination respectively. Figure 4.7 shows bioelimination curves for these seven combination consisting of modified starch, certain polyacrylates (which are not biodegradable but adsorbable to activated sludge), polyvinyl alcohol and certain galactomannans.

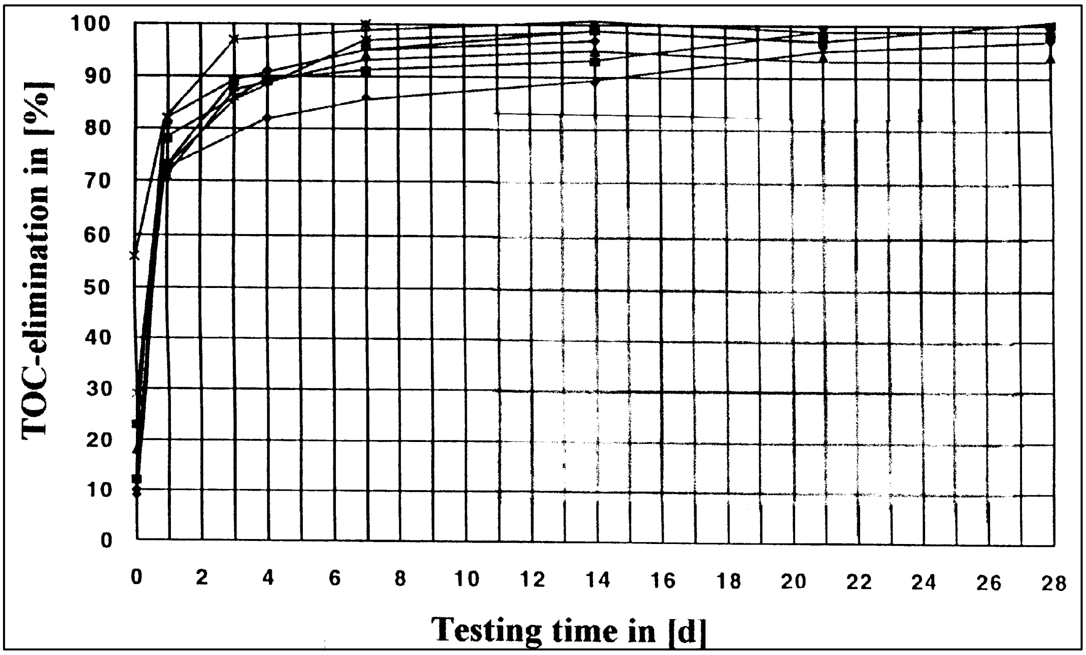


Figure 4.7: Bioelimination curves in the modified Zahn-Wellens-Test (EN 29888) of seven combinations of different sizing agents which are bioeliminated to more than 80% after 14 days - [Keller, 1992]

The testing method is the modified Zahn-Wellens-Test (EN 29888). The results (elimination rates after 14 days) can be transferred to real existing activated sludge systems.

All Suisse weaving mills have introduced one or several of these sizing agents combinations into practice and are applying them successfully.

Main achieved environmental benefits

The application of biodegradable/bioeliminable sizing agents lead to significant reduction of COD-load in the treated effluent of biological wastewater treatment plants to be discharged to natural waters.

Applicability

The described sizing agent combinations are applicable both to new and existing installations and cover most of the different kind of substrates, woven fabrics and weaving techniques.

Cross-media effects

Increased bioelimination/biodegradation and adsorption to sludge increase the amount of sludge to be disposed off. In many cases sludge is disposed on secured land-fills and is increasingly incinerated in plants according state-to-the-art. In case of biodegradation at low F/M-ratio, the compounds are converted to carbon dioxide, nitrate (in case of nitrogen-containing sizing agents), water and biomass. The disposal of the latter causes less problems than the application of non- or heavily biodegradable compounds

Reference plants

All the about twenty weaving mills in Switzerland apply one or several of these combinations of biodegradble/bioeliminable sizing agents. Also many weaving mills in Germany and Europe are applying such combinations successfully.

Operational data

The described combinations meet all the production requirements such as weaving efficiency, low dust generation, applicability to high speed weaving machines etc.

Concerning polyvinyl alcohol, it has to be stressed, that biodegradation needs certain system conditions of the activated sludge system such as adaptation, temperatures more than 15°C and especially low F/M-ratios (see 4.2.2.2.1).

Economics

In most cases, biodegradable/bioeliminable combinations of sizing agents are not more expensive than others not meeting the high elimination rates.

Driving force for implementation

The need to minimise discharged COD-loads to natural water and increasing awareness for environmental protection have been the main driving forces.

Reference literature

[Keller, 1992]
Tobler, H.P.; Baumann, U.; Bosshart, U; Keller, W.
Die Entwicklung umweltfreundlicher Schlichtemittel
Textilveredlung 27 (1992) 238-241

4.2.1.1.5 Minimisation of add-on of sizing agents by selection of more efficient products

Description

Sizing agents optimise the weaving process in terms of weaving efficiency and low warp thread breakage (resp. reduced loom stops). Desizing liquors load the effluent in finishing mills to a considerable amount (in finishing of woven fabrics COD load caused by desizing liquors is in a range between 30–70%).

As a first approach to minimise effluent load caused by sizes the minimisation of size add-on by means of process control (on-line monitoring/control of size add-on in sizing), prewetting technology (see 4.2.1.1.6), and other integrated measures in upstream yarn and fabric processing should be considered. On the other hand, if yarns with different technological properties can be accepted, yarns manufactured by compact spinning (see 4.2.1.1.12), high twisted yarns, intermingled yarns and plaid yarns which can be produced without or with a reduced amount of sizing agents are to be taken into consideration.

Ecologically optimised sizing agents have to fulfil the following requirements:

- High efficiency with low add-on
- Complete and easy removable from the fabric (low energy, temperature, and water consumption in desizing, reduced re-works and bad-works caused by insufficient desizing)
- High degree of bioelimination.

Changes in size recipes resp. use of high efficient synthetic sizes instead of natural starch esp. in the spun yarn segment can reduce size add-on, ecological loads in desizing without a decline in weaving efficiency. In some cases even increased weaving efficiency can be achieved.

Main achieved environmental benefits

Substantial reduction of COD-load caused by desizing liquors can be achieved (example in Table 4.7):

	Common recipe (modified starch, wax)	**Alternative recipe (modified starch, polyacrylate, wax)**
Size add-on	13%	10%
Specific COD	17800 g O_2/100kg warp yarn	11550 g O_2/100 kg warp yarn
Total COD/a	713 t	462 t
Reduction of COD-load	-	35%

Table 4.7: COD reduction after change in size recipe (calculated on an annual production of 4000 t warp yarn) - [Steidel, 1998]

Applicability

Regarding the world-wide textile chain it is hardly possible for non-integrated finishing mills esp. commission finishers to influence upstream weaving mills. However change to optimized recipes is possible for all sizing departments.

Cross-media effects

There are no cross-media effects to be mentioned. However, if alternative size recipes are used bioelimination degree of the sizes should be above 80% after 7 days according to OECD 302 B.

Reference plants

Ecologically optimised sizing agents are used in weaving mills world-wide. Various suppliers deliver ecological optimised sizing agents.

Operational data

A wholly synthetic universal size recipe for sizing staple fibre yarn (air jet loom, 650 rpm) is given below:

- Modified PVA: 7 kg
- Acrylate (liquid; 25%): 7 kg
- Wax: 0.4 kg
- Water: x kg
- Volume sizing liquor: 100 l
- Size add-on: 10%
- Nip pressure: 20 kN
- Sizing velocity: 100 m/min

Economics

In weaving mills higher prices for synthetic high efficiency sizes are compensated by cost savings due to a higher weaving efficiency (example in Table 4.8):

Costs/Savings per year /warp thread breakages	Common recipe (modified starch, wax)	Alternative recipe (acrylate, modified PVA, wax)
Costs for sizing agents	260,850 EURO	325,850 EURO
Warp thread breakages	5.8 thread break/10^5picks	3.0 thread break/10^5picks
Savings due to minimized thread breakages	-	225,000 EURO
Total savings	-	160,000 EURO

Table 4.8: Cost savings per year in a typical weaving mill (100 weaving machines, 310 rpm, 8000h/a) - [Steidel, 1998]

Driving force for implementation

In weaving mills substitution of conventional size recipes is economically motivated. In textile finishing COD-reduction and savings in energy and water consumption in desizing are the main items.

Reference literature

[Steidel, 1998]
Steidel, V.
Polyacrylatschlichten – Fokussierte Rezeptgestaltung im Stapelfaserbereich
13. Int. Symposium über das Schlichten, 16./17. Juni 1998, D-Denkendorf (1998)

4.2.1.1.6 Minimisation of add-on of sizing agents by prewetting the warp yarns

Description

In prewetting the warp yarn is run through hot water before sizing. The warp yarn is dipped into the hot water, additional spraying of hot water is possible. A squeeze roller provides the following sizing process for water surplus. Systems with two washing baths and two dipping and squeezing steps are also in use. The principal of prewetting devices is shown in Figure 4.8.

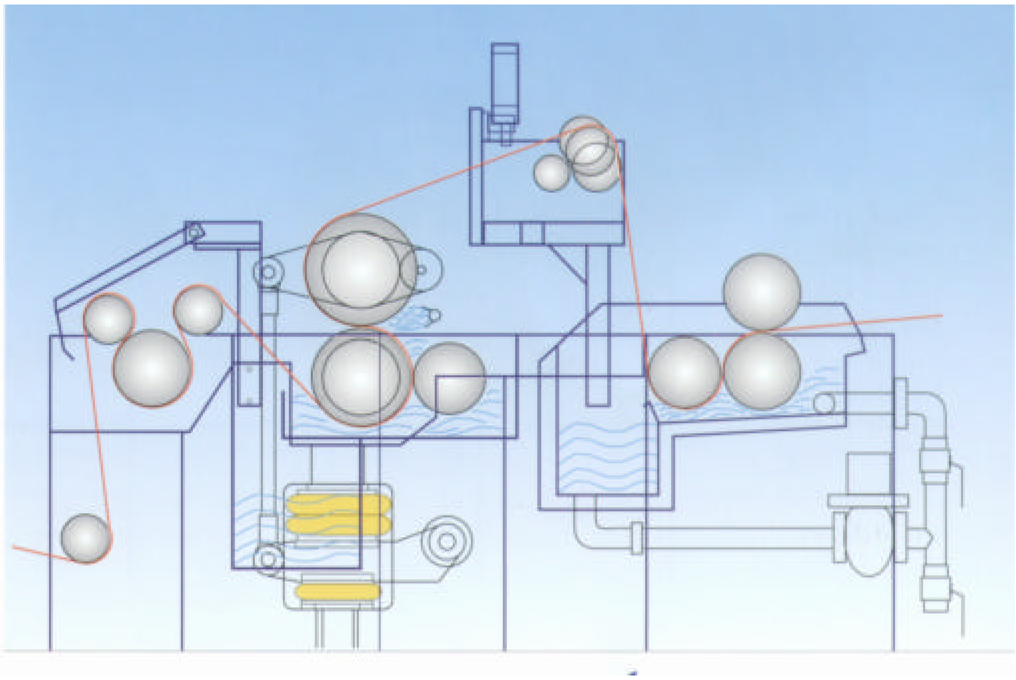


Figure 4.8: Combination of a prewetting and sizing box [Benninger, 2000]

Prewetting results in a more homogeneous sizing effect (lower amount of "core-sizing" is assumed), an increased adhesion of the size, and reduced hairiness and in consequence in a lower size add-on without affecting weaving efficiency. In some cases even an increase in weaving efficiency can be observed.

Main achieved environmental benefits

Benefits by prewetting arise from a considerable reduction of the size add-on. Thereby wastewater charge in pre-treatment is minimised (it is well-known that the desizing process is responsible for 30-70% of the wastewater charge of cotton processing finishing mills).

Depending on the setting of the warp beam and the warp yarns a reduction of the size add-on of about 20-50% is possible.

Applicability

Prewetting is tested in the practice with all cotton yarns as well as with blends of cotton/PES and viscose. Best results are achieved with medium to coarse yarn titres. Applicability is given for ring-spun yarns as well as for OE-yarns. Limited use is observed for dyed yarns. Existing sizing machines with two sizing boxes can be reconstructed by using the first sizing box for prewetting.

Cross media effects

No cross media effects are to be expected.

Reference plants

World-wide about 100 prewetting boxes are sold by Benninger Zell GmbH, Zell, Germany.

About 60 prewetting boxes of Deutsche Babcock Moenus Textilmaschinen AG, Mönchengladbach are running in 40 plants. Another supplier for prewetting systems is Karl Mayer Textilmaschinenfabrik GmbH, Obertshausen, Germany.

Economics

Additional investment costs for a sizing equipment with prewetting boxes are around 25,000 – 75,000 EURO compared to sizing equipment without prewetting. Operating costs are only marginally higher, because the additional expenditure for providing the prewetting water is parallel to the reduction of the sizing liquor consumption.

A direct comparison between sizing with and without prewetting (operational data of an Italian weaving mill) shows cost savings of about 27%, an increase in sizing machine speed of about 22%, and an increase in weaving efficiency of about 0.2%.

Driving force for implementation

Savings in consumption of sizing agents, increase of weaving efficiency, as well as reduction of the wastewater charge are the main reasons for implementation the prewetting technology.

Reference literature

[Babcock, 2000]
Voswinckel,G.
23. Int. Textile Conference, Slovakia (30.05-01.06.2000) (2000)

[Benninger Zell, 2000]
Product information on SaveSize and SaveSizecombi (2000)

[Benninger Zell, 2001]
Scherrer, A.
Written information after a request on IPPC-techniques (2001)

[ITV, 1998]
Abele, H.; Guo, J.; Trauter, J.; Schäfer, T.; Stegmaier, T.; Wunderlich, W.
Highlights aus der Schlichtereiforschung des ITV Denkendorf
13. Int. Schlichterei-Symposium, Denkendorf (16./17.06.1998) (1998)

[Karl Mayer, 2001]
Keimig, M.
Written information after a request on IPPC techniques (2001)

[Scherrer, 2001]
Scherrer, A.
Schlichtemittel-Einsparungen und verbessertes Laufverhalten durch Vornetzen
Melliand Textilberichte 82 (2001) 47-48

4.2.1.1.7 Environment-friendly surfactants

Description

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, non-ionic, cationic and amphoteric) are in use. However, anionic and non-ionic dominate. Surfactants in textile industry serve mainly as detergents, wetting agents, deaeration agents, levelling agents, dispersing agents, softening agents, emulsifying agents, spotting agents, anti-electrostatics, aftertreatment agents for fastness improvement, felting agents, fixing acceleration agents for continuous dyeing and printing.

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, emulsifiers in preparation agents etc.).

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, alkylnaphthol.

Cationic surfactants:
derivatives of quaternary ammonia salts.

Amphoteric surfactants (very rare):
Betain derivatives.

Due to their surface activity, aquatic toxicity of surfactants has to be taken into account. Fish toxicity between different types of surfactants can vary within a large range. For non-ionic surfactants with increasing ethylene oxide part, fish toxicity decreases but biodegradation decreases also [Schöberl, 1988; Stache 1990]. Cationic surfactants have by far highest fish toxicity compared to other classes of surfactants.

The rate of biodegradation also strongly depends on the chemical structure of the surfactants. For non-ionic surfactants chain length and number of side chains is a crucial point.

Substances with a low rate of biodegradation/bioelimination are adducts of ethylene oxide and propylene oxide (EO/PO´s; mainly used in preparation agents), lignine sulfonates and condensation products of naphthaline sulfonic acid and formaldehyde (mainly used as dispersing agents in dyestuffs and as levelling agent and aftertreatment agent for fastness improvement) and in the majority of cases fatty amine ethoxilates (mainly used in levelling agents).

The ethoxy chain in alkyl phenolethoxilates (APEO´s) is readily biodegradable but nonylphenol which is the main intermediate compound during biodegradation shows a very low degree of biodegradation, a high fish toxicity and reproductive toxicity [Schäfer, 1996]. Therefore TEGEWA (German association of textile auxiliaries suppliers) and other German associations decided in 1986 to phase out APEO´s in detergents [TEGEWA, 1986].

To minimise ecological load in wastewater caused by surfactants the following principles should be regarded:

- No use of APEO-containing products (with exception to APEO- containing coating pastes which are not released to wastewater).
- Use of readily biodegradable surfactants (OECD 301A-F tests: pass level > 60 resp. 70%; OECD 303 A: DOC or COD degradation > 80%; mod. Zahn-Wellens test: DOC-elimination > 80% in 7 days) if effectiveness of products is comparable to common products. For the choice of the products the ARS classification scheme (4.2.1.1.1) can be helpful.
- Aquatic toxicity of the products should be taken into consideration as well as possible critical by-products concerning working place atmosphere.

Main achieved environmental benefits

Degree of biodegradation of wastewater increases. Fish toxicity of the wastewater is reduced.

Applicability

There are manifold application fields for surfactants in textile finishing. Recipes and application techniques are process specific. There is no general difference for the application of ecologically optimised products. However if common surfactants are substituted by more environment-friendly products the process reliability and possible differences in effectiveness of the products should be regarded.

For textile finishing industries, the influence on the selection of surfactants is low if the products are used only as additives in textile auxiliaries and dyestuffs and a declaration in the Health and Safety Data Sheet is not needed.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

Various textile finishing industries in Germany as well as throughout the world use ecological optimised surfactants.

APEO-free surfactants and surfactants with a good biodegradability are delivered from many suppliers in Germany as well as world-wide.

Economics

Costs for ecological optimised products are comparable to costs for common products. However in some cases, a higher application amount has to be considered.

Driving force for implementation

Improvement of the environmental performance and national or local regulations are the main reasons for the use of more environment-friendly surfactants.

Reference literature

[Schäfer, 1996]
Schäfer, W.R.; Zahradnik, H.P.; Frijus-Plessen, N.; Schneider, K.
Anthropogene Substanzen mit unerwünschter Östrogenwirkung
Umweltmedizin 1 (1996) 35-42

[Schöberl, 1988]
Schöberl, P.; Bock, K.J.; Huber, L.
Ökologisch relevante Daten von Tensiden in Wasch- und Reinigungsmitteln
Tenside Detergents, Sonderdruck (1988) 86-107

[Stache, 1990]
Stache, H.; Kosswig, K. (ed.)
Tensid-Taschenbuch
Carl Hanser Verlag, München (1990)

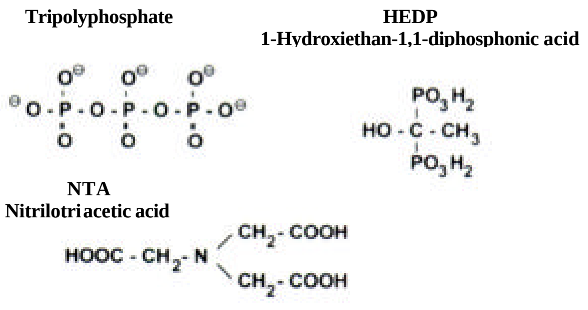
[TEGEWA, 1986]
Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoffindustrie and other German Associations
Freiwillige Verzichtserklärung auf Alkylphenolethoxylate (APEO)
D-Frankfurt/Main (1986)

4.2.1.1.8 Biodegradable/bioeliminable complexing agents for pre-treatment and dyeing processes

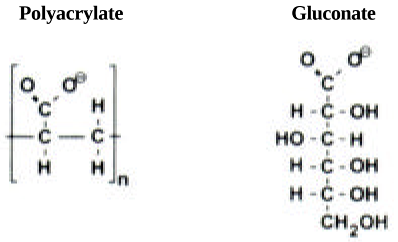
Description

Complexing agents (chelating agents) are applied to mask hardening alkaline-earth cations and transition-metal ions in aqueous solutions in order to eliminate their damaging effect esp. in pre-treatment processes (e.g. catalytic destruction of hydrogen peroxide).

Chemistry of conventional complexing agents is based on polyphosphates (e.g. tripolyphosphate), phosphonates (e.g. 1-hydroxyethane 1,1-diphosphonic acid) and amino carboxylic acids (EDTA, DTPA, and NTA). They all contain nitrogen and phosphorous in their chemical formula. With regard to restrictions on total-N and total-P in wastewater regulation N- and P-free products are convenient alternatives. Polycarboxylates resp. substituted polycarboxylic acids (esp. polyacrylates and polyacrylate-maleinic acid copolymerisates), hydroxy carboxylic acids (esp. gluconates, citrates) and sugar-acrylic acid copolymers are in use (Figure 4.9). The hydroxy carboxylic acids and sugar-acrylic acid copolymers have the additional advantage of ready biodegradability.



Structure of N-or P-containing complexing agents



Structure of N-and P-free complexing agents

Figure 4.9: Chemical structure of complexing agents [Bachus, 1999]

Selection of the best (in a technical, economical, and ecological sense) complexing agent for a special application affords that ecological properties and effectiveness (capacity to complex alkaline-earth cations, dispersing capacity, capacity to stabilise peroxide) are well balanced.

From the ecological point of view the following parameters are to be considered

- Biodegradation
- Bioelimination
- Remobilisation of heavy metals
- Ammonia content (eutrophication potential)
- Phosphorous content (eutrophication potential)

Main achieved environmental benefits

A qualitative assessment on the ecological properties of complexing agents is given in Table 4.9

Ecological properties	**EDTA, DTPA**	**NTA**	**Polyphosphate**	**Phosphonates**	**Poly-carboxylates**	**Hydroxy carboxylic acid**	**Sugar copolymers**
Biodegradation	No	Yes	Inorganic	No	No	Yes	Yes
Bioelimination	No	-	-	Yes [Nowack, 1997]	Yes	-	-
N-content	Yes	Yes	No	No	No	No	No
P-content	No	No	Yes	Yes	No	No	No
Remobilisation of heavy metals	Yes	Possible	No	No	No	No	No

Table 4.9: Qualitative assessment of different available and applied complexing agents - [Bachus, 1999]

Rate of bioelimination/biodegradation for phosphorous and nitrogen-free products is shown in the following examples:

- Sugar-acrylic acid copolymer: readily biodegradable, mineralisation: 100% (OECD 301 F): COD: 194 mg O_2/g; BOD_5 40 mg O_2/g [CHT, 2000]
- Sugar acrylic acid copolymer: readily biodegradable (OECD 301C); COD: 149 mg O_2/g [Stockhausen, 2000]
- Hydroxy carboxylic acid: elimination: 92% (OECD 302 B); COD: 144 mg O_2/g; BOD_5 51 mg O_2/g [CHT, 2000]
- Carboxylates: elimination > 90% (OECD 302 B); COD: 280 mg O_2/g; BOD_5 125 mg O_2/g [Petry, 1998]
- Modified polysaccharide: biodegradability 80% (OECD 301E) COD: 342 mg O_2/g; BOD_5 134 mg O_2/g [Clariant, 2000]

Applicability

Substitution of common complexing agents by more environmental friendly products should be done regarding the different effectiveness of the products (Table 4.10).

Properties	**EDTA, DTPA**	**NTA**	**Poly-phosphate**	**Phosphonate**	**Poly-carboxylates**	**Hydroxy carboxylic acid**	**Sugar copolymers**
Softening	+	+	+	++	+	0	+
Dispersing	-	-	0	0	+	-	+
Stabilisation of peroxide	+	-	-	++	0	-	+ (special products)
Demineralisation	++	+	0	++	0	0	0

**Table 4.10: Effectiveness of complexing agents - [Bachus, 1999]
(effectiveness increases in the following order -, 0, +; ++)**

Ecologically optimised products can be used in continuous and discontinuous processes.
It is to be noted that softening of fresh water in textile finishing should be carried out generally with ion exchangers.

Cross-media effects

In general there are no cross-media effects to be mentioned if N- and P-containing products are substituted. However for polyacrylate containing products residual monomer content in the polymer should be regarded.

Reference plants
N- and P-free complexing agents are applied world-wide. Consumption of polycarboxylates is significant higher than for sugar-acrylic copolymers and hydrocarboxylic acids.

Operational data
There are several application fields for complexing agents in textile chemistry. Recipes and application techniques are process specific. However there is no principal difference if ecologically optimised products are used.

Economics
Costs for N- or P-free compounds or especially for sugar-acrylic copolymers are comparable to other N- and P-free products. However in some cases, higher quantities may be necessary.

Driving force for implementation
Emission limit values for total-N and total-P in national and regional regulations are the main reason to change to N- and P-free complexing agents.

Reference literature

[Bachus, 1999]
Bachus, H.
Komplexbildner für den Markt von morgen
Melliand Textilberichte 80 (1999) 404-408

[CHT, 1999]
Chemische Fabrik Tübingen, D-Tübingen
Material Safety Data Sheet (1999)

[CHT, 2000]
Chemische Fabrik Tübingen, D-Tübingen
Product information (1999)

[Ciba, 1999]
Ciba Speciality Chemicals
Product information (1999)

[Clariant, 2001]
Clariant, D-Lörrach
Material Safety Data Sheet (2001)

[Stockhausen, 2000]
Stockhausen, D-Krefeld
Material Safety Data Sheet (2000)

[Novack, 1997]
Novack, B.
The behaviour of phosphonates in wastewater treatment plants in Switzerland
Water Research 32 (1998) 1271-1279

[Petry, 1998]
Dr. Petry, D-Reutlingen
Material Safety Data Sheet (1998)

4.2.1.1.9 Dispersing agents with higher bioelimination rates

Description

Disperse dyes are only sparingly soluble in water. To achieve an uniform dispersion which is not affected by temperature and shearing stress dispersing agents are added to disperse, vat and sulphur dyestuff formulations. Lignine sulfonates and condensation products of naphthalene sulfonic acid with formaldehyde are mainly in use. The dispersing agents do not have affinity to the fibres and contribute to a considerable amount to the problematic wastewater load in textile finishing (average COD: 1200 mg O_2/g (lignine sulfonates), resp. 650 mgO_2/g (naphthalene sulfonic acid condensation products).

Elimination in biological wastewater treatment is insufficient for both products. Thus, they contribute to residual (recalcitrant) COD in treated wastewater.

Disperse dyes in powder or granulated form contain 30-50 (in some cases up to 70%) of dispersing agents; disperse dyes in liquid form contain 10-30%. Usually, in case of dark shades, no additional dosage of dispersing agents is required whereas this may be necessary for pale shades. The quantities in vat and sulphur dyestuffs may be similar but precise information is not available.

There are two approaches to increase the bioelimination/biodegradation rate of dispersing agents. With the improved dispersing agents conventional dispersing agents can be substituted in the dyestuff formulations to an extend of max. 70%.

A)

Chemistry of optimised dispersing agent is based on fatty acid esters. A mixture of dispersing agents is applied and fatty acid esters are the main components. To date, this improvement is only for liquid formulations of disperse dyestuffs. The dispersing capacity of the product is improved; compared to conventional liquid dyestuff formulation. This means, that the concentration of dyestuffs per litre is significantly higher. Thus, the tinctorial strenght can be increased from 100% to 200%. In other words, the amount of dispersing agents in dyestuff formulations can be significantly reduced [Grütze, 2000].

B)

An alternative to common dispersing agents for powder and granulate formulations are dispersing agents based on mixtures of the sodium salts of aromatic carbon and sulfonic acids [Kilburg, 1997]. It is told that these products are modified common condensation products of naphthalene sulfonic acid with formaldehyde. This chemical modification leads to higher bioelimination rates because of increased adsorption rate to biomass. However they remain to be non-biodegradable.

Main achieved environmental benefits

A)

According to Modified Zahn-Wellens-Test (OECD 302 B), bioelimination rates are between 90 and 93%.

A comparison between common disperse dyestuff and optimised dyestuff formulations (average values considering the whole dyestuff palette) is given in Figure 4.10. Differences in tinctorial strength are taken into account.

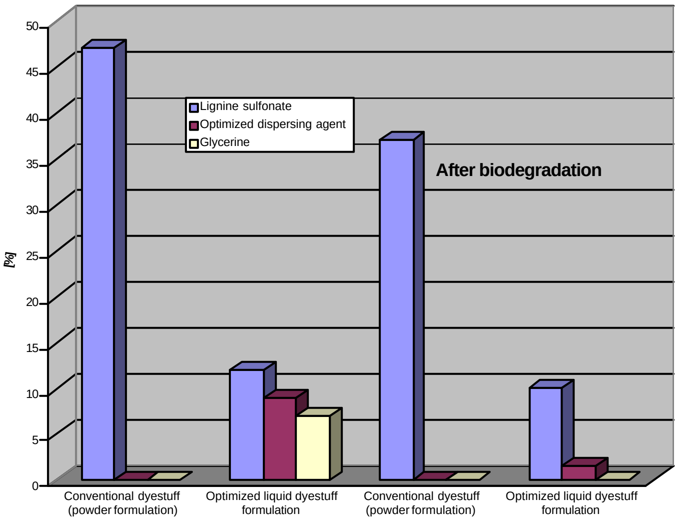


Figure 4.10: Comparison between the composition of conventional and new liquid formulations of disperse dyestuff types (before and after biological treatment) - [Grütze, 2000]; [%] means percentage of dispersing agents/glycerine related to the total formulation

B)
Figure 4.11 compares the bioelimination rates of conventional condensation products of naphthalene sulfonic acid with formaldehyde and the modified optimised ones. The degree of bioelimination of the modified dispersing agent is about 70% (test method according to OECD 302 B) compared to 20-30% of the conventional one.

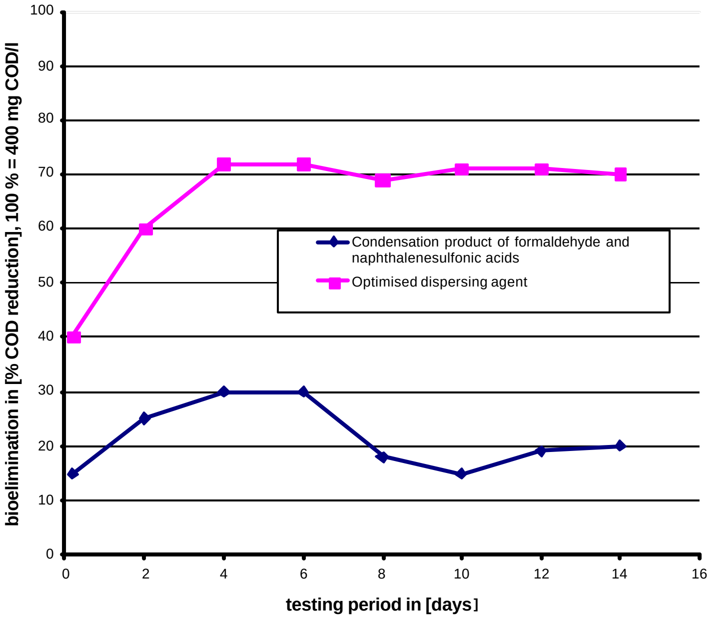


Figure 4.11: Comparison of biolelimination rates of conventional and modified dispersing agents which both base on condensation products of naphthalene sulfonic acid with formaldehyde - [Kilburg, 1997]

Applicability

Concerning case A), there are only liquid formulations of disperse dyestuffs available; there is no restriction in application fields with exception that the dyestuff palette is currently limited.
Concerning case B), these dispersing agents can be used both for disperse and vat dyestuffs (solid and liquid formulations).

Cross-media effects
There are no cross-media effects to be mentioned.

Reference plants
The ecologically advanced dyestuffs are in use in German finishing mills and world-wide as well.

Operational data
The ecologically optimised disperse dyes can be used similar to conventional disperse dyes.

Economics
The costs for the dyestuffs are higher compared to conventional liquid dyestuff formulations.

Driving force for implementation
Improvement of the environmental performance is the main motivation to use dyestuffs with a better degree of bioelimination.

Reference literature
[Grütze, 2000]
Grütze, J.
Eine neue Generation von Dispersionsfarbstoffen
Off print, DyStar Textilfarben , D-Leverkusen (2000)

[Kilburg, 1997]
Kilburg, H.
Innovative, Ecologically Advanced Dyeing of Polyester Fibres
Offprint, BASF AG, D-Ludwigshafen (1997)

4.2.1.1.10 Antifoaming agents

Description
Antifoaming agents prevent the formation of foam or destroy an existing foam. They are used in pre-treatment as well as in dye baths (esp. in jets), finishing liquors, and printing pastes. Antifoaming effects can be reached by products which are insoluble in water and have a low surface tension. They displace foam producing surfactants from the air/water boundary layer.
Antifoaming agents are often based on mineral oils (hydrocarbons). Typical active ingredients of alternative products are silicones, phosphoric acid esters (esp. tributylphosphates), fatty acid compounds, high molecular alcohols, fluorine derivatives, and mixtures of these components.

Main achieved environmental benefits
If alternative products are used, hydrocarbon content in wastewater- often limited in national/regional regulations - is minimised. Specific COD of the alternative products is lower compared to hydrocarbon-containing products; the alternative products can have a high bioelimination rate. For example, a product with a chemistry based on triglycerides of higher fatty acids and fatty alcohol ethoxylates (COD: 1245 mg/l; BOD_5: 840 mg/l) is eliminated in biological wastewater treatment to an amount of more than 90% (determined in the modified Zahn-Wellens-Test according to OECD 302 B). Furthermore organic-carbon content (VOC) caused by carry-over of the antifoaming agents into thermal processes (esp. drying after dyeing, heatsetting and finishing) is reduced.

Applicability
The products can be applied similar to conventional products. Effectiveness has to be regarded. If antifoaming agents based on silicones are used operational reliability (danger of silicone spots on the textile and silicone precipitates in the machinery) should be regarded.

Cross-media effects
It has to be taken into account that silicones are eliminated only by abiotic processes in wastewater and tributylphosphates are smell intensive and strongly irritant. Also high molecular alcohols are very smell intensive and can therefore not be used in hot liquors. Achieving certain concentrations, silicone oils may reduce oxygen input in activated sludge plants for wastewater treatment.

Reference plants
The alternative antifoaming agents are in use in German finishing mills and world-wide as well. There are various suppliers for these products.

Operational data
The products can be used similar to conventional products. If silicone products are used normally, due to the high effectiveness of these products, the required quantity can be reduced to a considerable amount.

Economics
Prices of mineral oil free products are similar to conventional products.

Driving force for implementation
Minimisation of hydrocarbons in the effluent as well as a reduction of the VOC content in the off-gas are the main reasons to substitute mineral oils containing antifoaming agents.

Reference literature
[Dobbelstein, 1995]
Optimierung von Textilhilfsmitteln aus ökologischer Sicht. Möglichkeiten und Grenzen
Nordic Dyeing and Finishing Conference 20.05.1995, F-Hämeenlinna (1995)

[Petry, 1999]
Dr. Petry GmbH, D-Reutlingen
Material Safety Data Sheet

4.2.1.1.11 Catalysts for polyester fibres

Description

The polymerisation reaction of polyethyleneterephthalate (main polyester type used in the textile industry) is carried out with catalysts based on antimony oxides or antimony acetates in more than 99,9% of the PES production world-wide. Antimony content in commercial PES fibres is in the range 200 to 300 ppm. In wet pre-treatment processes, HT-dyeing, and in alkalisation of PES some of the catalyst can be washed out.

PES fibres can also be produced with catalysts based on hydrolytically stable titanium/silicon mixed oxides or esters of the titanoic acid, components with no adverse health or environmental effects as far as known. A reduced antimony content compared to the well established antimony compound catalysts can be found. [Thier-Grebe, 2000].

Main achieved environmental benefits

The antimony content in the effluent of a finishing mill is summarised in Table 4.11 for PES fibres made with antimony and titanium based compound catalysts.

	Antimony content [µg/l]	
Process	**Sb compound catalyst**	**Ti compound catalyst**
Washing	12 ± 3	< 5
Rinsing	< 1	< 1
Dyeing (130 °C, 60 min)	2000 ± 70	< 3
Reductive after-treatment	16 ± 2	5 ± 2

Table 4.11: Antimony content in wastewater [Thier-Grebe, 2000]

Applicability

The fibre made with titanium compound based catalyst is only suited for a limited number of applications, especially where colour and dyeability are not required. PES fibres made with titanium compound based catalyst shows nearly the same mechanical properties as antimony compound based catalyst PES fibres (however ageing resistance in practise has to be proofed). The fibre made with titanium compound based catalyst can be converted like antimony compound based catalyst PES fibre types; e.g. for lower quality fibrefill and some non-woven products. However, there are limitations for the use of titanium compound based catalyst polyester fibres when good light fastness is required, e.g. for white polyester curtains.

Cross-media effects

To overcome the yellowish colour, optical brighteners have to be used.

Reference plants

Titanium compound catalyst based PES yarns are manufactured by TWD-KUAG, D-Deggendorf and Du Pont Sabanci Polyester GmbH. Weaving/finishing mills using these PES fibres include Schoeller, CH-Sevelen and Formosa Taffeta, TW-Touliu. Suppliers for catalysts are Acordis Industrial Fibers GmbH and Du Pont de Nemours (Deutschland) GmbH [Acordis, 2000; Du Pont, 2001].

Economics

The price of titanium compound catalyst based PES fibres is higher compared to the antimony compound based ones. But some advantages in dyeing lead to energy saving and dye stuff reduction: dyeing at lower temperature (at the same dyeing time), shorter dyeing cycles (at the same dyeing temperature), or reduced dyestuff concentration (at the same dyeing time and temperature).

Driving force for implementation

Titanium compound catalyst based PES yarns are manufactured on account of entrepreneurial initiatives.

Reference literature

[Acordis, 2000]
Acordis, D-Wuppertal
PET catalyst Titan Dioxide Based “C94”
Product information, 2000

[Du Pont, 2001]
Du Pont de Nemours /Deutschland) GmbH, D-Bad-Homburg
Personal information

[Thier-Grebe, 2000]
Thier-Grebe, R.; Rabe, M.
Polyester mit neuem Titandioxid-Katalysator
Melliand Textilberichte 81 (2000) 977-980

4.2.1.1.12 Compact spinning

Description

Normally, in ring spinning, after the draft system a spinning triangle is generated. In the moment of passing the spinning triangle the fibres are not strengthened by twisting. Yarn breaks and yarn hairiness occurs. In compact spinning the fibre strands are compressed after the draft system by means of pneumatic devices (application of low pressure) [Artzt, 1995]. A higher yarn quality results (increased fibre strength and elongation, reduced hairiness, increased abrasion resistance).

Main achieved environmental benefits

Compared to conventional ring spun yarns, compact yarns have better running properties and less thread breaks during weaving even if the size add-on is reduced up to 50%. This leads to a considerable reduction in wastewater load in desizing. Due to the reduced hairiness, paraffine-application of yarns to be knitted is no longer necessary [Binternagel, 2000].

Applicability

Applicability is proofed for pure cotton yarns. It has to be mentioned that appearance and technological properties of compact spinning yarns (and also of fabrics made of them) are different compared to conventional manufactured yarns. The lower hairiness of the yarns is in case of yarns which are produced for knitted goods an undesired effect. Reconstruction of existing spinning machines is partially possible.

Reference plants

At time around 250.000 spindles are installed, mostly in Italy [ITV, 2001]:
Compact spinning machines are manufactured by

- Rieter Textile Systems, CH-Winterthur
- Zinser Textilmaschinen, D-Ebersbach
- Spindelfabrik Süssen, D-Süssen

Cross media effects

There are no cross media effects to be mentioned.

Economics

Additional yarn costs are compensated partially or totally by cost savings in weaving mills due to a better weaving efficiency and reduced size add-on. Reduced costs in finishing are assumed (e.g. lower dyestuff consumption) [Binternagel, 2000].

Driving force for implementation

A better yarn quality and the possibility to create new effects/designs are the main reasons for installing compact spinning machines.

Reference literature

[Anonymous, 2000]
Verdichtungsspinnen lässt Kosten sinken und Qualität steigen
Melliand Textilberichte 81 (2000) 701

[Artzt, 1995]
Artzt, P.; Betz, D.; Schneider ,J.; Sonntag, E.
Innovationen in der Ringspinnerei – neue Impulse für ein altes Spinnverfahren
Melliand Textilberichte, 76 (1995) 1061-1064

[Artzt, 1999]
Artzt, P.
Entwicklung neuer Garne auf der Basis des Verdichtungsspinnens
Melliand Textilberichte 80 (1999) 689

[Binternagel, 2000]
Binternagel, T.
Neue Möglichkeiten in der Weiterverarbeitung von COM4-Garnen
Melliand Textilberichte 81 (2000) 702-707

[ITV, 2001]
Personal information
Institut für Textil- und Verfahrenstechnik, D-Denkendorf

[Stalder, 2001]
Stalder, H; Hellwig, A.
Vorteile und neue Möglichkeiten durch COM4-Garn im Gestrick
Melliand Textilberichte 82 (2001) 138-140

4.2.1.2 Textile pre-treatment

4.2.1.2.1 Substitution of hypochlorite for bleaching

Description

Hypochlorites have been used as bleaching agents for textile substrates for a long time. The main two forms are chloride of lime and sodium hypochlorite. In Europe, chloride of lime is no more in use because of awkward application properties. Sodium hypochlorite has been widely substituted by hydrogen peroxide but is still in use. In Germany and other European countries, for bleaching of woven fabric consisting of cotton and cotton blends, hypochlorite has been completely substituted more than ten years ago. For knit fabric consisting of cotton or cotton blends, a combination of hypochlorite and hydrogen peroxide has been widely applied because it is cheap and a soft handle (because natural wax is removed to a low extend only) is achieved. Thus, for continuous bleaching of knit fabric, sodium hypochlorite has been used in the first bleaching stage and hydrogen peroxide in the second. Today, this process has been substituted by a two-stage bleaching with hydrogen peroxide. Thereby, the first stage is carried out at room temperature (cold bleach) and the second one at higher temperatures (hot bleach). Also for discontinuous bleaching processes of knit fabric, hypochlorite has been substituted. In some cases hypochlorite is still in use as a cheap and effective auxiliary for boiling out of dyeing machines.

Main achieved environmental benefits

The application of hypochlorite causes chlorinated hydrocarbons as by-products, such as trichloromethane (chloroform) and many other unspecified compounds, depending on impurities of cotton and applied bleaching auxiliaries; as a total most of these by-products can be detected by means of a sum parameter called adsorbable organic halogens (AOX). This severe disadvantage of formation of chlorinated by-products is prevented by use of hydrogen peroxide.

Applicability

The substitution of hypochlorite as bleaching agent is applicable both to existing and new installations. Today, there are no limitations to the application of hydrogen peroxide only, both for woven fabric and knit fabric consisting of cellulosic fibres and concerned blends. Also for yarns consisting of cellulosic fibres, hydrogen peroxide is the appropriate bleaching agent. In some cases (esp. in finishing knitted PES fabrics for use as home textiles) bleaching with sodium chlorite is in use. If processes are well controlled, AOX generation is 10 times lower compared to hypochlorite bleaching [UBA, 1994].

Cross-media effects

There is no cross-media effect to be mentioned.

Reference plants

There are many textile finishing industries in Europe and world-wide having successfully replaced hypochlorite by hydrogen peroxide.

Operational data

As already indicated, for continuous bleaching of woven and knit fabric, usually two stage-bleaching is applied at different temperatures (cold - hot).

Economics

For knit fabric, cost for the application of a two stage bleaching with hydrogen peroxide may be two up to six times higher compared to two stage bleaching with hypochlorite (first stage) and hydrogen peroxide (second stage) [Wurster, 1990]. However, hypochlorite has widely replaced, e.g. in Germany practically completely.

Driving force for implementation
Market demands for chlorine free bleached textiles and requirements to wastewater disposal have been the major driving forces for the implementation of this technique.

Reference literature

[Wurster, 1990]
Wurster, P.; Conzelmann, F.
Bleichprozesse mit Natriumhypochlorit im Spannungsbereich zwischen Qualitätsanforderungen, Wirtschaftlichkeit und Umweltschutz
Textilpraxis International 45 (1990) 1269-1273

[UBA, 1994]
Schönberger, H; Kaps, U.
Reduktion der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

4.2.1.2.2 Recovery of sizing agents by ultrafiltration

Description

Sizing agents are applied to warp yarns in order to protect them during the weaving process. However, sizing agents have to be removed practically completely during textile pre-treatment because they would disturb further processing, especially dyeing and/or printing. In case of finishing woven fabric, sizing agents represent the major part of COD-load which is 30-70% [UBA, 1994]. Sizing agents can be recovered from washing liquor by ultrafiltration. However, this is possible for water-soluble synthetic sizing agents only, such as polyvinyl alcohol, polyacrylates and carboxymethyl cellulose. Recently, it has been confirmed that modified starch can also be recycled such as carboxymethyl starch. The principle of recovery by ultrafiltration is shown in Figure 4.12. After sizing and weaving, sizing agents are removed during textile pre-treatment by hot washing with water in a concerned continuous washing machine. For minimising washing liquor flow, the washing process may need to be optimised. Sizing agents concentration in the washing liquor is about 20-30 g/l. In the ultrafiltration plant, they are concentrated to 150-350 g/l and the concentrate can be reused for sizing again. It is kept at high temperature (80-85°C) and has not to be heated up again. The permeate can be recycled to the washing machine.

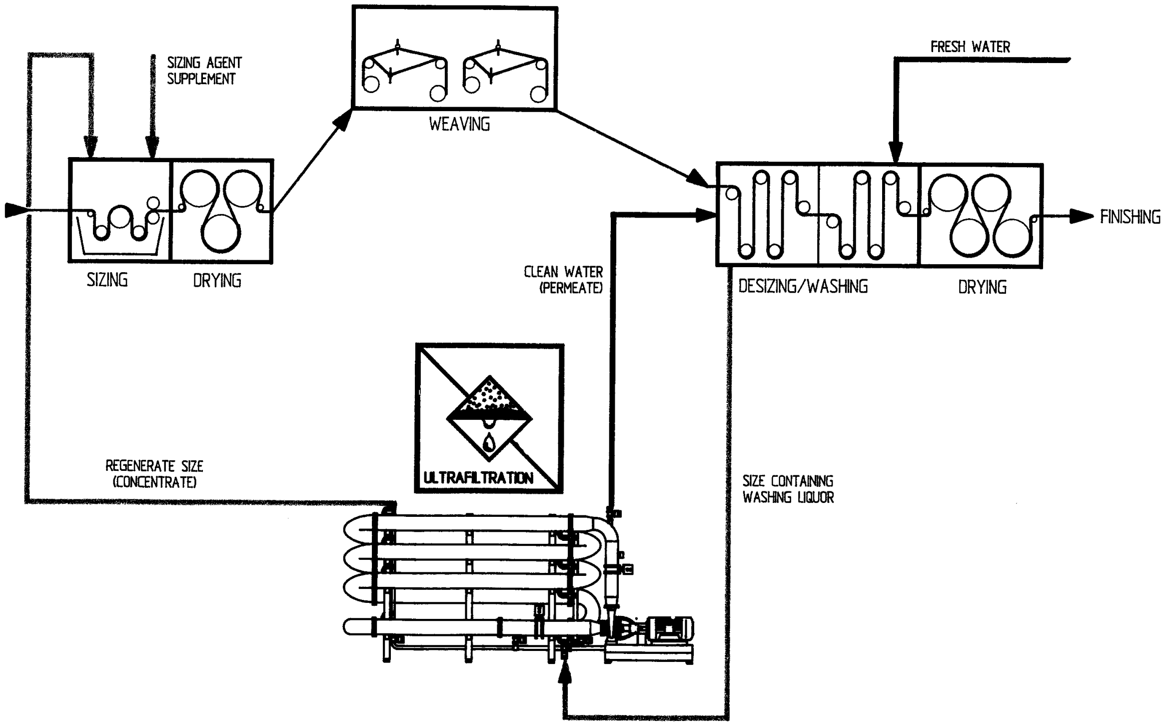


Figure 4.12: Principle of application and recycling of sizing agents by ultrafiltration

Figure 4.13 shows an example for the material balance of sizing agents and water for the process without and with recovery of sizing agents. It is obvious that there are various losses of sizing agents at different processes, especially during weaving. Also, on the desized fabric some sizing agents remain and there is also some loss with the permeate. Thus the percentage of sizing agents which can be recovered is 80-85%.

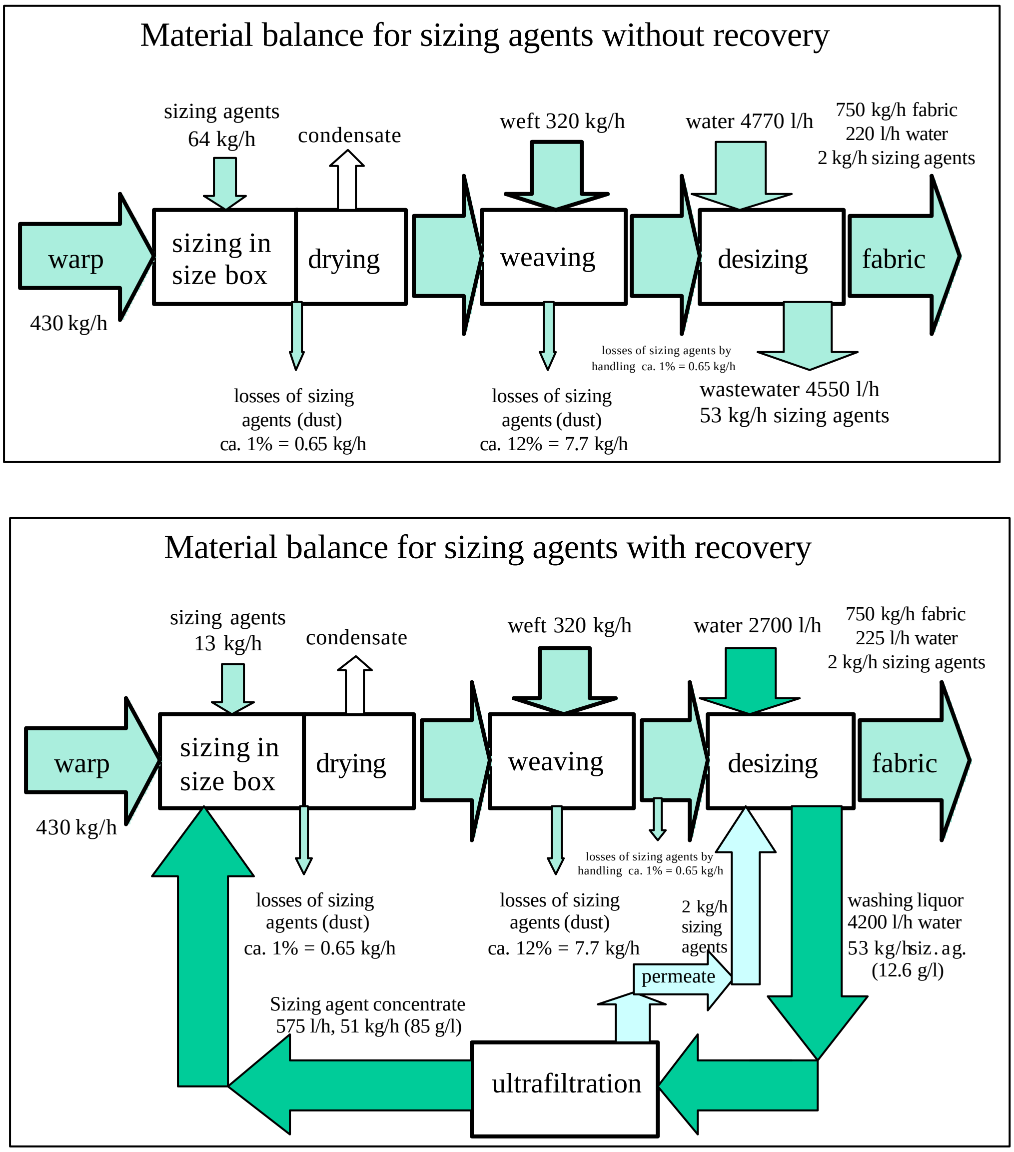


Figure 4.13: Representative example for balancing of sizing agents and water without and with recovery of sizing agents - [Langer, 1997]

Main achieved environmental performance

COD-load of wastewater from finishers of woven fabric is significantly reduced by 30-70%. Sizing agents are recovered by 80-85%. In addition, sizing agents in wastewater have not to be treated. Thus energy consumption for treatment is reduced significantly as well as quantity of sludge to be disposed of.

Applicability

Usually, sizing agents are recovered in integrated mills only having a weaving and finishing section at the same site. There are cases with considerable distance between weaving mill and finishing department (up to 300 km in one case in USA) and desizing liquor is transported by insulated tankers. However, weaving mills can offer desized fabric by installation of a washing machine and dryer and thus can recycle sizing agents also.

In case of an integrated mill, the minimum quantity of processed fabric is about 1000 t/a; in case of a weaving mill offering desized fabric the limit is much higher (about 5000 - 8000 t fabric/a) because in addition to the ultrafiltration plant a washing machine and a dryer have to be implemented. To date, the textile finishers' acceptance of already de-sized fabric is still limited. Certain effects like minting can be carried out with non-desized fabric only.

Cross-media effects

Ultrafiltration needs energy but compared to the energy required to produce new sizing agents (if they are not recovered and have to be treated in wastewater treatment plants) it is much less.

Reference plants

The first plant for recovery polyvinyl alcohol went into operation 1975 in USA. Meanwhile there are two plants in operation in Germany for many years and various plants in Brazil, Taiwan and USA. There is a small number of suppliers only.

Operational data

In order to minimise scaling and fouling, fibres have to be removed before ultrafiltration. The same is for fine particles, such as singeing dust. To this purpose pre-filtration is applied. There are difficulties to remove dyestuff particles in case of coloured woven fabric (dyed warp yarns) because desizing liquor is slightly coloured. Here microfiltration is applied for pre-filtration, however in such cases it is more difficult to operate the plant but is possible and carried out successfully for many years. Usually, for recovery synthetic sizing agents are used, mostly mixtures of them, such as polyvinyl alcohol and polyacrylates but also carboxymethyl cellulose and meanwhile (in Brazil) carboxymethyl starch.

The operation of ultrafiltration units for recovery of sizing agents require qualified staff and maintenance.

Economics

Regarding economics, the specific price for sizing agents in [EURO/kg] may not be taken into consideration only but also both the cost for the whole recipe and the whole process, especially increased weaving efficiency which can be the dominant cost factor. This is important when changing from starch and starch derivatives (which can not be recycled but are cheaper in specific price) to synthetic sizing agents which are more costly but application amounts are less and weaving efficiency may be higher.

Table 4.12 presents a typical example for savings when introducing recovery of sizing agents.

Input for sizing	**without recovery**		**with recovery**	
		[EURO/a]		[EURO/a]
Produced woven fabric [t/a]	8750		8750	
Quantity of warp yarns [t/a]	5338		5338	
Load of sizing agents referred to yarn - in weight-%	13.8		10.0	
Recovered sizing agents [t/a]			427	76095
Starch derivative [t/a]	470	261435		
PVA [t/a]	264	722500	75	205100
Polyacrylates (100%) [t/a]			32	158400
Wax [t/a]	59	133040	26.7	30485
Fresh water [m^3/a]	5075	5840	755	830
Steam [t/a]	890	10780	350	4235
Electricity [kWh/a]	155680	8560	32000	1760
Man power [h/a]	4450	58700	1680	22180
Total cost		**1200855**		**499085**
Cost [EURO/t warp yarn]		225		93.5

Table 4.12: Cost for sizing agents with and without recovery - [Armbruster, 1999]

With respect to the example given in Table 4.12, additional savings have to be considered because of higher weaving efficiency, reduced cost for finishing (time saving and significantly reduced consumption of chemicals for degradation and removal of starch/starch derivatives) and wastewater treatment. Then, the pay back time of an ultrafiltration plant may be less than one year.

Thereby the investment in [EURO] cost for the example, illustrated above are following:

- ultrafiltration plant:	990000
- transport:	16500
- equalisation tank:	105000
- installation:	77000
- start up	27500
- miscellaneous:	27500
total investment cost	**1243500**

Driving force for implementation
Wastewater problems (high pollution load) and cost reduction have been the most important driving forces to implement recovery sizing agents.

Reference literature

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduzierung der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

[Langer, 1997]
Langer, H.; Armbruster, W.
Schlichterückgewinnung mittels Ultrafiltration
Abschlussbericht Nr. 8011 zu einem UBA-Forschungsvorhaben (1997)

[Armbruster, 1997]
Armbruster, W.
Die Rückgewinnung von Schlichtemitteln aus dem Abwasser der Textilveredlungsindustrie
Manuskript zum Vortrag anläßlich der Sitzung der ATV-Arbeitsgruppe "Textilindustrie" am 18.03.1999 (1999)

[Rescom, 2001]
Rescom Engineering GmbH, D-Noerdlingen
Recovery of Sizing Agents (2001)

4.2.1.2.3 Recovery of caustic soda from mercerisation process

Description

During the mercerisation process, cotton yarn or fabric (mainly woven fabric but also knit fabric) is treated under tension in a solution of concentrated caustic soda (270-300 g NaOH/l respectively 170 - 350 g NaOH/kg textile substrate) for about 40-50 seconds. Subsequently, textile substrate is rinsed in order to remove caustic soda. This rinsing water is called weak lye (40 - 50 g NaOH/l) and can be concentrated by evaporation for recycling. The principle is shown in Figure 4.14. After removal of lint, fluff and other solids (in self-cleaning rotary filters or pressure micro filtration), the weak lye first is concentrated, for instance in a three stage evaporation stage (Figure 4.15). In many cases, purification of the lye is required, normally carried out after evaporation. The purification technique depends on the extend of lye contamination and can be simple sedimentation but also oxidation/flotation by injection of hydrogen peroxide.

The driving force of the evaporation process is a temperature and pressure drop over the stages, with the highest temperature and pressure in the first stage and the lowest temperature and pressure in the last stage. To use the vapours of one stage to heat the next one, the boiling point in the next stage must obviously be lower. This is achieved, despite the higher concentration, by lower pressure in the next stage. The concentration increases over the stages, the temperature decreases. The vapours of the last stage are used to pre-heat the weak lye feed and are then condensed to liquid phase in a condenser by heating up cold water for process use.

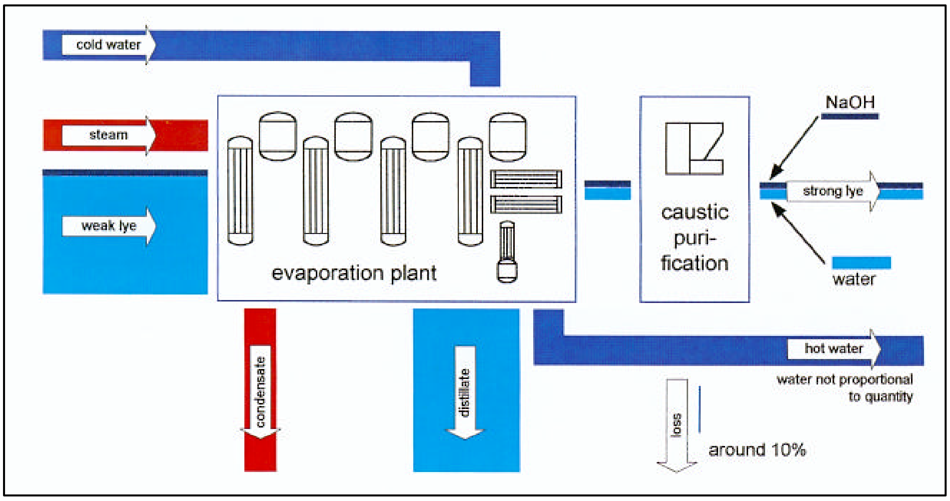


Figure 4.14: Scheme for illustrating the principle of caustic soda recovery from mercerisation with evaporation and -usually- subsequent purification

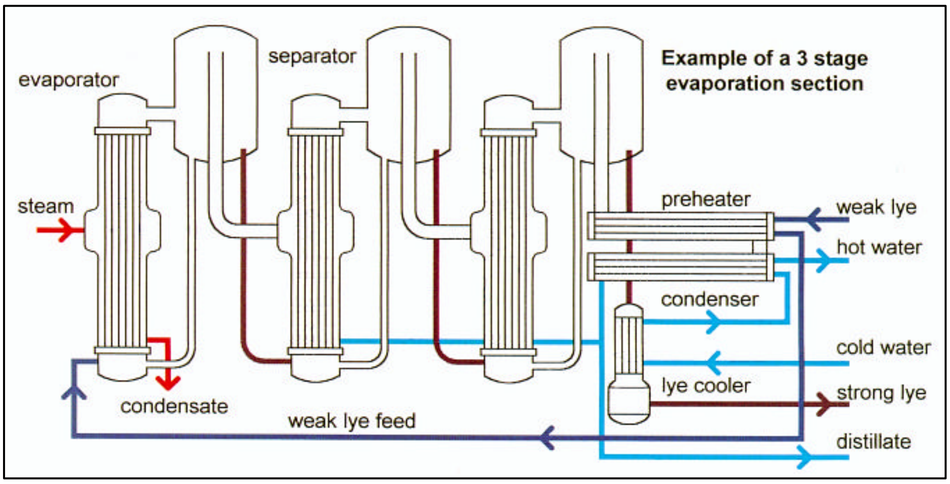


Figure 4.15: Evaporation of weak lye from rinsing as part of the mercerisation process

Main achieved environmental benefits

Alkaline burden of wastewater is reduced drastically and required acid for wastewater neutralisation is minimised.

Applicability

The technique is applicable both to existing and new installations.

Cross-media effects

Evaporation requires approx. 0.3 kg steam/kg water evaporated in a 4-stages evaporation plant. This corresponds to 1.0 kg steam/kg recovered NaOH (28 °Bé) or 1.85 kg steam / kg NaOH (40 °Bé). However, energy consumption for production of caustic soda by chloroalkali electrolysis is also considerable.

Reference plants

First caustic soda recovery plant went into operation more than one hundred years ago. Today, there are more than 300 plants in operation world-wide, especially for recovery of caustic soda from woven fabric mercerisation and yarn mercerisation and some from knit fabric mercerisation; the latter process is not applied very often.

Main suppliers in Europe are:

- KASAG Export AG, CH-9259 Kaltenbach, Switzerland
- Körting Hannover AG, D-30453 Hannover, Germany

Operational data

The concentration of weak lye usually is 5-8 °Bé (30-55 g NaOH/l) and is concentrated to 25-40 °Bé (225-485 g NaOH/l), depending on the mercerising process applied; in case of raw mercerisation (dry textile substrate is treated) the concentration is 25-28 °Bé and is 40 °Bé in case of non-raw mercerisation. In case of raw mercerisation, the concentration of impurities is significantly higher and thus viscosity which do not allow to go for higher concentrations (circulation in evaporators is disturbed).

Economics

The more stages for evaporation, the more often the heat is re-used and the lower is the steam consumption and herewith the running cost. Investment however, obviously increases with more stages.

Investment cost mainly depend on plant size and purification technique and typically vary from 200,000 to 800,000 EURO. Amortisation time depends on plant size and operation time per day. If mercerisation is permanently practised, pay back time is less than one year. In case, non-recovered caustic soda lye has to be neutralised with acid, pay back time is less than six month. Thus, from the economic point of view, caustic soda recovery may be very attractive.

Driving force for implementation

High alkali content of wastewater and economical aspects of caustic soda losses have been the main driving forces.

Reference literature

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduzierung der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

4.2.1.2.4 Enzymatic scouring

Description
Desizing, scouring with strong alkali and bleaching are typical pre-treatment steps for cotton finishing mills. Often scouring and bleaching steps are combined. Scouring improves wettability of cotton fibres. Hydrophobic impurities as pectines, waxes are removed from the fibres.
With the use of enzymes (generated from genetically modified microorganisms) the alkaline scouring process can be replaced. The enzymes are used in combination with surfactants (wetting agents and emulsifiers) and complexing agents. Due to a better bleachability of enzyme scoured textiles bleaching can be carried out with reduced amounts of bleaching chemicals and auxiliaries.

Main achieved environmental benefits
Sodium hydroxide used in common scouring is not necessary.
Furthermore in comparison to common pre-treatment sequences the following environmental benefits can be achieved (Table 4.13):

	Enzymatic scouring	Enzymatic scouring + bleaching with reduced concentration of peroxide and alkali
Reduction in rinsing water consumption	20%	50%
Reduction in BOD-load	20%	40%
Reduction in COD-load	20%	40%

Table 4.13: Environmental benefits of an enzymatic scouring process

Applicability
The enzymatic scouring process can be applied to cellulosic fibres and their blends (woven and knitted goods) in continuous and discontinuous processes. The enzymatic pre-treatment can be combined with enzymatic desizing. Existing machines (jets, overflows, winches, pad batch, pad steam, and pad roll) can be used. Cotton seed capsules are removed in downstream bleaching process.

Cross-media effects
There are no cross-media effects to be mentioned.

Reference plants
The enzymatic scouring is applied in several German finishing mills and world-wide as well.

Operational data
A typical recipe for a pad batch process with joined enzymatic desizing is given below:
- impregnation at 60 °C
- 2-3 ml/l wetting agent
- 2-5 ml/l emulsifier
- 5-10 ml enzymatic compound
- 4-6 ml/l amylase
- 2-3 g/l common salt
- pH 8-9.5
- storing for 3-12 h depending on amount and type of starch, extraction, and rinsing.

Economics
Substantial savings in water, time, chemicals/auxiliaries, and energy depending on on-site situation are possible.

Driving force for implementation

Quality aspects (good reproducibility, reduced fibre damages, fabrics have a good dimensional stability, colour yield is increased, soft handle of the fabrics) technical aspects (no corrosion of metal parts) as well as ecological and economical aspects are reasons for the implementation of the enzymatic scouring technique.

Reference literature

[Kahle, 2000]
Kahle, V.
Bioscouring ein neues, modernes BioTech-Konzept
Product information, Bayer AG, D-Leverkusen (2000)

4.2.1.2.5 Enzymatic removal of residual hydrogen peroxide after bleaching

Description

To achieve reproducible bleaching results residual hydrogen peroxide content of 10-15% of the initial quantity should be still available after bleaching. The residual hydrogen peroxide content must be completely removed to prevent any change of shade with dyestuffs which are sensitive to oxidation. Reducing agents and several rinsing steps are necessary in common peroxide removal techniques. High energy and water consumption and the use of sulphur containing reducing agents are the main disadvantages of the conventional technique.

Special enzymes (peroxidases) catalyse the reduction of hydrogen peroxide to oxygen and water. No side reactions with the substrate or with dyestuffs occur.

Main achieved environmental benefits

Peroxidases are completely biodegradable. Rinsing steps after peroxide bleaching can be reduced (normally only one rinsing step with hot water is necessary). Peroxidases have no negative influence on downstream dyeing process. Therefore, after treatment with the enzymes in an exhaust process the liquor does not have to be drained prior to dyeing. Savings in energy and water consumption can be achieved. Wastewater pollution with reducing agents (used for conventional processes) is avoided.

Applicability

Enzymatic peroxide removal is possible in a discontinuous, semi-continuous, and continuous way. The method is applicable both in new and existing installations.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

The technique is applied in European textile finishing mills and world-wide as well.
A selection of suppliers for enzymatic peroxide removal agents is given below:

- Bayer AG, D-Leverkusen
- Dr. Petry GmbH, D-Reutlingen
- Kapp Chemie GmbH, D-Miehlen
- Chemische Fabrik Tübingen, D-Tübingen
- Ciba Speciality Chemicals, CH-Basel

Operational data

A typical process sequence is given below:
Peroxide bleaching - liquor change - one rinsing bath (hot water) - liquor change – enzymatic peroxide removal – dyeing without previous liquor change.
Typical application amounts for the peroxidases in exhaust techniques are in the range of 0.5-2.0 ml/l (40-60 °C; 20 min) [Bayer, 1999], resp. 0.2 ml/l (20-50 °C; 10-15 min) [Stöhr, 1997]. In padding liquors a peroxidase concentration between 1-6 ml/l (100% liquor up-take) is used [Bayer, 1999].

Economics

Due to savings in water and energy consumption cost savings in a range between 6-8% (exhaust technique) can be achieved [Gebhart, 2000].

Driving force for implementation

The use of environmental friendly auxiliaries and cost saving potentials are the main motivation for the application of enzymatic peroxide removal techniques.

Reference literature

[Bayer, 1999]
Bayer AG, D-Leverkusen
Product information (1999)

[Ciba, 1998]
Ciba Speciality Chemicals, CH-Basel
Product information (1998)

[Gebhart, 2000]
Gebhart, P.; Etschmann, M.; Sell, D.
Entfernung von Bleichmittelresten mit Enzymen bringt Vorteile
Melliand Textilberichte 81 (2000) 56-58

[Stöhr, 1997]
Stöhr, R.
Simplified procedure for bleaching and dyeing cotton knitwear
Peprint from Int. Dyer (1997)

4.2.1.2.6 Optimisation of pre-treatment of cotton warp yarn

Description

For producing of white, non-dyed sheets to be used under bed sheets and table cloth, cotton woven fabric is in use. To this purpose, cotton warp yarn is bleached before weaving because the fabric is not desized after the weaving process. A five-step process has been applied, consisting of wetting/scouring, alkaline peroxide bleaching and three subsequent rinsing steps whereas the last rinsing water has been reused for the first bath. The existing process has been studied in detail. With the results, the optimised process has been developed. Wetting, scouring and bleaching is combined to one step and rinsing is performed in two steps; the second rinsing bath is reused.

In addition, heat recovery has been introduced. The hot scouring/bleaching bath (110°C) is heating fresh water for first rinsing in a heat exchanger. The bath is cooled down to about 80°C and fresh water is heated to 60-70°C. This cooled scouring/bleaching bath is collected in a tank which also receives the warm rinsing water from first rinsing. Energy of this wastewater then is recovered in a second heat exchanger to heat mixed fresh water and rinsing water from second rinsing. After that, cooled scouring/bleaching bath and first rinsing bath is discharged to a municipal wastewater treatment plant whereas second rinsing water is reused for preparing the scouring/bleaching bath.

Main achieved environmental benefits

Water consumption and wastewater discharge before and after optimisation can be seen from Table 4.14.

Process sequence	Process	Water consumption for conventional process [l]	Water consumption for optimised process [l]
1. step	wetting/scouring	6400	6400
2. step	bleaching	5000	
3. step	cold rinsing	5000	5000
4. step	warm rinsing	5000	
5. step	rinsing and pH adjustment with acetic acid	5000	5000
All steps		26400	16400
Recycling of last rinsing bath		- 5000	- 5000
Overall water consumption		21400	11400
Specific water consumption (800 kg yarn/batch)		26.8 l/kg	14.3 l/kg
Residual water content in the yarn		1400	1400
Wastewater flow		20000	10000
Specific wastewater flow		25 l/kg	12.5 l/kg

Table 4.14: Optimisation of warp yarn scouring/bleaching - absolute and specific water consumption and wastewater discharge before and after process optimisation - [van Delden, 2001]

The consumption of chemicals and energy has also been reduced drastically. Following savings are achieved:

Process time	about 50%
Water consumption/wastewater discharge (Table 4.14)	about 50%
NaOH	about 80%
H_2O_2	no reduction
Complexing agents/stabilisers	about 65%
Surfactants	about 70%
Optical brightener	no reduction
COD load of wastewater	about 20%
Energy	1.2 kg steam/kg warp yarn

Applicability
The optimisation of the process is possible both for exiting and new installations. Regarding the recovery of heat, space for additional tanks is required which may be a limiting factors in some cases. The quality of the cotton yarn has to be considered (content of iron, seeds etc.) in order to make to sure that the process can be applied.

Cross-media effects
There is no cross-media effect to be mentioned.

Reference plants
Two textile finishing industries in Germany are practising the described optimised process successfully.

Operational data
In Table 4.15, the conditions of the optimised process are compiled. It also contains the calculation of COD-input and COD-output respectively.

Process and Input			
	quantity	spec. COD-value and -concentration [mg O_2/g] resp. [mg O_2/l]	COD-load per 800 kg batch [kg O_2]
Wetting/scouring/bleaching			
• Recipe			
➢ NaOH 38° Be/33%	3.5 g/l	-	-
➢ H_2O_2 35%	3.0 g/l	-	-
➢ Complexing agent and stabiliser	1.0 g/l	85	0.53
➢ Surfactant	1.9 g/l	1610	19.35
➢ Optical brightener	0.15 weight-%	2600	3.12
			total : 23
• Conditions: pH ca. 12, 110°C, 10 min			
• Extracted COD from CO warp yarn			56
First rinsing			
• Conditions: 70°C, 15 min		3000 mg O_2/l	15
Second rinsing			
Conditions: 70°C, 15 min		1000 mg O_2/l	5
Total			**99 kg COD resp. 124 g/kg**

Table 4.15: Recipe and conditions of the optimised process as well as COD-input resp. COD-output (however, affinity of textile auxiliaries to cotton yarn is not taken into account) - [van Delden, 2001]

Economics

The considerable savings of time, water, chemicals and energy makes the process highly economical. The optimised process does not require new pre-treatment equipment but tanks, heat exchangers, pipes and control devices for energy recovery from wastewater.

Driving force for implementation

Environmental motivation has been the main driving force for the development of the process; however the economical benefit pays back the invested efforts and investigations.

Reference literature

[van Delden, 2001]
van Delden, S.
Prozessoptimierung durch Wasserkreislaufführung und Abwasservermeidung am Beispiel einer Kettbaumbleiche
Proceedings of BEW-Seminar "Vermeidung, Verminderung und Behandlung von Abwässern der Textilindustrie" on 06.03.2001 (2001)

4.2.1.3 Dyeing

4.2.1.3.1 Discontinuous dyeing with airflow dyeing machines

Description

Discontinuous processing of textile substrates require more water and energy compared to continuous processes. However, for a long time efforts are undertaken to optimise discontinuous processes with respect to productivity, efficiency and also to minimise energy and water consumption respectively. This lead to dyeing jets. Thereby liquor ratios have been reduced step by step. The latest developments have LR of 1:3 (for woven PES fabric) and 1:4.5 (for woven CO fabric). To achieve such low LR, within the machine (jet), the fabric is moved by moisturised air or a mixture of steam and air only (no liquid) along with a winch. The prepared solutions of dyestuffs, auxiliaries and basic chemicals are injected into the gas stream. The bath level is always below the level of processed textiles in order to maintain low LR. The principle of such an airflow dyeing machine is illustrated in Figure 4.16.

Rinsing is carried in a continuous manner. During the whole rinsing process, the bottom valve is open and rinsing water is discharged without additional contact with the fabric (which is the case in conventional machines) (Figure 4.17). This also allows the discharge of hot bath liquors, also after high-temperature dyeing at 130°C. Thus, in addition to time saving, optimum heat recovery can be performed. The fabric itself is processed with low tension and crease formation is minimised.

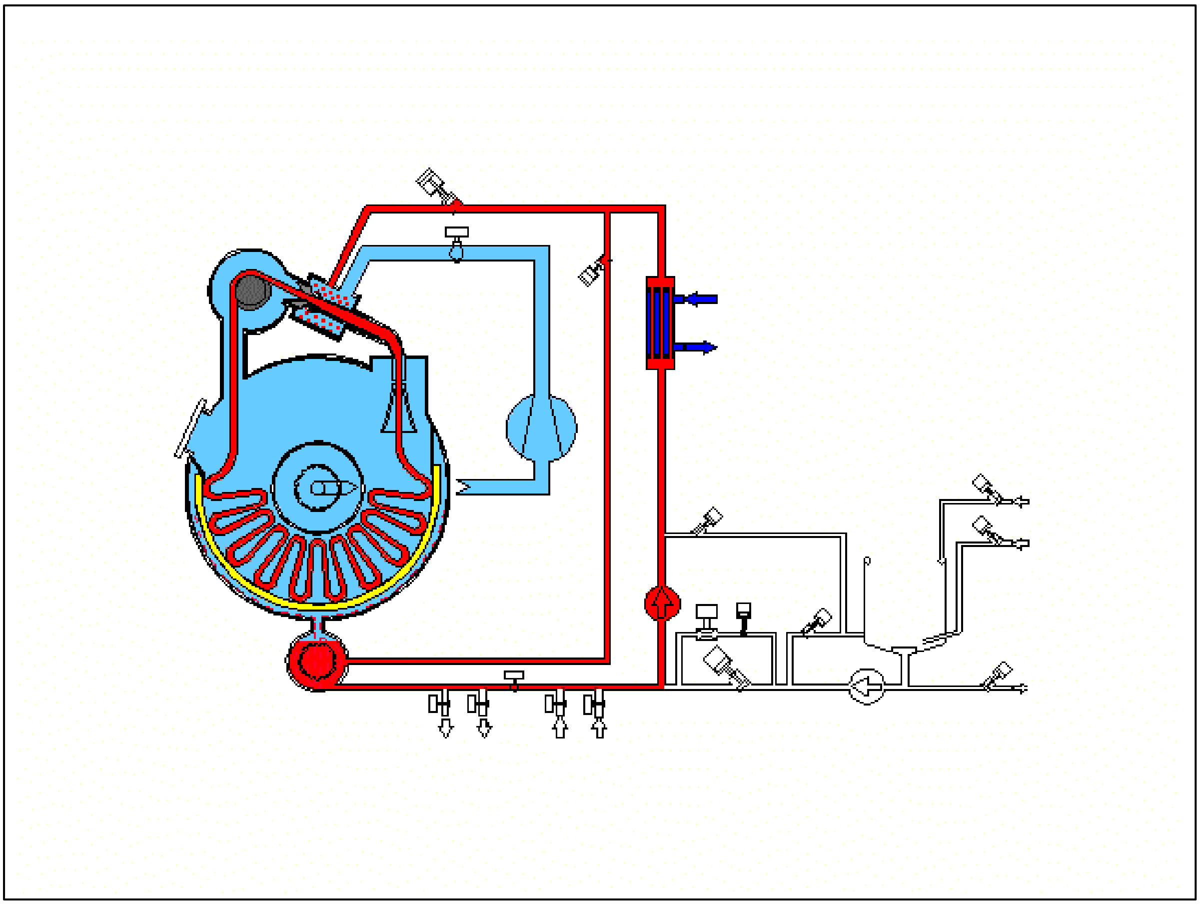


Figure 4.16: Scheme of an airflow dyeing machine (jet) with indication of air ventilation and injection of the concerned bath

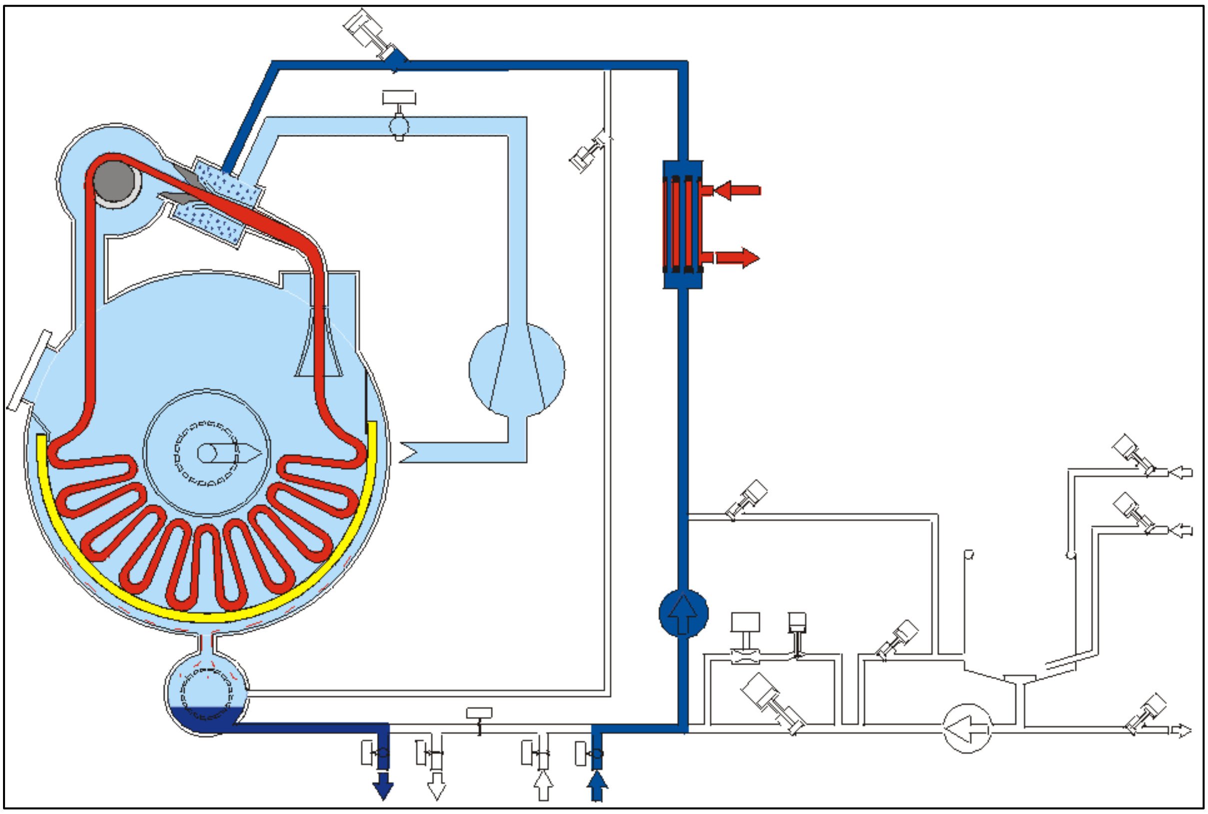


Figure 4.17: Rinsing performance in an airflow machine (jet), showing the open valve in order to achieve continuous rinsing

Main achieved environmental performance

Textile processing at low LR and practically continuous rinsing, water saving of about 50% are achieved compared to machines having a hydraulic system (the fabric is moved by injection of process liquor and a winch) at LR of 1:8 up to 1:12. The same is for heating energy. There are also savings of auxiliaries and basic chemicals of about 40%. The savings are compiled in Table 4.16 for exhaust dyeing with reactive dyestuffs

Input	unit	Conventional exhaust dyeing at LR 1:8 up to 1:12	Exhaust dyeing in an airflow system at LR 1:4.5
Water	[l/kg]	100 - 150	20 - 80
Auxiliaries	[g/kg]	12 - 72	4 - 24
Salt	[g/kg]	80 - 960	20 - 320
Dyestuffs	[g/kg]	5 - 80	5 - 80
Steam	[kg/kg]	3.6 – 4.8	1.8 – 2.4
Electricity	[kWh/kg]	0.24 – 0.35	0.36 – 0.42

Table 4.16: Comparison of specific input factors for exhaust dyeing with reactive dyestuffs in dyeing jets at LR 1:8 up to 1:12 (conventional) and in an airflow system

Applicability

The application of this technique needs investment in new dyeing machines (e.g. Figure 4.18). Existing machines can not be retrofitted. The machines can be used both for knit and woven fabric and for nearly kinds of textile substrates. Fabrics consisting of wool or wool blends with a percentage of wool of more than 50% can not be dyed because of felting. It can not be recommended to dye linen fabric with the described system because of scaling of the machines with linen fluffs. For silk, the system has been approved but is still rarely applied for it.

Concerning dyeing with vat and sulphur dyestuffs, a process has been developed to minimise the oxidation of dyestuffs by oxygen from injected air (minimisation of oxidation by heating up to steam atmosphere).

Elastic fabrics containing polyurethan fibres (lycra) are always difficult to dye with respect to dimension stability but they can be dyed in the airflow system. Also other substrates, such as PES or PES/WO blends are difficult or impossible to process in case of low dimension stability of the fabric.

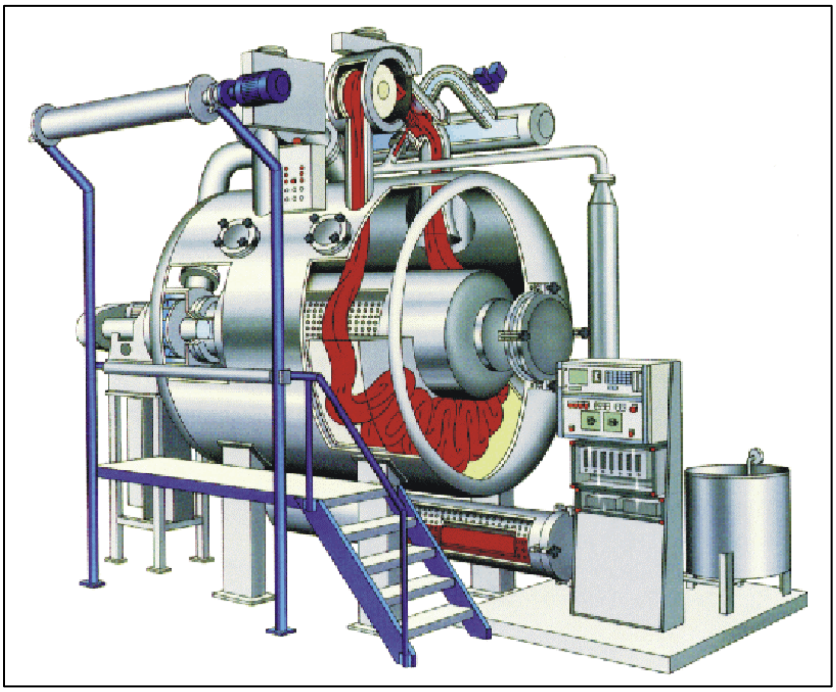


Figure 4.18: Example for an airflow dyeing machine

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

Airflow dyeing machines are in operation in many textile finishing industries world-wide. There is only one producer of machines in which the textile substrate is moved by air only (THEN GmbH, D-74523 Schwäbisch Hall) achieving lowest water consumption. There are several other producers of machines using air and liquor for moving the textile substrates (e.g. Thies GmbH, 48653 Coesfeld; MCS, I-24059 Urgnano - Bergamo; Scholl AG, CH-5745 Safenwil; Krantz Textiltechnik, D-41006 Mönchengladbach).

Operational data

The airflow dyeing machine offer combination of high productivity and reproducibility and reduction of water, chemicals and energy consumption.

Economics

Investment cost for airflow dyeing machines, compared to conventional dyeing jets are around one third higher but due to high savings a short payment period can be achieved.

Driving force for implementation

High productivity and reproducibility and minimisation of water, chemicals and energy consumption have been and still are the main driving forces for the application of this technique.

Reference literature

[Adrion, 1997]
Vielfalt der Veredlung durch das aerodynamische System
Textilveredlung 32 (1997) 16-21

[Adrion, 2001]
Ökofärben - Perspektiven mit dem aerodynamischen System
Manuskript zum Seminar "Vermeidung, Verminderung und Behandlung von Abwässern der Textilveredlung" am 06.03.2001 (2001)

4.2.1.3.2 Minimisation of dyeing liquor losses in cold pad batch dyeing

Description

Cold pad batch (cpd) dyeing is a widespread technique for the semi-continuous dyeing of cellulosic (mainly cotton or viscose) woven and knit fabric with reactive dyestuffs. The dyeing liquor and the necessary alkali for fixation and other auxiliaries are fed to a containment (padder or dyeing trough) for impregnating the textile (Figure 4.19).

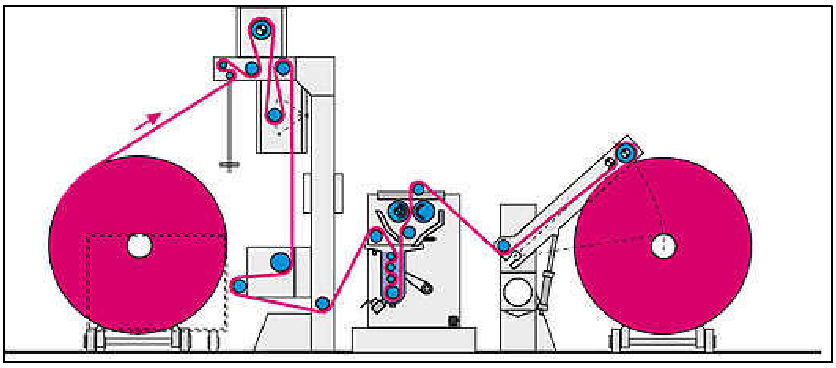


Figure 4.19: Typical scheme for cold pad batch dyeing

In order to minimise the losses from impregnation bath, the add-on of dyeing liquor can be carried out in a nip (Figure 4.20) or in volume minimised trough (Figure 4.21).

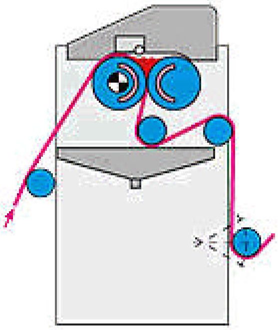


Figure 4.20: Scheme of cold pad batch dyeing by application of the dyeing liquor in a nip

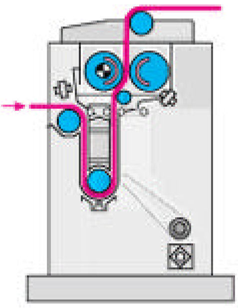


Figure 4.21: Scheme of cold pad batch dyeing by application of the dyeing liquor in a volume-minimised trough, here in a U-shaft

In case of application of the dyeing liquor in a nip, the loss can be minimised down to about 5 l per batch, in case of a U-shaft down to 12 l. Both values are for a trough width of 1800 mm.

The losses of dyeing liquor can be significantly reduced not only by minimising the trough volume but also by additional measures:

- Minimisation of auxiliaries` consumption by dosage of auxiliaries depending on shade depth which results in lower wastewater pollution. Dyestuff solution and auxiliaries are dispensed separately and recipe-specific, and are mixed before feeding into the padder and dyeing trough respectively.
- On-line measurement of pick-up (measurement of consumption of dyeing liquor and determination of quantity of processed fabric (measurement of length and specific weight)). The determined values are automatically processed and are used for the preparation of the next comparable batch in order to minimise surplus and thus losses of padding liquor
- Application of rapid batch technique; residual dyestuff liquor in the feeding tanks (Figure 4.22) can be minimised which is at least as important as the minimisation of trough volume. This system do not prepare the whole dyestuff solution (for the whole batch) before starting dyeing but prepare it just-in-time in different steps. This can be performed by on-line measurement of pick-up (see above). Figure 4.22 shows dosing of the dyeing liquor and different auxiliaries, needed for fixation of reactive dyestuffs.

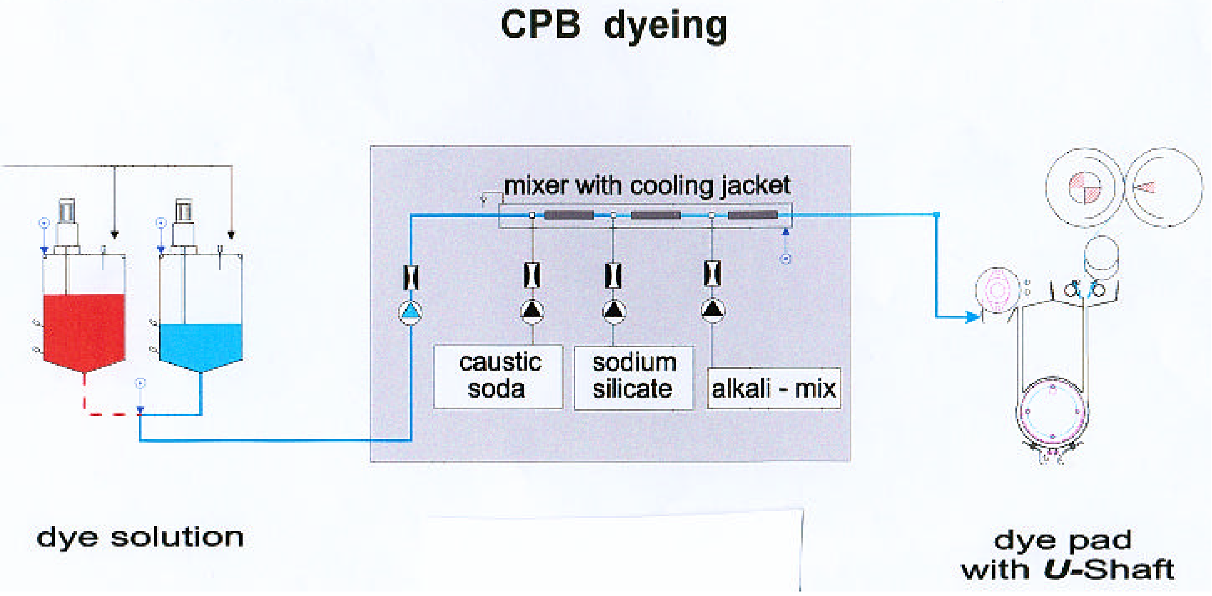


Figure 4.22: Typical scheme of an automated dispensing system for cold pad batch dyeing

The automated process control system guarantees high precision operation corresponding with high accuracy in dyeing liquor preparation with automated control of dosing tolerances. Thus, a bundle of techniques enable the highest reduction of dyeing liquor losses.

Main achieved environmental benefits

The volume minimisation of the whole pad batch dyeing system enables the reduction of losses from troughs from 30 up to 100 l per batch down to about 12 l, in case of nip dyeing even down to about 5 l.
Automated dispensing system along with on-line measurement of pick-up allow the minimisation of residual dyestuff liquor in the feeding tanks from up to 150 l down to 5-15 l.
In addition, new systems are operated with minimised flow of rinsing water (about 25% savings).

Applicability

The technique is applicable both to existing and new cold pad batch dyeing systems.
Dyeing in the nip is only possible for light fabrics (up to 220 g/m) and fabric with good wettability.
In case of brushed or sheared textile, the pick-up time may be to short and reproducibility is adversely affected. Special attention has to paid to knit fabric and elastic fabric.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants
In Europe and countries outside Europe, there are about 40 plants successfully in operation. These plants are equipped with the online dosage system for individual dosing of alkali products. The rapid batch dosing system for liquid dyes is successfully applied in a TFI and can be considered to be in the stage of market introduction.
Suppliers:

- E. Küsters Maschinenfabrik GmbH & Co. KG, devision textile, D-47805 Krefeld
- Kleinewefers Textilmaschinen GmbH, D-47803 Krefeld
- Seybert & Rahier GmbH & Co. Betriebs-KG, 34376 Immenhausen

Operational data
The regular control of the dosage system, such as pumps is very important. The determination of the pick-up has to be checked from time by time. This means the check of the length metering system and the determination of specific weight under standardised conditions of the fabric to be dyed (not of the raw material before textile pre-treatment). Thus, precision of the system can be maintained.

Economics
Investment of the automated dosage system and a volume minimised trough (e.g. U-shaft) is about 85,000 EURO (related to a width of 1800 mm). In case of 15 batches per day, 230 working days per year, reduction of loss of at least 50 l per batch and price of dyeing liquor of 0.5 EURO/l, savings of also about 85,000 EURO result. This means a short pay back time. Thereby, cost for additional wastewater disposal are not taken into account.

Driving force for implementation
The need for increased reproducibility and productivity, and wastewater problems because of colour have been the main driving forces.

Reference literature
[Hartmann, 1997]
Hartmann, W.
Bessere KKV-Färberesultate mit innovativer Maschinentechnologie
ITB Färbrei/Druckerei/Ausrüstung (1997), Nr. 3, 39-46

4.2.1.3.3 Silicate free fixation method for cold pad batch (cpb) dyeing

Description
World-wide, the spreading of cpb-dyeing is approx. 16%. Thus, it became an important dyeing method with increasing relevance. In the early 70ties, sodium silicate was introduced as a problem solver in cpb, mainly to increase the pad liquor stability and to avoid selvage carbonisation with state of the art application technique at these days. However, from this time onwards, the dyehouses had handling problems with sodium silicate. Now, silicate free, highly concentrated aqueous alkali solutions have been designed and developed especially for modern and advanced dosing techniques using a new designed application technique with reduced liquor content as well. The solution is ready-made and is directly applied for cpb-dyeing; it has not to be prepared by TFI. It is a carefully adjusted mixture of specific alkaline in aqueous solution.

Main achieved environmental benefits
In combination with reactive dyestuffs with high fixation rates (see concerned described technique), there are following advantages:

- No rests of alkali in formulation tank because alkali can be added as a ready-made solution and TFI has not to prepare it
- No deposits (like in case of silicates) on the cpb-dyeing equipment and easy to wash-off
- No need to add auxiliaries in the padding liquor to avoid deposits
- Low electrolyte content which reduces the substantivity of the hydrolysed dyestuff in the washing off procedure (reduced energy and water consumption)
- It allows wastewater treatment based on membrane technique (no crystallisation in filters, pipes and valves and no membrane blocking which is the case for sodium silicate)

Applicability
The technique is applicable both to existing and new installations. However, for existing installations, additional measures for process optimisation and control may be needed.

Cross media effects
There are no cross media effects to be mentioned

Reference plants
In Europe, there are many TFI applying ready-made alkali solutions, mainly in Italy (e.g. Miroglio) but also in France (e.g. T.I.L., F-Lyon), Germany (e.g. Riedel&Tietz Textil GmbH, D-09212 Limbach-Oberfrohna) and Austria (e.g. Fussenegger, A-Dornbirn).

Operational data
The aqueous alkali solution has been designed for direct dosing units. Thus, the delivered, ready-made solutions can be applied.
Available state of the art online dosing technique are for instance:

- Küsters, D-47805 Krefeld: Contidos SF
- Kleinewefers KTM, D-47803 Krefeld: Inline-Mix
- Mutschink, D-47918 Tönisvorst: KM Inline Mix

The aqueous alkali solution can be used in conventional state of the art membrane pumps dosing units like from sera - Seybert&Rahier GmbH, D-34376 Immenhausen or from Bran&Lübbe GmbH, D-42499 Hückeswagen with 4:1 ratio (dyestuff to alkali solution) as well.

Figure 4.23 shows the typical dosing curve. The advantage of using a curve instead of conventional step dosage of alkali is to increase reproducibility because of adjusted alkali amount referring to the amount of dyestuff in the recipe.

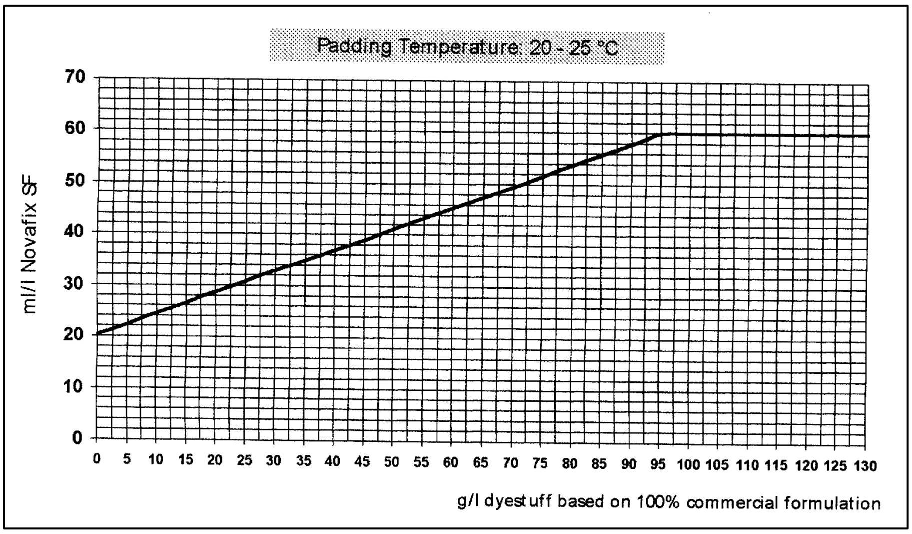


Figure 4.23: Dosage of ready made alkali solution depending on applied dyestuff concentration

Suppliers: Bilgram GmbH, D-88348 Bad Saulgau

Economics

Compared with conventional fixation methods, the ready-made alkali solution is more expensive in price per kg. In addition, as a silicate-free alkali with the tendency to lower pad liquor stability, its application needs more efficient temperature control (cooling/heating concepts). Generally spoken it means more additions in the infrastructure around the padder to guarantee constant conditions. The ready-made alkali solution is developed for modern optimised trough designs (described technique "Minimisation of dyeing liquor losses in cold pad batch dyeing") with very low liquor content and short pad liquor exchange time and therefore there is no need to have this extremely long pad liquor stability time. Also the benefits of indirect cost have to be taken into account as well:

- Investment in advanced dosing unit is cheaper because you need only 2 dosing units (1 for dyestuff solution, 1 for the ready-made alkali solution).
  Conventional fixation methods based only silicate need always minimum 3 dosing units (1 for dyestuff solution, 1 for silicate, 1 for caustic soda).
  1 dosing unit using advanced technique is around 12,000 EURO.
- No need to remove rubbers in short time periods because of silicate deposits. In Germany, the cost are 7,000 - 10,000 EURO to remove rubbers of a padder.
- Much better washing off of hydrolysed dyestuff means less energy and water consumption.
- Higher productivity of padders and washing machines.
- Better reproducibility because of defined and monitored conditions.

Driving forces for implementation

The main driving forces are:

- Better reproducibility
- Reduction of total process costs
- Easy handling, no deposits and better washing off behaviour
- Possibility using membrane technique for wastewater treatment
- Possibility having a liquid form of alkali dosable in supplied concentration without crystallisation problems

Reference literature

The cold pad-batch process – future oriented technology
Melliand Textilberichte 81 (2000)

[Patent, 1998]
German patent application (19849898.5), (November, 1998)
„Wässrige alkalihaltige Formulierung und deren Verwendung in Verfahren zum Färben von cellulosischen Textilmaterialien"

4.2.1.3.4 Exhaust dyeing of cellulosic fibres with polyfunctional reactive dyestuffs

Description

Polyfunctional reactive dyes contain more than one reactive group in each molecule and offer very high levels of fixation by exhaust dyeing which leads to lower colour usage to achieve a given depth of shade and a lower unfixed colour load in the effluent. Figure 4.24 shows an example for the chemical structure.

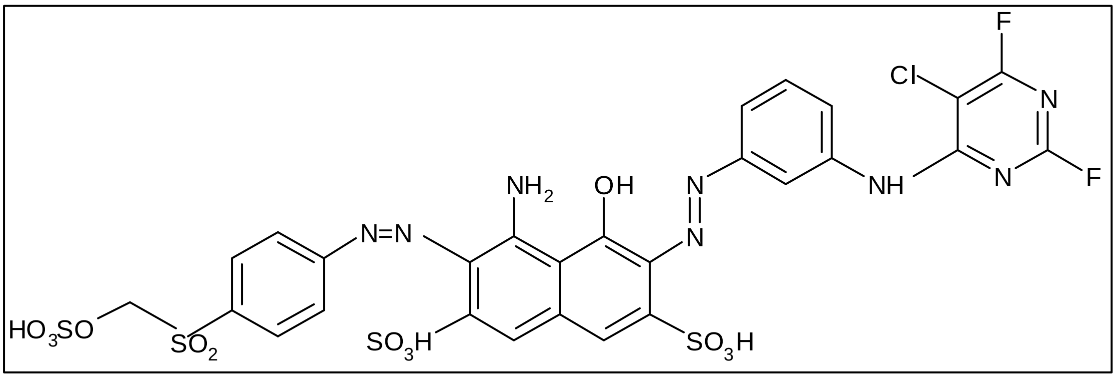


Figure 4.24: Example for the chemical structure of a polyfunctional reactive dyestuff having two different kind of reactive groups

Innovative manufacturers have introduced dye ranges of this type over the last few years as pressure to reduce the colour load to wastewater has increased particularly in Western Europe. Examples of these high fixation dye ranges are:

Cibacron FN dyes (exhaust warm) (Ciba)
Cibacron H dyes (exhaust hot) (Ciba)
Drimarene HF dyes (Clariant)
Levafix CA dyes (Dystar)
Procion H-EXL/XL+ dyes (DyStar)
Sumifix HF dyes (Sumitomo)

Main achieved environmental benefits

Reduced Colour Load

The main benefit achieved by the use of polyfunctional high fixation reactive dyes is the reduced colour and COD load to the effluent.

In the case of a reactive dye containing two or more reactive groups of similar reactivity, the potential for achieving a covalent linkage with the cellulose hydroxyl groups is significantly increased.

The fixation of a reactive dye with cellulose can be expressed either as a percentage of total dye applied (fixation rate, sometime also called absolute fixation) or as a percentage of dye exhausted (exhaustion rate, sometimes also called fixation efficiency).

In the case of a monofunctional dye the fixation rate is approximately 60% (with an exhaustion rate of approximately 70%) so that 40% of the dye applied is lost to the effluent which has to be treated to remove colour before it can be discharged to a river or other receiving water.

In the case of a reactive dye containing two reactive groups, the increased probability of reaction with cellulose can give rise to figures of 80% fixation rate and over 90% exhaustion rate. This leads to a significant reduction in the amount of colour lost to the effluent.

Reduced Salt Consumption

High exhaustion rate also means that a lower amount of colour is required to achieve a given depth of shade and hence salt loading can be reduced as this normally increases with increasing dyestuff concentration. But this reduction is small compared to the application of low salt reactive dyestuffs which are also polyfunctional (see described technique "Exhaust dyeing of cellulosic fibres with low salt reactive dyestuffs").

Reduced Water and Energy Consumption
High fixation rate minimises the amount of unfixed dye that must be removed at the end of the fixation stage to achieve the desired level of fastness performance. This means that shorter rinsing and soaping sequences are required which leads to considerable savings in water and energy consumption.
For example the recently introduced Levafix CA dyes (DyStar) and Cibacron FN (Ciba) have very high levels of fixation and consequently require less water and energy in the wash-off stage.
A further recent innovation from Dystar (Procion XL+ dyes) allow much shorter processing times on certain substrates by combining the pretreatment and dyeing steps using polyfunctional dyes which fix at 90°C. Savings of up to 40% in water and energy consumption are claimed.

Reduced AOX Load
Some of the most recent polyfunctional dyes use a combination of reactive groups based on modified vinylsulphone or heterocyclic fluoro components, which means that there is no contribution to Adsorbable Organic Halogen (AOX) in the effluent. Examples include

Levafix CA dyes (Dystar)
Cibacron FN dyes (Ciba)
Selected Drimarene HF dyes (Clariant)

Applicability
High fixation reactive dyes can be applied on all types of dyeing machines but offer particular advantage on the most modern low liquor ratio dyeing machines fitted with multi-tasking controllers where additional advantages of reduced energy and water consumption can be exploited.

Cross-media effects
There are no cross media effects to be mentioned.

Reference plants
High fixation, polyfunctional reactive dyes have been in widespread use for many years in all European countries and world-wide as well.

Operational data
Individual manufacturers provide comprehensive technical information for their high fixation dye ranges including detailed salt recommendations according to depth of shade, type of substrate, equipment in use, etc. These recommendations should also have been designed to ensure a high level of reproducibility and maximise Right-First-Time performance.

Economics
Compared to conventional monofunctional reactive dyestuffs, polyfunctional reactive dyestuffs are more expensive when considering the price per kilogram only. However the high fixation efficiency, the savings on salt usage, and reduced water and energy consumption means that the total cost of processing can be significantly reduced.

Driving force for implementation
The main driving force for the development of high fixation, polyfunctional reactive dyes has been the introduction of legislation restricting the colour of effluents discharged to sewer (indirect discharges) or river (direct discharges). Most European countries set colour absorbance limits at various wave lengths which have to be complied with by the discharger. This has meant an increase in charges for colour removal treatments either on-site or at the local municipal wastewater treatment plants.
In some countries legislation also exists to limit AOX levels in effluent.
An equally important factor has been the drive to reduce the total costs of processing, and high fixation dyes giving high levels of Right-First-Time production can make a significant contribution in this respect.

Reference literature

[Buettler, 2000]
Buettler, B.; Galafassi, P.; Hannemann, K.
Vorteilhafte Kombination-Umweltverträgliche Produkte mit besserer Ökonomie
Melliand Textilberichte 81 (2000) 382-385

[Easton, 1995]
Easton, J.R.
The dye maker's view
in "Colour in Dyehouse Effluent", edited by Cooper, P.
Society of Dyers and Colourists, Bradford West Yorkshire BDI 2JB, England (1995) 9-21

[Ebenezer, 2001]
Ebenezer, W.J.; Hutchings, M.G.
Super-Efficient Dyes for the Coloration of Cotton: The Procion XL+ Range
Green Chem. (2001) 3, G10-G13

[Eden]
Eden, B.;Schaffeld, M.
Levafix CA – ein neues, Hochleistungs-Reaktivfarbstoffs-Sortiment
Melliand Textilberichte 81 (2000) 386-390.

[Taylor, 2000]
Taylor, John A.
Recent Developments in Reactive Dyes
Review of Progress in Coloration 30 (2000) 93-107

4.2.1.3.5 Exhaust dyeing of cellulosic fibres with low salt reactive dyestuffs

Description

Traditionally, exhaust dyeing of cellulosic fibres with reactive dyestuffs required high amounts of neutral salts usually 50-60 g/l but up to 100 g/l for dark shades. However several manufacturers have developed innovative dyestuff ranges and application processes that only need about two thirds of this quantity.

Examples of these systems are

Cibacron LS dyes (Ciba)
Levafix OS dyes (Dystar)
Procion XL+ dyes (Dystar)
Sumifix HF (Sumitomo)

Low salt reactive dyestuffs are also polyfunctional reactive dyes (see the described technique "Exhaust dyeing of cellulosic fibres with polyfunctional reactive dyestuffs") but have additional special properties. They have higher affinity to cellulosic fibres and allow very high fixation rates which brings the added benefit of reduced unfixed colour load in the effluent. At the same time, the required amount of salt for dyeing can be significantly reduced. Figure 4.25 illustrates two examples.

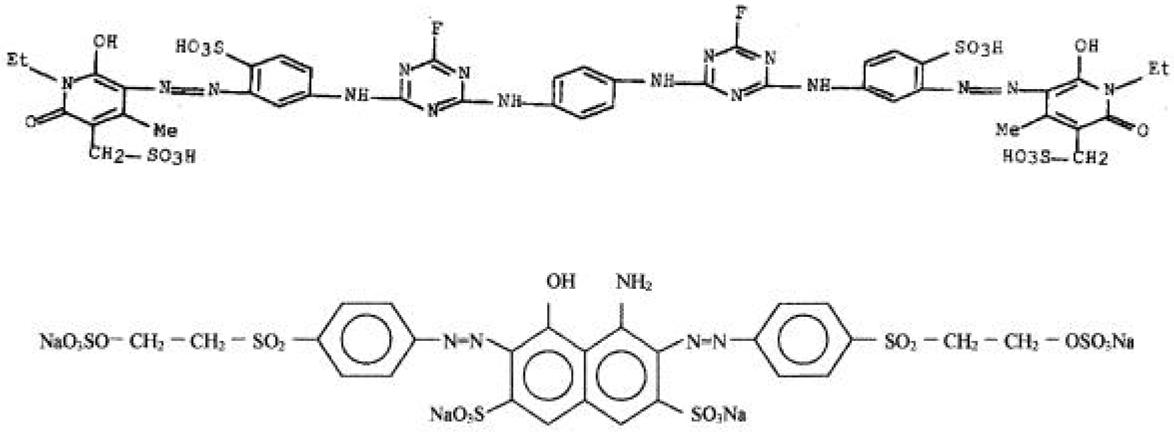


Figure 4.25: Two examples of polyfunctional reactive dyestuffs with high affinity to cellulosic fibres - the first has two monofluoro triazine reactive groups bridging the chromophores and the second (reactive black 5) two vinyl sulfone reactive groups; there are also reactive dyestuffs with two different reactive groups

These dyestuff ranges have also been designed to perform well on modern low liquor ratio dyeing machines which offer further possibilities for reducing the overall salt requirement as illustrated in Table 4.17.

	Winch LR 20:1	Jet LR 10:1	Low LR Jet LR 5:1
Traditional Reactive Dyes (60g/l salt)	1200 kg	600kg	300kg
Low Salt Reactive Dyes (40g/l salt)	800 kg	400 kg	200 kg

Table 4.17: Quantities of salt required to dye 1000 kg fabric to a medium depth of shade

Main achieved environmental benefits

Salt consumption for exhaust dyeing is reduced by about one third of the quantity needed for conventional reactive dyestuffs, with positive impact on effluent salinity and on smooth running of wastewater treatment units. The significantly lower salt usage translates into reduced salt handling and dissolving time. An automation of salt or brine additions is facilitated by lower required salt quantity.

When reducing salt levels it is important to ensure that reproducibility levels are maintained as this can have a major impact on water and energy consumption per unit of production. Under low liquor ratio (LR) dyeing conditions the substantivity of a dyestuff is increased due to increased mechanical pick-up and the exhaustion and fixation levels are also increased, but to a lesser extent. However migration and level dyeing behaviour are adversely affected unless there is a compensating reduction in salt concentration. Therefore, salt addition can, even has to be reduced.

It should also be mentioned that rinsing after dyeing needs efficient washing machinery because the non-fixed compounds of the high-affinity type, low salt reactive dyestuffs are not as easy to wash out as low- or medium-affinity dyestuffs.

High affinity low salt reactive dyestuffs can also be favourably used for one-bath dyeing of polyester-cellulose blends, which saves time, water and energy. The lower salt concentration reduces the tendency of disperse dyestuffs to stain the cotton fibres of the blend (beneficial for fastness and reproducibility of shades). High affinity dyestuffs can be applied to a wide range of liquor ratio with good reproducibility. Thus, they also allow efficient coloration under conditions of longer liquor ratios with respect to cotton such as those that exist when dyeing polyester/cellulose blends.

Applicability

The technique is applicable both to existing and new dyeing machines. Low salt reactive dyestuffs can be applied on all conventional exhaust dyeing machines but offer particular advantage on the most modern low liquor ratio dyeing machines where additional advantages of reduced energy and water consumption can be exploited.

Cross-media effects

There are no cross media effects to be mentioned.

Reference plants

Low salt reactive dyestuffs have been in use for the last five years in all European countries and throughout the world-wide.

Operational data

Individual manufacturers provide comprehensive technical information for their low salt dyestuff ranges including detailed salt recommendations according to depth of shade, type of substrate, equipment in use etc. These recommendations should also have been designed to ensure a high level of reproducibility and maximise Right-First-Time performance. Figure 4.26 shows an example for a dyeing curve.

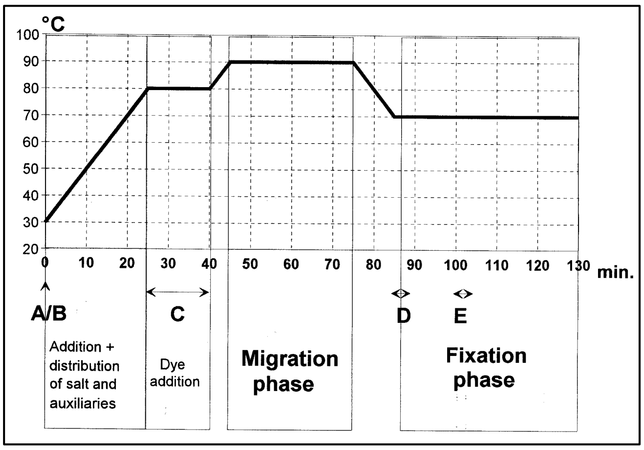


Figure 4.26: Typical dyeing curve for low salt dyestuffs with indication of the addition of dyestuff, salt and alkali

Economics

Compared to conventional reactive dyestuffs, low salt reactive dyestuffs are significantly more expensive when considering the price per kilogram only. However the high colour strength, the savings for salt and increased reproducibility have to be taken into account as well. Depending on the special circumstances of each dye house, the application of low salt reactive dyestuffs can be of economic benefit.

Driving force for implementation

In areas having arid climate conditions and negative water balance, low salt reactive dyestuffs have been introduced first (e.g. North Carolina in the US and Tirupur, Tamil Nadu in India). They have also found success in areas where the dyehouses are discharging directly to freshwater areas and there is a need to minimise salination effects.

Reference literature

[Buettler, 2000]
Buettler, B.; Galafassi, P.; Hannemann, K.
Vorteilhafte Kombination-Umweltverträgliche Produkte mit besserer Ökonomie
Melliand Textilberichte 81 (2000) 382-385

[Ebenezer, 2001]
Ebenezer,W.J.; Hutchings, M.G.
Super-Efficient Dyes for the Coloration of Cotton: The Procion XL+ Range
Green Chem. (2001) 3, G10-G13

[Hildebrand, 1988]
Hildebrand,D.; Renziehausen,B.;Heilmann,D.
Lineare Alkalidosierung und Salzreduktion beim Farben von Cellulosefasern mit Levafix E/EA/EN-farbstoffen

[Jaeger, 1996]
Jaeger, C.A.
Cibacron LS: Reduktion der Elektrolytmenge im Ausziehverfahren
Textilveredlung 31 (1996) 138-140

[Taylor, 2000]
Taylor, John A.
Recent Developments in Reactive Dyes
Review of Progess in Coloration 30 (2000) 93-107

4.2.1.3.6 Enzymatic aftersoaping in reactive dyeing

Description
Dyeing and printing with reactive dyes affords soaping and rinsing steps to remove non-fixed reactive dyestuffs resp. dyestuff hydrolysates. Consumption of energy, water, and chemicals for the soaping and rinsing steps is high.
With enzymatic techniques the removal of non-fixed dyestuffs from the fibre as well as from the exhausted dyebath can be achieved. Usually the application of the enzymatic compounds takes place in the fourth or fifth rinsing step (Table 4.18).

Common aftertreatment (example)	Enzymatic aftertreatment
5 min overflow rinsing	5 min overflow rinsing
10 min 40 °C	10 min 40 °C; neutralisation
10 min 40 °C; neutralisation	10 min 60 °C
10 min 95 °C	10 min 95 °C
10 min 95 °C	15 min 50 °C; enzymatic treatment
10 min 50 °C	10 min 30 °C
10 min 30 °C	-

Table 4.18: Comparison between common and enzymatic aftertreatment (exhaust dyeing) [Bayer, 2000]

Enzymatic decolourisation of reactive dyestuffs is proofed with Levafix, Remazol, Cibacron, Procion, and Synozol types [Bayer 2000].

Main achieved environmental benefits
The amount of rinsing steps can be reduced by means of an enzymatic aftertreatment. Therefore besides the application of environment-friendly enzymes, savings in consumption of detergents, water, and energy are the main advantages concerning environmental aspects.

Applicability
The technique is applicable for exhaust dyeing with reactive dyestuffs. Application in continuous processes and printing are currently under development. Most of the reactive dyestuffs can be enzymatically decolourised. However, a test on laboratory scale should be performed.

Cross-media effects
There are no cross-media effects to be mentioned.

Reference plants
Enzymatic aftertreatment is applied in several German finishing mills as well as world-wide.

Operational data
The enzymatic rinsing step is carried out as follows (exhaust technique):
- Fresh water (50 °C)
- Addition of a process regulator mainly for adjusting optimal pH (1 g/l)
- Control of pH; addition of acetic acid if necessary
- Addition of enzymatic compound (0.25 g/l);
- Running time: 10 min
- Draining of the liquor.

Economics
Savings in water and energy consumption and reduced process times are advantages in an economical sense.

Driving force for implementation
Implementation of the enzymatic technique is motivated by cost saving potentials and improved quality (better fastness properties can be achieved).

Reference literature

[Bayer, 2000]
Product information (2000)

[Haas, 2000]
Haas, J.; Koenemund, B.; Vogt, U.
Neuer und besserer Weg beim Seifen von Reaktivfärbungen
Melliand Textilberichte 81 (2000) 847-848

4.2.1.3.7 Exhaust dyeing of polyester and polyester blends - carrier-free or use of ecologically optimised carriers

Description

Due to the high glass transition point of polyethyleneterephthalate, which is in the range of 80-100 °C, the diffusion rate of disperse dyestuff molecules into the PES fibres at normal dyeing temperatures is very low. Therefore, dyeing conditions used for other substrates are not applicable. Exhaust dyeing of single polyester and polyester blends can be carried out either in autoclaves at high temperature (HT-dyeing; 130 °C, which is usually applied for PES and wool-free blends) or at normal dyeing temperatures (95 °C – 100 °C or 106 °C – 120 °C with wool protection agent, which is applied for PES/wool-blends) with the help of so-called carriers.

Carriers are absorbed to a great part on the PES fibre. They improve the swelling of the fibres and increase the amorphous parts in the fibre structure. After dyeing and rinsing steps a particular amount is emitted to wastewater. The other part, fixed on the textile, enters the off-gas in downstream drying and heat setting steps or remain on the fibre with possible problems concerning consumer health.

Common substances which can be used in carrier formulations are

- Chlorinated aromatic compounds (mono-chlorobenzene, trichlorobenzenes etc.)
- o-phenylphenol
- Biphenyl and other aromatic hydrocarbons (trimethyl benzene, 1-methyl naphthaline etc.)
- Phthalates (diethylhexylphthalate, dibutylphthalate, dimethylphthalate)

Human toxicity, aquatic toxicity, high volatility, and high odour intensity are the main problems in using common carriers.

For special applications (esp. in carpet industry) modified polyethylenterephthalate which is dyeable with cationic dyestuffs can be used.

For pure polyester and wool-free blends, HT-dyeing without use of environmental problematic carriers is the best method.

However, dyeing of polyester blends esp. polyester/wool blends and poyester/elastane blends afford the use of carriers because the sensitivity of the wool substrate to high temperatures. Chemistry of carrier systems which are optimised concerning human toxicology and environmental properties are based on

- Carbonic acid esters/benzylbenzoate
- and N-alkylphthalimide.

Regarding polyester/elastane blends, it is recently possible to apply certain dyestuffs at 120 – 125 °C. These dyestuffs provide very high washing fastness on these blends [CIBA, 2001].

Main achieved environmental benefits

In HT-dyeing of PES wastewater and off-gas is carrier-free. The amount of environmental problematic substances is reduced.

Carbonic acid esters/benzylbenzoate based carriers are readily biodegradable (degree of mineralisation: 79%). Due to their low volatility odour nuisance (esp. regarding working place atmosphere) is negligible [CHT, 1999].

In dyeing with carriers based on N-alkylphthalimide odour nuisance is minimised due to the low volatility of the products [Bayer, 2000].

Applicability
HT-dyeing can be carried out for all PES qualities. Special HT-dyeing equipment is necessary. Application for PES blends is limited regarding the sensitivity of the fibre blends (esp. PES/WO blends) to high temperature.

Dyeing with optimised carriers is applicable for all PES blends. The effectiveness of the products in comparison to common products has to be kept in mind.

Cross-media effects
Carriers based on N-alkylphthalimide derivatives are not biodegradable and only partially eliminated in biological wastewater treatment.

Reference plants
HT-dyeing and optimised carriers are applied European- as well as world-wide.

Operational data
Carbonic acid esters/benzylbenzoate carriers are used in a range between 2,0-5,0 g/l (dyeing at boiling temperature; average liquor ratio) [CHT, 1995].

N-alkylphthalimide carriers are applied in a range of 2% (liquor ratio 1:10) to 1% (liquor ratio 1:20) for dyeing of light shades. For dark shades the amount of carrier is in a range between 6% - 3% [Bayer, 2000].

Economics
The price for ecological optimised carriers is approximately the same as for common carriers.

Driving force for implementation
To keep environmental limit values and to improve conditions concerning working place atmosphere is the main motivation to use HT-dyeing or optimised carrier systems.

Reference literature

[Bayer, 2000]
Bayer AG, D-Leverkusen
Material Safety Data Sheet and product information (2000)

[CHT, 1995]
Chemische Fabrik Tübingen, D-Tübingen
Product information (1995)

[CHT, 1999]
Chemische Fabrik Tübingen, D-Tübingen
Material Safety Data Sheet (1999)

[Ciba, 2001]
Ciba Internet homepage "Idea of the month", July 2001 in connection with Ciba brochure "Polyester/elastane blends" (2000)

[DWI, 1997]
Deutsches Wollforschungsinstitut
AIF Vorhaben 10187 (1997), Forschungskuratorium Textil e.V. Eschborn, Germany

[EnviroTex, 1996]
EnviroTex GmbH, D-Augsburg
Erweiterte, wichtige immissionsschutzrechtliche Fragestellungen beim Betrieb von Textilveredlungsanlagen; Teilbericht 3: Trocknen und Fixieren carriergefärbter Ware
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, München (1996)

[Fiebig, 1984]
Fiebig, D.
Ökologische Aspekte und Gebrauchseigenschaften von Polyesterfärbungen mit Carriern
Textil praxis international (1984) 144-148

[Fischer, 1979]
Fischer, H.; Weber, R.
Möglichkeiten zur Verminderung der Abwasserbelastung durch gezielte Veränderungen an Textilhilfsmitteln
Textil praxis international (1979) 578-582

[Keller, 1978]
Keller, K.H.
Der Einsatz von Carriern – Chemie und Wirkungsmechanismus
Textilveredlung 13 (1978) 140-145

4.2.1.3.8 More environment-friendly reductive aftertreatment in PES dyeing

Description

Customers demand a high washing fastness. In order to meet the requirement, aftertreatment is practised to remove non-fixed disperse dyes from the fibres. Aftertreatment in PES-dyeing can be carried out with surfactants or more effective by means of reducing agents. In conventional aftertreatment, sodium dithionite is used as reducing agent. The pH of aftertreatment bathes has to be changed two times:

- Dyebath: acidic
- Reducing step: alkaline
- Rinsing step: acidic (pH of the textile: 4-7.5).

Reducing agents based on special short chain sulfinic acid derivatives can be used directly in the exhausted acidic dyebath. The reducing agents with high biodegradability cause a lower sulfur (resp. sulfite) load in the effluent [BASF, 2000]. Further sulfinic acid products – not mentioned in detail here - with a similar ecological performance (readily biodegradable, lower sulfite load in effluent) are available; they have to be applied in alkaline conditions [Textilcolor 2000].

Main achieved environmental benefits

The reducing agent based on aliphatic short chain sulfinic acid derivatives is readily biodegradable (Biodegradation > 70% (OECD 302 B - DOC-reduction after 28 d). The sulfur content of the product is approx. 14% (sodium dithionite: approx. 34%). Savings in water consumption up to 40% are possible.

Sodium dithionite primarily reacts to sulfite; sulfate is generated slowly. The sulfinic based reducing agent primarily reacts to 50% sulfite and 50% sulfate. Amount of inorganics (sodium sulfate, sodium sulfite) is minimised compared to dithionite (Table 4.19).

Recipe	Sulfur concentration in mixed effluent [mg/l]	Spec. sulfur load [mg/kg PES]	Max. sulfite concentration in mixed effluent [mg/l]	Max. spec. sulfite load [mg/kg PES]
Sodium dithionite (3 g/l) 2 rinsing baths	260	4100	640	10300
Sulfinic acid compound (6.25 ml/l) 2 rinsing baths	290	4700	360	5800
Sulfinic acid compound (6.25 ml/l); 1 rinsing bath	390	4700	490	5800

Table 4.19: Loose fibre dyeing (liquor ratio 1:4); sulfur and sulfite concentration in mixed effluent (dyebath, aftertreatment bath, and rinsing baths are considered) and specific sulfur and sulfite load - [BASF 2000]

Furthermore working place safety compared to auto-inflammable dithionite is improved, odour nuisances are minimised.

Applicability

The technique can be performed on PES, PAC, CA, and their blends. In case of blends with elastane fibres applicability is limited. The alternative auxiliaries can be used in all types of dyeing machines.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants
The technique is applied in more than five finishing mills in Germany and world-wide as well.

Operational data
A typical process is described below:
- 1.0-1.5 ml/l (medium shades) resp. 1.5-2.5 ml (dark shades) reducing agent is added to the exhausted dyebath (10-20 min; 70-80 °C)
- Hot rinsing
- Cold rinsing.

Economics
Cost-savings due to savings in energy, time, water, and chemicals are possible.

Driving force for implementation
Cost savings and improvement of the environmental performance (esp. reduction of sulfite content in wastewater) is to be seen as main reason for the substitution of conventional reductive aftertreatment.

Reference literature

[BASF, 2000]
BASF AG, D-Ludwigshafen
Product information and personal information (2000)

[Karl, 1997]
Karl, U; Beckmann, E.
Innovatives neues Produkt für die PES-Nachreinigung im Färbebad
Melliand Textilberichte 78 (1997) 332-334

[Karl, 1999]
Karl, U.; Freyberg, P.
Neue reduktive Verfahren in der Textilveredlung
Melliand Textilberichte 80 (1999) 616-618

[Textilcolor, 2000]
Textilcolor AG, CH-Sevelen
Product information (2000)

4.2.1.3.9 Substitution of afterchrome dyestuffs for dyeing of wool (all make-ups)

Description

In 1995, world market for wool dyestuffs was about 24,000 t, whereas the percentage in Asia, especially in China and Japan, is higher and is lower in Europe (Figure 4.27).

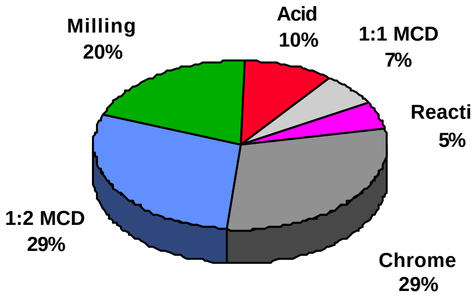


Figure 4.27: Percentages of applied quantities of dyestuff classes for wool dyeing on global base - [Hannemann, 1997]; MCD = Metal Complex Dyestuffs; Milling = acid milling dyestuffs

Due to their lack of brilliance, afterchrome dyestuffs are used for muted shades: 50-60% of afterchrome dyestuffs for wool are applied for black shades, a further 25-30% for navy, and the remaining 10-25% for other restrained colours, such as brown, bordeaux or green [Hannemann, 2000]. Part of the chrome used in dyeing appears in wastewater, however its quantity can be minimised by process optimisation, especially by exact pH control (ideal is 3.5 - 3.8) and by adding anionic auxiliaries [Langmann, 1976; Duffield, 1991]. However, still considerable amounts of chromium may be present in wastewater, not only in the exhausted dye bath but also in rinsing water and from after-treatment processes [Thomas, 1992].

Quite recently, there are reactive dyestuffs available to substitute afterchrome dyestuffs, also for dark shades. There are six different colours available which are compiled in Table 4.20, along with information on composition and biodegradation.

Trade name	Chemical characterisation all dyestuff products are pulver formulations	danger symbol	Biological degradation and elimination resp. [%], testing method	spec. COD-value [mg O_2/g]	spec. BOD_5-value [mg O_2/g]	Content heavy metals [mg/g]	Content orga-nohalogens [mg/g]	Content of nitrogen [mg/g]
Lanasol Yellow CE	mixture of azo dyestuffs	Xn	40-50, OECD 303A	790	55		65	39
Lanasol Golden Yellow CE	formulation of an azo dyestuff	Xi	<10, OECD 302B	909	0		<1	ca. 10
Lanasol Red CE	mixture of azo dyestuffs	Xi	<10, OECD 302B	700	0		<1	56
Lanasol Blue CE	mixture of azo and anthraquinone dyestuffs, contains reactice black 5	Xn	40-50, OECD 303A	928	329		<1	36
Lanasol Navy CE	mixture of azo dyestuffs, contains reactive black 5	Xn	20-30, OECD 302B	1032	57		<1	64
Lanasol Black CE	mixture of azo dyestuffs, contains reactive black 5	Xn	20-30, OECD 303A	ca. 800	0			96
applied auxiliaries for Lanasol Dyes								
Cibaflow CIR	anionic de-aerating agent containing alkylpolyalkylene-glycolethers and esters	Xi	80-90, OECD 302B	410	135			
Albegal B	amphoteric hydroxyethylated fatty acid amine derivate	Xi	60-70, OECD 302B	1.025	0			33

Table 4.20: Name and data on six reactive dyestuffs for wool dyeing and concerned auxiliaries

These dyestuffs are based on bifunctional reactive dyestuffs mainly from the bromo-acrylamide or vinylsulfone type in order to achieve the required wet-fastness. A typical structure of a bifunctional reactive dyestuff from the bromo-acrylamide type is shown in Figure 4.28. The dye range is based on a trichromy with Yellow CE or Golden Yellow CE, Red CE and Blue CE for the coloured shade area and Navy CE and Black CE as basis for high fast navies and blacks.

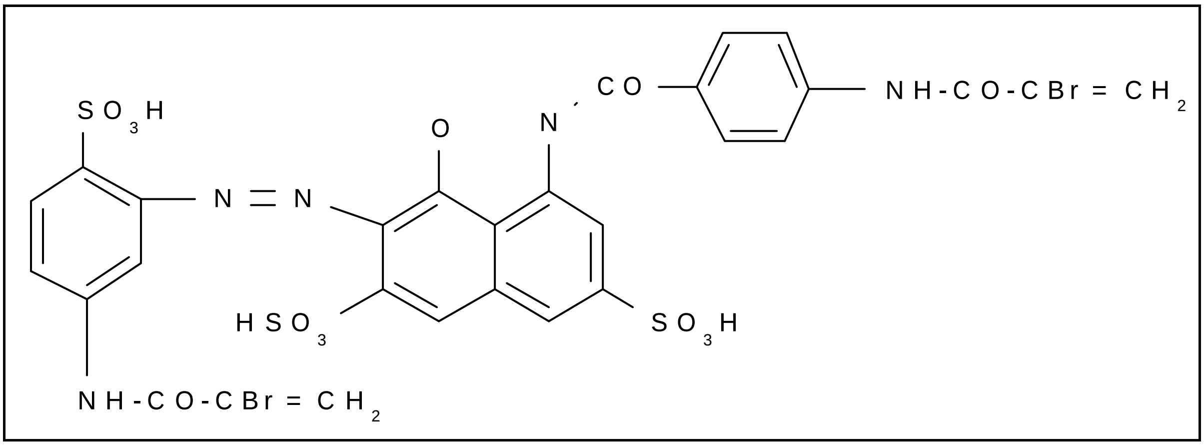


Figure 4.28: Typical example for the chemical structure of a metal free reactive dyestuff for dyeing of wool, appropriate to substitute afterchrome dyestuffs

The reactive dyestuffs meet the very high standards of fastness like afterchrome dyes.
In Table 4.21 the properties of the reactive dyestuffs, in comparison to afterchrome dyestuffs, are compiled.

	Afterchrome Dyestuffs	Reactive dyestuffs
Fixation mechanism	small acid dye molecule, which is complexed with chromium	covalent chemical bond
Formulation	only one chromophore to yield black	dye mixture necessary to yield black
Levelling properties	good fibre levelness	fibre levelness depends on dyeing auxiliaries and combination partners
Dyeing process	two-step dyeing process: dyeing and chroming	one-step dyeing but for dark shades, after-treatment is required
Reproducibility	shade matching difficult	very good
Impact on wool fibres	fibre damage	wool protection by the dyestuffs themselves
Health and safety aspects	handling of hexavalent chromium (carcinogenic compound)	metal free
Effluent characteristic	chromium in the effluent	more coloured but metal free

Table 4.21: Properties of reactive dyestuffs for wool dyeing in comparison to afterchrome dyestuffs

Main achieved environmental benefits

Effluent and wool is free of chromium. Handling of hexavalent chromium, which requires special safety precautions (due to its chronic toxicity and carcinogenic properties) can be avoided.

Applicability

The reactive dyestuffs can be applied for all make-ups in all concerned existing dyeing machines. When controlling pH and temperature properly, adding a suitable levelling agent and carrying out adequate after-treatment exhaustion rates of more than 90% and exceptional fastness level of afterchrome dyestuffs are achieved [Hannemann, 2000]. In special cases, such as chlorination of the wool after dyeing, high level fastness can not be achieved.

Cross-media effects

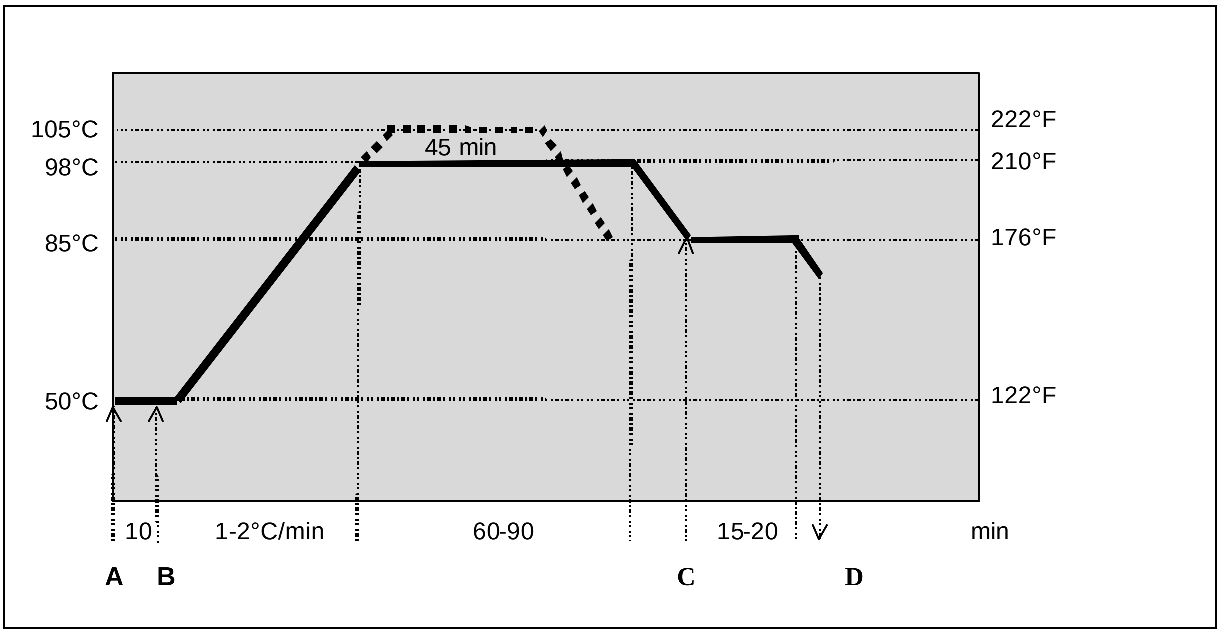
Dyeing with reactive dyestuffs require levelling agents which are heavily or non-biodegradable but are eliminated in wastewater treatment plants by adsorption. These compounds have affinity to wool fibres and remain there to an extend of about 50%.

Reference plants

Reactive dyestuffs for wool dyeing are applied for a few years all over Europe and other countries.

Operational data

Figure 4.29 shows a typical dyeing curve.



A	0.5 g/l Deaeration agent on basis fatty alcohol ethoxilates 0-5% Glauber's salt 1-2% Levelling agent (alkylaminethoxilates and alkylaminethersulfates) x % acetic acid (80%) and /or formic acid - pH 4.5 - 6
B	y % reactive dyestuffs (Table 4.20)
C	z % ammonia or soda ash
D	Rinse warm and cold; acidify with 1% formic acid (80%) in the last rinsing bath

- ✓ For yarn and piece dyeing, a 15 min temperature hold at 70°C is recommended
- ✓ For shrink-resist wool, a starting temperature at 30°C and a 15 min temperature hold at 60°C are recommended

Figure 4.29: Dyeing curve for the application of reactive dyestuffs (Lanasol CE) for wool exhaust dyeing

Economics

Reactive dyestuffs can be applied to the same cost compared to afterchrome dyestuffs.

Driving force for implementation

The avoidance of handling of hexavalent chromium and wastewater problems as well pushed the introduction of reactive dyestuffs substantially. The same is for the attractive cost of these dyestuffs.

Reference literature

[Hannemann, 1997]
Hannemann, K.; Flensberg, H.
Reaktivfarbstoffe für Wolle - eine Alternative zu den Nachchromierungsfarbstoffen
Melliand Textilberichte 78 (1997) 160-164

[Hannemann, 2000]
New developments in the substitution of afterchrome dyes
Proceedings of 10th International Wool Textile Research Conference, 26.11.-01.12.2000
Melliand Textilberichte 82 (2001) in print

[Langmann, 1976]
Langmann, W.; Meier, G.
Untersuchung des Chromierungsprozesses beim Färben von Wolle im Hinblick auf Abwasserprobleme
Melliand Textilberichte 57 (1976) 580-582

[Duffield, 1991]
Duffield, P.A.; Holt, R.R.D.; Smith, J.R.
Färben mit geringem Restchromgehalt im Abwasser
Melliand Textilberichte 72 (1991) 938-942

[Thomas, 1992]
Thomas, H.
Neue Aspekte zur Abwasserbehandlung beim Färben von Wolle mit Nachchromierungsfarbstoffen
Taschenbuch Textilindustrie (1992) 324-331

4.2.1.3.10 Dyeing of Wo and PES in standing bath

Description

It is well-known that wool can be dyed with high exhaustion rates. This is for afterchrome dyes and 1:2 metal complex dyes (also 4.2.1.3.9). Also disperse dyes have high exhaustion rates. In such cases, the exhausted dye bath can be reused for the next batch. In the following, an example for doing so is described. The concerned company is finishing loose material consisting either of wool or of polyester with subsequent spinning unit. The produced yarn is used for the formation of fabrics (in an other company) which are also finished. The latter is the reason for that rinsing of the loose material after dyeing can be minimised. Thus, in case of wool dyeing with afterchrome dyestuffs or metal complex dyestuffs, there is only one rinsing. Disperse dyeing is carried out with reductive after-treatment directly subsequent to dyeing and one rinsing bath. The rinsing and after-treatment bath are discharged (after neutralisation, reduction of hexavalent chromium and chromium(III) precipitation) to a municipal wastewater treatment plant. Along with the introduction of dyeing in standing bath, all ten dyeing stations with 50 to 1000 kg capacity (LR 1:8) have been equipped with temperature and pH control and automated acid dosage. In addition, acetic acid had been replaced by formic acid in order to reduce COD load. The dyeing processes for wool are carried out conventionally. The so-called "Lanaset TOP" process (see the concerned described process) has not been introduced yet. However, dyeing in standing bath is possible. Per day, about 65 batches are dyed.

For dyeing in standing, for 10 storage tanks have been introduced with 17m^3 each along with a concerned piping system (Figure 4.30). The exhausted dye baths are moved to the tanks by compressed air. A ring pipe is therefore used in order to minimise the installation of new pipes. Most of the tanks are constantly used for the same type exhausted dye baths (e.g. afterchrome bath for dark shades, such as black and marine or exhausted bath from dyeing with metal complex dyestuffs etc.). For preparation of new dyeing baths, the dyestuffs and chemicals are supplied manually.

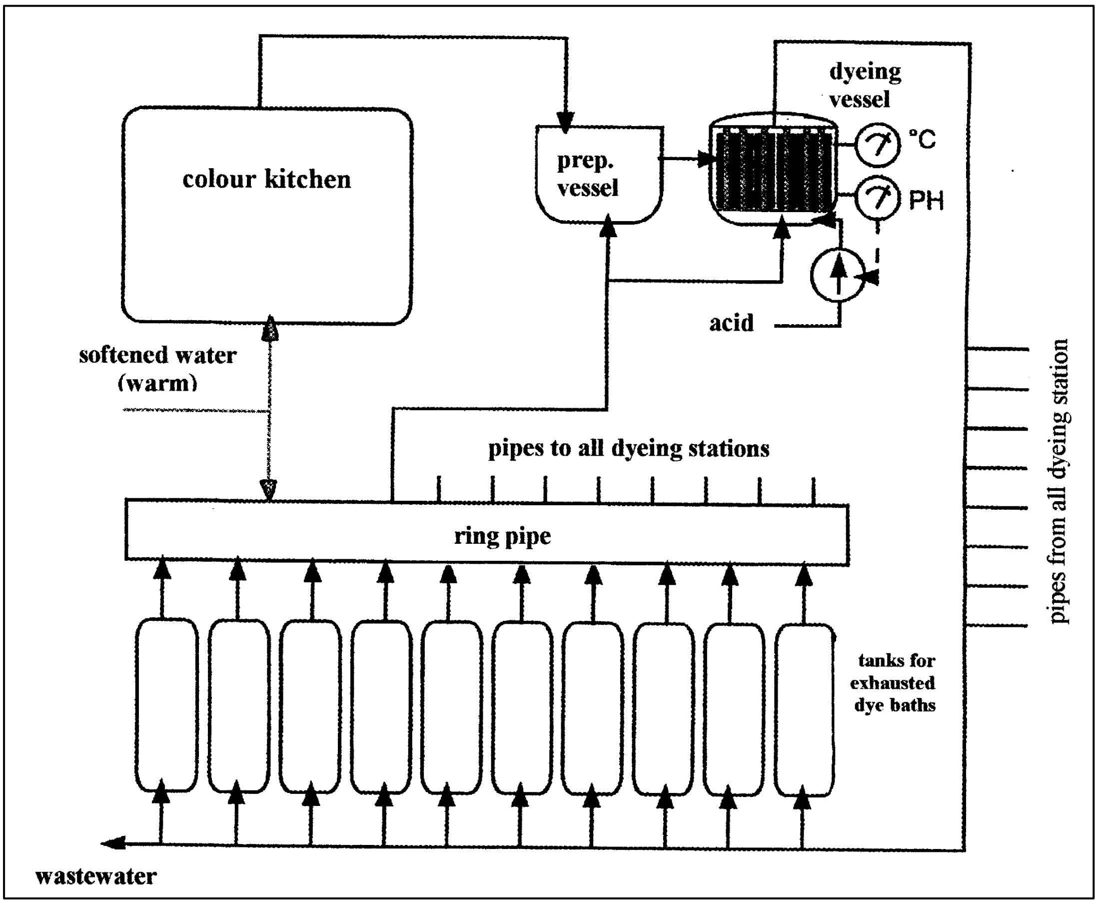


Figure 4.30: Scheme indicating the installations (tanks and piping system) for dyeing in standing bath - [Fembacher, 1997a]

Main achieved environmental benefits

The process optimisation measures resulted in a 70% reduction of chromate consumption. Dyeing in standing bath lead to the reduction of specific water consumption from 60 to 25 l/kg (absolute: reduction from 150,000 m^3/a to 65,000 m^3/a) and wastewater flow respectively which is nearly 60%. In case of wool dyeing, the application of sodium sulfate can be completely avoided because of protein degradation compounds -originating from wool- guarantee sufficient levelling; these even improves further wool processing.

Applicability

Dyeing in standing bath is possible at new and existing installations. Space for the tanks must be available and the number of different shades may not be too large. In case of the described example, the technique has been introduced in practice in a 35 years old dyehouse.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

Kammgarnspinnerei Stöhr GmbH, D-41199 Mönchengladbach

Operational data

Dyeing in standing bath is successfully in operation since 1996. In the start-up phase, experience has to be collected how to prepare new dyeing baths from exhausted ones; but soon it becomes daily routine.

Economics

Investment for building for the tanks, the tanks themselves, piping and control devices 0.8 million EURO. Fresh water and wastewater cost are 3.20 EURO/m^3 (0.6 EURO/m^3 for fresh water including treatment and 2.60 EURO/m^3 wastewater fee). Thereby, cost for pre-treatment (neutralisation, reduction of hexavalent chromium and precipitation of chromium(III)) and disposal of sludge is not taken into account. Thus, annual savings of about 250,000 EURO are achieved which allows an acceptable pay back time.

Driving force for implementation

Increasing cost for wastewater and increasing requirements on wastewater discharge (especially regarding chromium) have been the driving forces for the company to install the described techniques.

Reference literature

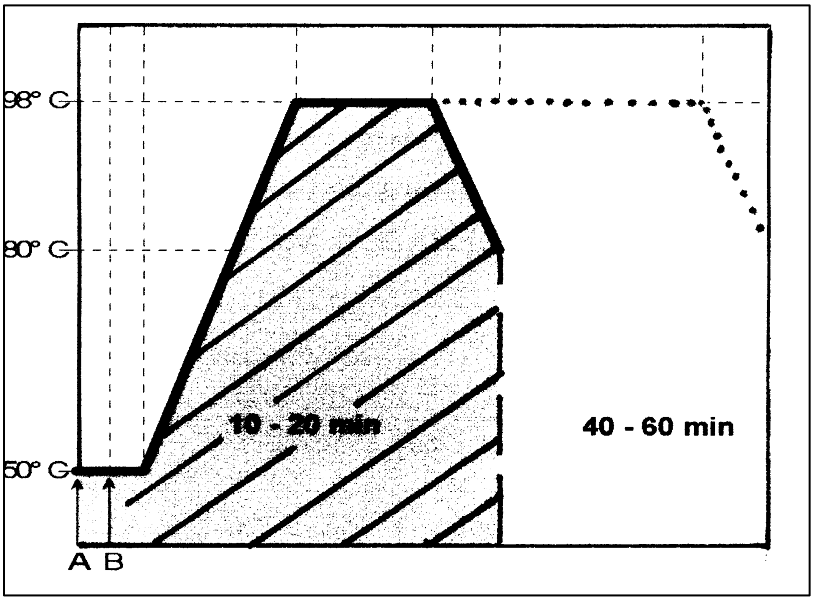
[Fembacher, 1997a]
Fembacher, K.; Brummerhop, H.J.; Mocken, R.
Entwicklung, Erprobung und Optimierung eines umweltverträglichen Färbereiverfahrens zur Reduktion der Abwasserbelastung bei der Kammgarnspinnerei Stöhr GMbH, D-41199 Mönchengladbach
Abschlussbericht über ein Entwicklungsprojekt, gefördert von der Deutschen Bundesstiftung Umwelt (1997)

[Fembacher, 1997b)
Fembacher, K.; Fembacher, U.
Abwasserbehandlung und Prozessoptimierung in der Kammzugfärberei
Melliand Textilbereichte 78 (1997) 159

4.2.1.3.11 Dyeing of loose wool fibre and combed tops - minimisation of wastewater emissions

Description

Dyeing of loose wool fibre and combed tops is still carried out with afterchrome dyestuffs and metal complex dyestuffs as well. These chromium containing dyestuffs can be substituted by metal free reactive dyestuffs in many cases (see 4.2.1.3.9). However, when substitution is not possible, the conventional dyeing process can be optimised by applying proper process control (especially pH control). For 1:2 metal complex dyestuffs, the dyeing process can be improved (not suitable for afterchrome dyes) by using a special auxiliary for increasing dye bath exhaustion within shorter time and to replace acetic acid by formic acid. The optimised process is well-known as "Lanaset TOP process" which has been released by a dyestuffs and textile auxiliaries supplier in 1992 [Hannemann, 1992]. It is mainly for dyeing loose wool fibre and combed tops which are still major make-ups (about half of the world-wide annual processed quantity). The control of pH and the application of a mixture of different fatty alcohol ethoxilates (having fibre and dyestuffs affinity) shorten the dyeing time drastically compared to the conventional process (Figure 4.31). In addition exhaustion rate is almost 100%. This makes dyeing on standing bath easier (see 4.2.1.3.10)



A **Adding of auxiliaries and formic acid**
B **Adding of dyestuffs**

Figure 4.31: Dyeing of loose wool fibre and combed tops - comparison of the dyeing curve for the conventional process (whole curve) and the optimised process (Lanaset TOP process) (hatched part of the curve) - [Bauhofer, 1995]

In addition to environmental advantages, the process enables fast shade and fastness development, leading to reproducible dyeings with very high fastness properties.

Main achieved environmental benefits

Because of higher exhaustion and fixation rate respectively, colour in exhausted dye bath is reduced which directly correlates with chromium content. Residual chromium contents in exhausted dye bath down to 0.1 mg/l are achievable. When dyeing in standing bath, no build-up of chromium occurs. The substitution of acetic acid (having a specific COD of 1067 mg O_2/g) by formic acid (having a forth time lower specific COD of 235 mg O_2/g and being a stronger acid than acetic acid) leads to lower COD load in the effluent. During dyeing, boiling time can be shortened to one third which saves not time only but also energy.

Applicability
The technique is applicable in new and existing installations for dyeing loose wool fibre and combed tops.

Cross-media effects
There is not cross media effect to be mentioned.

Reference plants
The process has been successfully introduced into practice in many dyehouses world-wide.

Operational data
See description of this technique.

Economics
Savings are achieved due to shorter process time and less rinsing water.

Driving force for implementation
The requirements to reduce the chromium content in wastewater and the need to increase productivity have been the main driving forces for the implementation of this technique.

Reference literature

[Hannemann, 1991]
Hannemann, K.; Grüner, F.
A new short-time process for dyeing loose wool fibre and combed tops
International Textile Bulletin (1992), no. 4, 3-9

[Bauhofer, 1995]
Bauhofer, R.; Hannemann, K.
Environmental aspects of wool dyeing
Proceedings of the 9th International Wool Research Conference - 28.06. - 05.07.1995 in I-Biella, Vol. I (1995) 96-100

4.2.1.3.12 Environment-friendly dyeing with sulphur dyestuffs

Description

World-wide sulphur dyestuffs are of great importance in dyeing cotton in medium to dark shades (esp. black) with a high fastness to light and washing. Sulphur dyes are synthesised by reaction of aromatic nitrogen containing compounds with sulphur or polysulfides. The molecular structure of sulphur dyes which are water insoluble pigments is in most cases not well defined. Dyeing process is carried out with the reduced water soluble „leuco-compound“. Common sulphur dyes are available in powder form; before dyeing they have to be reduced with sodium sulfide in an alkaline solution. Also liquid pre-reduced dyestuff formulations are available (sulfide content > 5%). Surplus of sulfide in wastewater (caused by the dyestuffs and the reducing agent) is responsible for wastewater toxicity and odour nuisances (esp. in working place atmosphere).

The following sulphur dyes with an optimised ecological performance are available:

- Prereduced dyestuffs with reduced amount of sodium sulphide (liquid formulations; sulfide content < 1%) [DyStar, 2001]
- Non-prereduced sulfide-free dyestuffs (water soluble in the oxidised form) [DyStar, 2001]
- Non-prereduced sulfide-free stabilised dispersed dyestuffs (in powder or liquid form); reduction with sodium dithionite alone is possible [DyStar, 2001]
- Non-prereduced sulfide free dyestuffs (stable suspension); reduction with glucose alone is possible [Clariant, 2001].

Alternative reducing techniques are possible for all non-prereduced sulphur dyestuffs and sulphur dyes with a reduced sulfide content. The following binary systems are in use (glucose is added to sodium dithionite to prevent over-reduction) [DyStar, 2001a]:

- combination of dithionite and glucose
- combination of hydroxyacetone and glucose (seldom)
- combination of formamidine sulfinic acid and glucose (seldom).

Stabilised sulfide free dyestuff types can be reduced with sodium dithionite without addition of glucose [Hähnke, 1995]. For another type of non-prereduced sulphur dyestuffs the reduction step can be carried out with glucose alone [Clariant 2001].

AOX-free re-oxidation is possible with peroxide instead of potassium dichromate and halogenated compounds (bromate, jodate, chlorite or N-chloro-p-toluene sulfamide) and is meanwhile widely applied.

Main achieved environmental benefits

Sulfide content in wastewater is minimised, if sulfide-low or sulfide-free sulphur dyes are used in combination with sulfide free reducing agents. If peroxide is used for re-oxidation instead of dichromate or halogenated compounds chromium respectively AOX-content in wastewater is avoided.

Applicability

The dyestuffs and reducing agents can be used in existing and new dyeing machines (exhaust dyeing as well as continuous techniques). Differences of shade compared to common sulphur dyeing are to be regarded.

Cross-media effects

Using sodium dithionite as reducing agent, the sulfite content in wastewater is to be taken into account.

Reference plants

The dyestuffs and reducing agent system are in use in Europe and world-wide as well.

Operational data

A typical recipe for cotton dyeing on a jet machine (liquor ratio 1:6 to 1:8; dyeing for 45 min at 95 °C is given below [DyStar, 2001a]:

Non-prereduced sulphur dye:	10%
Wetting agent:	1 g/l
Caustic soda solution (38 Bé):	15-20 ml/l
Soda ash:	8-10 g/l
Salt:	20 g/l
Glucose:	10-12 g/l
Sodium dithionite:	8-10 g/l or hydroxyacetone: 4-5 g/l or formamidine sulfinic acid: 4-5 g/l.

Economics

Stabilised non-prereduced sulfid-free dyestuffs are more expensive in comparison to common sulphur dyes.

Driving force for implementation

Main motivation in application of sulfide-free or sulfide-low techniques in dyeing with sulphur dyes is to minimise wastewater problems and to meet requirements to wastewater disposal, as well as to reduce odour nuisances and to improve working place atmosphere.

Reference literature

[DyStar, 2001]
DyStar, D-Frankfurt/Main
Product information. Schwefelfarbstoffe von DyStar: Wirtschaftlich seit 1897 (2001)

[DyStar, 2001a]
DyStar, D-Frankfurt/Main
Technical information (2001)

[Clariant, 2001]
Clariant, CH-Muttenz
Product information. Ihre schwarzen Zahlen (2001)

[Hähnke, 1995]
Hähnke, M.; Schuster, C.
Schwefelfarbstoff und Ökologie – ein Widerspruch?
Melliand Textilberichte 76 (1995) 414-420

4.2.1.3.13 One-step continuous vat dyeing in pastel to pale shades

Description

Conventional continuous (pad steam) vat dyeing comprises padding of the dyestuff pigments, intermediate drying, padding chemicals/auxiliaries (reducing agents), steaming, oxidising and washing (several soaping and rinsing steps).

One-step continuous vat dyeing is possible with special vat dyes and auxiliaries. Padding, intermediate drying and fixation is carried out in a continuous way.

The following auxiliaries have to be used:

- Special selected vat dyes with low migration tendency
- Auxiliaries based on polyglycols and acrylic polymers for pad liquor stability, high fastness level and little influence on handle

Main achieved environmental benefits

The process can be carried out without steaming and subsequent washing. Wastewater is only loaded with residual padding liquors. Water consumption is minimised to approx. 0.5 l/kg textile. Savings in chemicals consumption and energy are additional environmental benefits.

Applicability

The technique can be performed on cellulose and cellulose/polyester blends. Applicability of the technique is restricted on pastel to pale shades (up to approx. 5 g dyestuff/l at 50% liquor pick up).

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

The technique is applied in several finishing mills in Germany as well as world-wide.

Operational data

Typical recipe of padding liquor:

- 30-40 g/l auxiliary I
- 5-10 g/l sodium sulfate
- 10-20 g/l auxiliary II
- up to 2.5 g/kg dyestuff

Typical process parameters:

- padding: liquor pick-up: 50-65% (as low as possible); liquor temperature: < 35 °C
- intermediate drying: 100-140°C
- thermofixation: cellulose 30 s at 170 °C; polyester/cellulose: 30 s at 190 °C

Economics

Considerable cost-savings due to savings in energy, time, water, and chemicals can be achieved compared to conventional pad-steam vat dyeing.

Driving force for implementation

Cost savings are the main motivation to implement the one-step technique.

Reference literature

[BASF, 1998]
BASF AG, D-Ludwigshafen
Product information (1998)

[DyStar, 2001]
DyStar AG, D-Frankfurt
Personal information (2001)

[Schrott, 2000]
Innovationen bei Textilfarbstoffen auf Basis des integrierten Umweltschutzes
20. Fortbildungsseminar des VTCC und VDF, March 2000 (2000)

4.2.1.4 Printing

4.2.1.4.1 Substitution of urea in reactive printing pastes

Description

Urea is used in reactive printing paste up to 150 g/kg paste. Urea is also used in printing pastes containing vat dyes but at significant lower concentrations (about 25 g/kg paste). The main functions of urea are:

- to increase the solubility of dyestuffs with low water solubility. This hydrotropic effect does not influence fixation rates significantly
- to increase the condensate formation necessary for the migration of dyestuffs from paste to textile fibres
- to form condensates with increased boiling point (115°C); thus the requirements on steam quality can be reduced.

Urea can be substituted by controlled addition of moisture (10 weight-% in case of cotton fabric, 20 weight-% in case of viscose fabric and 15 weight-% in case of cotton blends). This substitution is practised for reactive printing on cotton, viscose and concerned blends.

Application of moisture is either performed by spraying defined quantity of water mist or by add-on as foam. The latter has been qualified best, especially in case of reactive printing on stable viscose fibre fabrics. Figure 4.32 and Figure 4.33 show a plant for controlled application of moisture by spraying water mist and a plant by adding moisture in form of foam.

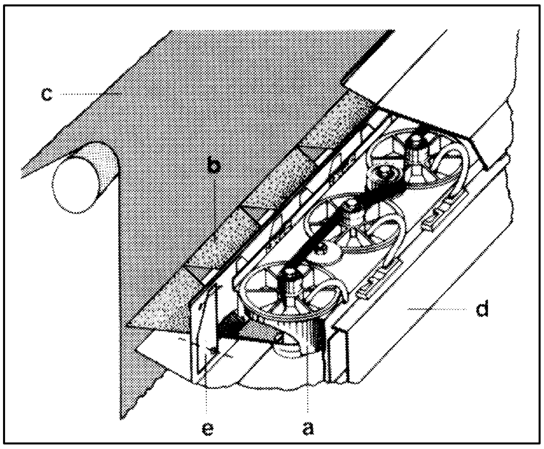


Figure 4.32: Spraying system for the controlled add-on of water on textile fabric
a = discs, b = spray; c = textile fabric; d = discs frame; e = control of spray intensity

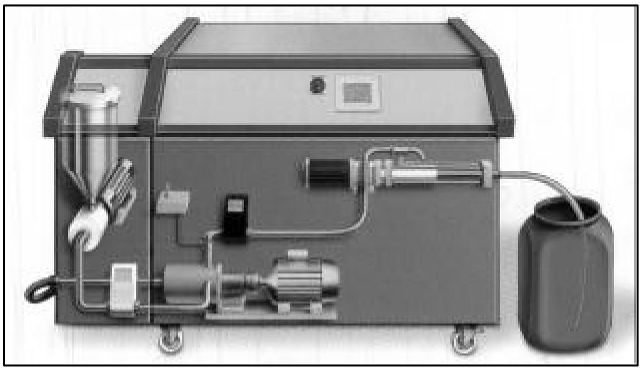


Figure 4.33: Water foam preparation system; the foam is added by a screen like in rotary printing

Main achieved environmental performance

In textile finishing industries the printing section is the main source of urea and its decomposition products (NH_3/NH_4^+). During wastewater treatment excess of ammonia needs high consumption of air and energy respectively for nitrification. Discharge of ammonia and nitrate contribute to eutrophication. Substitution/minimisation of urea at source significantly reduces these adverse effects.

In case of reactive printing the urea content in the printing paste can be reduced from 150 g/kg paste to zero by application of moisture. In case of phthalocyanine complex reactive dyes reduction to 40 g/kg paste is possible only because of bad migration properties of these big dyestuff molecules. In mixed wastewater of a textile finishing industry with a printing department the ammonia concentration went down from about 90-120 mg NH_4-N/l to about 20 mg NH_4-N/l.

Applicability

The substitution of urea is applicable both to new and existing plants performing reactive printing on cotton, viscose and concerned blends.

Cross-media effects

The application of moisture needs energy but this consumption is significantly lower than energy consumption for the production of urea.

Reference plants

Ulmia, D-Ravensburg-Weissenau; KBC, D-Lörrach; Textilveredlung Wehr, D-Wehr

Operational data

Cases have been reported where spraying systems did not meet the quality standards of prints on viscose stable fibres. The foam system is applied in practice since several years with very satisfactory results.

Economics

Regarding investment cost the spraying system is significantly cheaper compared with the foam system. Investment cost for the spraying system including on-line moisture measurement is about 30,000 EURO, for the foam system about 200,000 EURO.

Driving force for implementation

Stringent limits applied by local authorities for NH_4-N in wastewater, due to eutrophication in surface water have promoted the introduction of this technique. Because of high energy consumption for biological nitrification, many municipalities have changed their fee system and now also charge industrial indirect dischargers on nitrogen emissions also. Such fee systems also strongly promoted the application of the described technique.

Reference literature

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduzierung der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

4.2.1.4.2 Pigment Printing with low emissions to air

Description

Due to processing conditions during drying and fixation volatile organic components charge the off-gas in pigment printing. Especially if fixation of the printed goods and finishing is carried out in a one-step process kind and quality of the off-gas pollutants are of essential interest.

In Europe white spirit printing seemed to be eliminated, but nevertheless the main sources for off-gas charges in pigment printing are based on aliphatic hydrocarbons. These substances arise from the mineral oil content in thickeners. Their emission potential can be in a range up to 10 g Org.-C/kg textile. Nowadays optimised products are available. These new products are based on polyacrylic acid with a reduced hydrocarbon content. Also hydrocarbons can be substituted by polyethylene glycol. Another kind of new developments is based on synthetic granules/powders, free of hydrocarbons.

Another source of emissions in pigment printing (formaldehyde and alcohols (mainly methanol)) is the fixation agent (crosslinking agents based on methylol compounds (melamin compounds or urea-fomaldehyde pre-condensates)). New formaldehyde-low products are available.

In addition to the above mentioned items with optimised printing pastes ammonia emission in the off-gas caused by ammonia solutions used as additives in the binder systems can be reduced to a considerable amount.

Furthermore optimised printing pastes are APEO-free. Conventional products should be substituted due to the high aquatic toxicity and reproductive toxicity of nonylphenols.

Main achieved environmental benefits

Table 4.22 shows concrete examples of the emission rates for the thermal processing steps during pigment printing (emission mearurements were carried out on a laboratory stenter):

Process	Pigment print recipe I [g Org.-C/ kg textile]	Pigment print recipe II [g Org.-C/ kg textile]	Pigment print recipe III [g Org.-C/ kg textile]
Drying	2.33	0.46	0.30
Fixation	0.04	0.73	0.06
Sum	2.37	1.19	0.36

Table 4.22: Emissions during pigment printing [EnviroTex, 2000]

In recipe I an already optimised thickener with hydrocarbons was used, in the optimised recipe II the mineral oil is exchanged for polyethylene glycol, and in the optimised recipe III the thickener is based on a powder. Formaldehyde emissions below 0.4 g CH_2O/kg (assumed air textile ratio: 20 m^3/kg textile) can be achieved. Carry-over of volatile substances from printing to finishing processes can be reduced to a level < 0.4 g Org.-C/kg (assumed air/textile ratio: 20 m^3/kg). For optimised printing paste recipes ammonia emission can be reduced below 0.6 g NH_3/kg textile (assumed air textile ratio: 20 m^3/kg).

Applicability

The technique is applicable in new and existing installations. Thickeners based on powders can lead to raising dust or closing the stencils.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

The technique is applied in Europe as well as world-wide.

Selection of suppliers

BASF Aktiengesellschaft
D-67056 Ludwigshafen

Bayer AG
Geschäftsbereich Spezialprodukte
D-51368 Leverkusen

BFGoodrich Diamalt GmbH
D-80972 München

CHT R. Beitlich GmbH
D-72072 Tübingen

Ciba Speciality Chemicals Inc.
GB-BD12-OJZ Bradford, West Yorks

Economics

Economical benefits are given by saving end-of-the-pipe technologies concerning off-gas cleaning.

Driving force for implementation

To keep the limit values concerning off-gas (Organic-C, formaldehyde, ammonia) is the main motivation for the use of VOC-reduced printing pastes.

Reference literature

[EnviroTex, 2000]
EnviroTex GmbH, D-Augsburg
Erweiterte, wichtige immissionsschutzrechtliche Fragestellungen beim Betrieb von Textilveredlungsanlagen – Teilbericht 2: Pigmentdruck
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, München (2000)

[Fay, 1994]
Fay, R.
Pigmentdruck im Spannungsfeld zwischen hohem Qualitätsstandard und ökologischen Anforderungen
Melliand Textilberichte 75 (1994) 1007

[Grund, 1994]
Grund, N.
Ökologische Parameter im Pigmentdruck
Melliand Textilberichte 75 (1994) 630

[Grund, 1995]
Grund, N.
Environmental considerations for textile printing products
JSDC 111 (1995) 7

[Schneider, 1996]
Schneider, R.
Emissions- und abwasserfreier Textildruck – nur eine Vision?
Melliand Textilberichte 77 (1996) 478

4.2.1.4.3 Volume minimisation of printing paste supplying systems of rotary screen printing machines

Description

The printing paste supplying system is indicated in Figure 4.34. The volume depends on the diameter of pipes and squeegee as well as on pump construction and length of pipes.

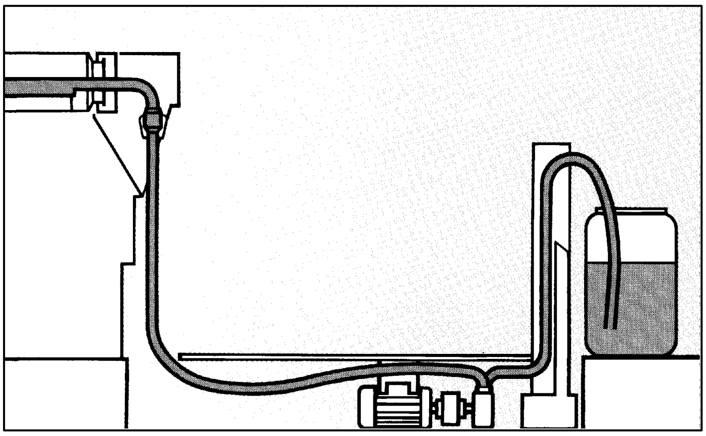


Figure 4.34: The printing paste supplying system of rotary screen printing machines, showing the printing paste drum, the pipes, the pump and (the front part of the) squeegee

When changing the colour or pattern, the printing paste supplying systems have to be cleaned and considerable amounts of printing pastes find its way to wastewater. Thereby, printing machines can have up to 20 printing paste supplying systems. For fashion designs, a typical number of different colours per dessin are 7 to 10. Typical system volumes of conventional and modern printing paste supplying systems are compiled in Table 4.23. In addition to this volume, residual printing paste in the rotary screens have to be taken into account which may be 1-2 kg. Thus, in conventional systems the loss per supplying system is up to 8 kg. This quantity has to be related to consumed amount of paste printed on the textile fabric (Table 4.23). Then it is obvious that the quantity of the supplying system may be higher than the amount printed on the fabric (in case of printing pattern having about 120 m). In Europe, in the past years, average printing batch has significantly decreased and is 400-800 m only.

Minimising the system volume is a major measure to reduce printing paste losses to wastewater. Diameters of pipes and squeegees have been reduced to 20-25 mm leading to substantial reductions (Table 4.23).

Printing width	Volume of conventional printing paste supplying systems in [l] including pipes, pump and squeegee	Volume of optimised printing paste supplying systems in [l] including pipes, pump and squeegee
164	5.1	2.1
184	5.2	2.2
220	5.5	2.3
250	5.8	2.4
300	6.2	2.6
320	6.5	2.7

Table 4.23: Volume of conventional and optimised printing paste supplying systems of rotary screen printing

Especially for small run lengths, additional measures may be taken, such as

- non-usage of the supplying system but manual injection of small quantities of printing paste (1-3 kg) directly into the screen or manual insertion of small troughs (with a cross-section of 3x3 cm or 5x5 cm)
- minimisation of the lenghts of pipes by supplying the printing pastes by funnels directly positioned above the pumps - in case of small run length
- minimisation of residual printing pastes in the screens by application of squeegees with homogenous paste distribution over width
- manual stop of printing paste supply shortly before finishing a run in order to minimise the residual printing pastes in the rotary screens
- nowadays the pumps can be operated in both directions; thus after finishing a run, some of the printing paste can be pumped back to the drum but there are limits because of sucking air via the holes in the squeegee

Main achieved environmental performance

Depending on the age of existing printing paste supplying systems, the system volumes and thus the losses can be reduced significantly. Taking into account pumps which can be operated in both directions, the reduction is about one third.

Applicability

The described measures are applicable both to existing and new installations.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

Many plants in Europe and world-wide have been retrofitted with minimised printing paste supplying systems being in operation successfully.

Operational data

The manual injection or insertion of printing pastes and the manual stop of printing paste supply shortly before the end of the run needs well educated and motivated staff. Meanwhile some industries are practising the manual injection or insertion, others report that even for small lots (up to 120 m), the technique is difficult to apply. Reproducibility may be affected because the quantity of printing pastes to be inserted vary with different designs which is difficult to manage for the stuff and a constant level of printing pastes within the screen can not be maintained which may affect constant printing quality.

Economics

The installation of 12 sets of volume minimised pipes and squeegees requires investment cost of about 25,000 EURO.

Driving force for implementation

The need of minimising production cost by minimising the loss of printing pastes and problems wirh wastewater disposal have been the main driving forces.

Reference literature

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduzierung der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

Information material of suppliers of rotary screen printing machines, especially Stork Brabant B.V., NL-5830 AA Boxmeer and J. Zimmer Maschinenbau GesmbH, A-6330 Kufstein

4.2.1.4.4 Recovery of printing paste from supplying system of rotary screen printing machines

Description

This technique may be combined with the described technique "Volume minimisation of printing paste supplying systems of rotary screen printing machines" (see 4.2.1.4.3). The printing paste remaining in the paste supplying system is recovered. Before filling the system, a ball is inserted in the squeegee and then transported by the incoming paste to its end. After finishing a print run, the ball is pressed back by controlled air pressure. At the same time, the pumping direction has been changed and the printing paste in the supplying system is pumped back to the drum. Then, the drum contains a defined printing paste which can easily be reused. Therefore, there are different systems available (see 4.2.1.4.5).

This process of printing paste recovery from the supplying system is illustrated in Figure 4.35; the ball is indicated in the moment, the pump is transporting the paste back to the drum.

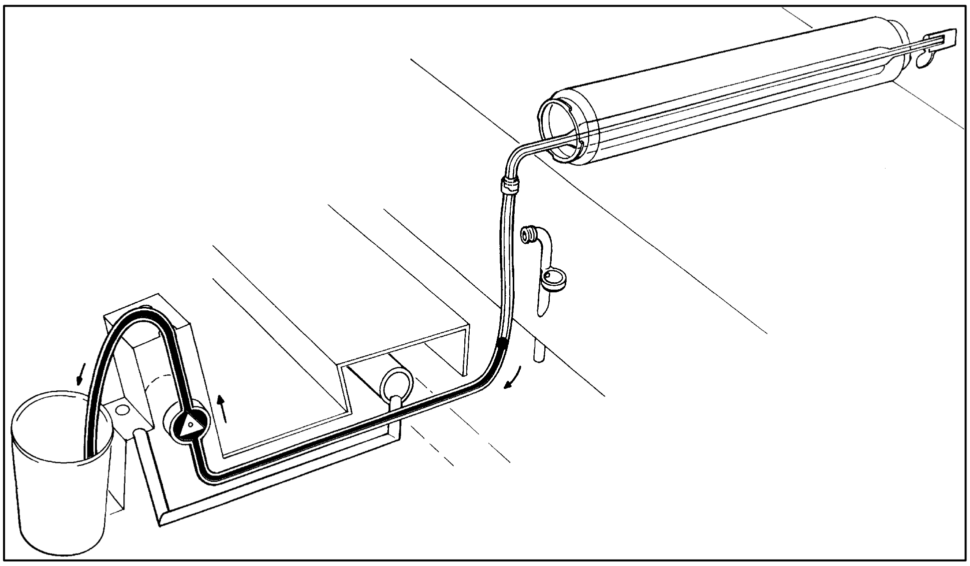


Figure 4.35: Recovery of printing paste from the paste supplying system by pumping back by hand of an inserted ball - [Stork, 2001]

Main achieved environmental performance

The loss of printing paste are reduced drastically. For instance, at a printing width of 1620 mm, the loss is reduced from 4.3 kg (in case of a non-optimised printing paste supplying system) to 0.6 kg. Rotary screen printing machines have up to 20 supplying systems. However, in practice, for fashion designs 7-10 different printing pastes are common. So, the saving of 3.7 kg per supplying system has to be multiplied. Thus water pollution can be minimised considerably.

Applicability

The technique is applicable for new installations (new rotary screen printing machines). Certain existing machines can be retrofitted. In the market, there is only one supplier for this technique which is Stork Brabant B.V., NL-5830 AA Boxmeer. All their machines newer than so-called RD-III (means RD-IV and all subsequent models) can be retrofitted with the described system.

Cross-media effects

There is no cross-media effect to be mentioned.

Reference plants

World-wide, especially in Europe, there are many rotary screen printing machines in operation, equipped with the described technique.

Operational data

The textile finishing industries apply the technique successfully, especially in combination with recycling of the recovered printing paste.

Economics

Investment for retrofitting of a rotary screen printing machine with 12 new squeegees and pipes for a printing width of 1850 mm and the recovery system is about 42,000 EURO. From Table 4.24, the amortisation period can be seen.

Number of changes of printing pastes per day	8
Number of working days per year	250 d
Average number of printing pastes per dessin	7
Saving of printing paste per supplying system	3.7 kg
Price of printing paste	0.6 EURO/kg
Savings per year	**31080 EURO/a**

Table 4.24: Calculation of savings by installation of the printing paste recovery system; the number of changes may be higher in practice, also average number of printing pastes per dessin

The example according Table 4.24 is in case of using the existing pumps. Then, normally a certain range of viscosity has to be maintained. In case of unlimited range of viscosity, the pumps have also to be replaced by new ones. Then, investment cost are about 90,000 EURO. So, amortisation time is not about one year like for the example in Table 4.24 but about two years. However, with respect to the above mentioned example, there are indications from textile finishing industries that cost are 25% higher (112,000 EURO instead of 90,000 EURO).

In addition, in practice it has to be taken into account, that not the whole quantity of recovered printing pastes can be reused. This is especially the case in industries having various kinds of printing pastes due to logistic problems (limited storage and handling capacities). Rates of reuse of only 50-75% are reported which significantly extends the amortisation time.

Driving force for implementation

Severe wastewater problems and the need to decrease losses of printing paste because of economical and environmental reasons have been the main driving forces.

Reference literature

[Stork, 2001]
Stork Brabant B.V., NL-5830 AA Boxmeer
The 3E-squeegee - Lower cost by reduced paste losses
Brochure

[Kool, 1993]
Kool, R. J. M.
Rotary-screen printing, alive and kicking
Journal of the Society of Dyers and Colourists 109 (1993) 318-322

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduzierung der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

4.2.1.4.5 Recycling of residual printing pastes

Description

Printing pastes are high concentrated and consist of dyestuff, thickener and various other chemicals specific for the different kind of printing pastes (mainly pigment, reactive, vat and dispers printing pastes). Typically the loss of printing pastes (mainly to wastewater) is 40-60% in case of non-optimised systems. Thus, considerable environmental problems have to be tackled. For a long time, printing pastes have been prepared manually in a concerned colour kitchen. Thereby, since the very beginning, residual printing pastes have been reused but was strongly depending on responsible staff and actual production. Today, printing pastes are usually prepared with computerised systems. Every printing paste has its certain recipe which are saved electronically. Printing pastes are prepared in surplus in order to avoid stop of printing runs. So, considerable amounts of residual printing pastes have to be tackled and a lot are still discharged to effluent which causes severe wastewater problems and are also less acceptable from the economical point of view. When recovery printing paste from the supplying system for rotary screens (see 4.2.1.4.4) the need for recycling increases.

There are different systems available to recycle residual printing pastes. One option is to weight every paste and direct it to a certain place in a storage facility. The composition is saved electronically and available computer programmes calculate the formulation of new printing pastes considering the reuse of residual printing pastes which are fetched manually from its storage place and is brought to an automatic printing preparing system (Figure 4.36 as an example).

Figure 4.36: Example for an automatic printing paste preparing system, in which residual printing pastes can be reused for the formulation of new printing pastes

Another possibility is to empty all drums with residual printing paste and sort it according to their chemical characteristic, which is mainly kind of dyestuff (e.g. pigments or reactive dyestuffs) and kind of thickener. The drum is cleaned with a scraper to minimise the printing paste loss, then is washed and reused for the preparation of new printing pastes. An example for such an approach can be seen from Figure 4.37. Here, the storage of residual printing pastes is minimised.

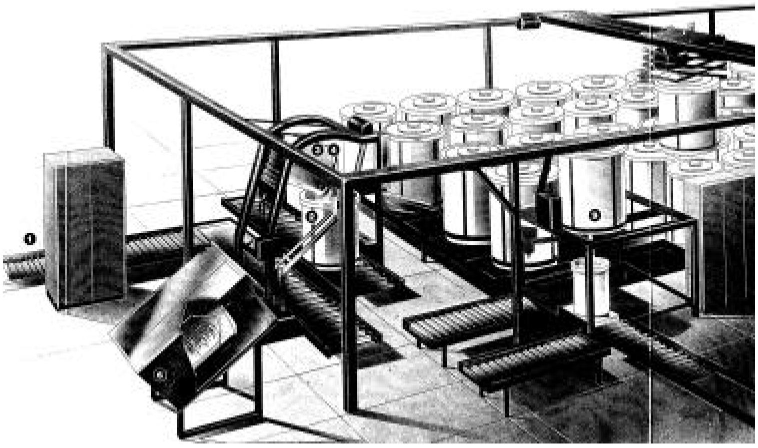


Figure 4.37: Example for printing paste recycling; the drums are emptied to certain storage tanks according to their characteristic - [Eing, 1997]

Main achieved environmental benefits

The quantity of residual printing pastes to be disposed off is significantly reduced both in wastewater and solid waste. The amount of residual printing paste are reduced to 50% at least, in many cases to about 75%.

Applicability

Systems for recycling of printing pastes are applicable both in existing and new installations. However, for totally computerised systems, the printing section must have a minimum size which is 3 rotary screen and/or flat screen printing machines.

Cross-media effects

There are no cross-media effects to be mentioned.

Reference plants

World-wide, especially in Europe, there are various plants from different suppliers in operation.
Important suppliers are:

- Stork Brabant B.V., NL-5830 AA Boxmeers
- GSE Klieverik Dispensing, NL-6971 GV Brummen
- I.A.S. Industrial Automation Systems S.R.L., I-22077 Oligate Comasco

Operational data

From applying textile finishing industries, it is reported that such systems need some time for implementation in daily routine but after managing starting problems, available systems work satisfyingly. In case of textile finishing industries having only one or two kinds of printing pastes (e.g. pigment printing pastes), the systems are most efficient. In case of industries having various kinds of printing pastes, the number of different single and mixtures of printing pastes may be difficult to manage with respect to logistic aspects. Then, achieved recycling rates may be in the range 50-75% only.

Economics

Investment cost are about 0.5-1 million EURO depending on size and number of different printing pastes to be recycled. Pay back periods reported, vary between two and five years depending on individual circumstances.

Driving force for implementation

Economical considerations and needs respectively and problems of residual printing paste disposal have been the main driving forces.

Reference literature

[Eing, 1997]
Anonymous
Report on the new printing paste recycling plant at H. Eing Textilveredlung GmbH & Co, D-48712 Gescher
Melliand Textilberichte 78 (1997) 512

4.2.1.4.6 Reactive 2-phase printing

Description

In conventional 1–phase printing with reactive dyes urea is used to increase solubility of the dyestuffs and to enhance formation of condensate which is important for diffusion of the dyestuffs from the printing paste on the textile. Depending on the substrates, quality of pre-treatment, fixation conditions and dyestuffs urea is added in an amout of 20 to 200 g/kg printing paste. In 1-phase printing minimization or even substitution of urea is possible by controlled addition of moisture (see chapter 4.2.1.4.1). Application of urea in printing is accompanied with the following ecologial disadvantages

- High nitrogen content in waste water with the potential of eutrophication.
- Sublimation of urea and degradation to ammonia in the printing mansardes with consequences for working place atmosphere and off-gas emission.

2-phase printing can be carried out without urea. The process steps are as follows:

- Printing of the printing paste which contains thickener, reactive dyes and water
- Intermediate drying
- Padding with alkaline solution of fixating agents (esp. water-glass)
- Fixation by means of overheated steam
- Washing steps (removal of thickeneres, improve of fastness properties)

Main achieved environmental benefits

Significant reduction of the ammonia content in waste water and reduced off-gas problems are the main ecological improvements. In addition shelf life of printing pastes and therefore the recycling rate of residual printing pastes is increased.

Applicability

2-phase reactive printing can be carried out on cotton and viscose substrates. Application of the fixation liquor needs the combination of an impregnation device with a steamer. Overheated steam is necessary. Reactive dyes based on monochlortriazine and vinylsulfone types can be used. For printing of turquoise and green shades an addition of urea (100 g/kg printing paste) should be made.

Cross-media effects

No cross-media effects have to be regarded.

Reference plants

The technique is applied in 3 French finishing plants, 1 Italian finishing plant and is currently to be installed in Germany.

Operational data

A typical recipe for the printing paste is given below:

Thickening stock solution:

Alginate based thickening agent (3-12%)	700 g
Oxidising agent	10 g
Complexing agent	3 g
Preserving agent	0,5-1 g
Water	x g
Total	1000 g

Printing paste:

Thickener stock solution	800 g
Reactive dyestuff	x g
Water	y g
Total	1000 g

Fixation is carried out by means of overheated steam (90 s at 125 °C).

Economics
Low energy consumption is to be mentioned as economical advantage.

Driving force for implementation
Ecological aspects as well as quality and economic aspects are the reasons for implementation of 2-phase printing. In detail the opportunity to correct mistakes in printing before fixation and the insensivity to variations in drying conditions (speed, stoppages) have to be mentioned.

Reference literature

[DyStar, 2000]
DyStar, D-Frankfurt/Main
Product information (2000)

4.2.1.5 Finishing

4.2.1.5.1 Stenter with optimised energy consumption

Description
Stenters are mainly used in textile finishing for

- heatsetting
- drying
- thermosol processes
- and finishing.

It can be assumed (rough estimation) that in finishing as an average every textile material is treated 2.5 times in a stenter which is therefore often the bottle neck in textile finishing mills.
Regarding the invest costs and running costs for a stenter it is obvious that energy consumption of stenters is the main item concerning ecology of stenter technology (see Figure 4.38).

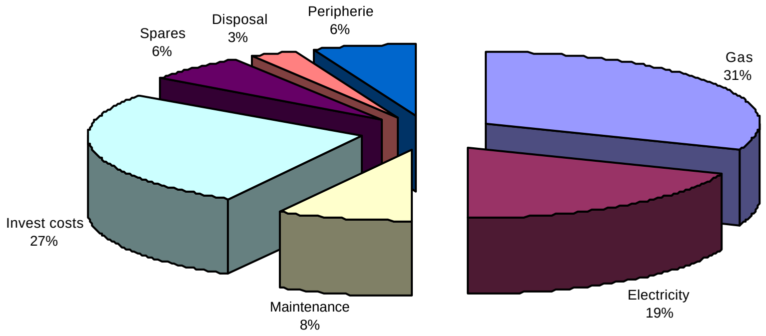


Figure 4.38: Costs concerning a stenter (10 years running time considered)

To give a –surely rough - assessment energy consumption of energetic optimized stenters is in the range of 3500-4500 kJ/kg textile. However energy consumption depends strongly on the process that is carried out.

Main heat demand needed in a stenter is caused by water evaporiation and the heat losses due to the output of hot air resp. the heating of the fresh air.

Therefore as a first step before heating in a stenter is carried out mechanical dewatering of the textiles should be done in a efficient way. In addition air/textile ratio should be kept as low as technical and economical possible.

Technologies reducing energy consumption of stenters including heat recovery systems are compiled below. Thereby it has to be kept in mind that a change of processes resp. auxiliaries used can also reduce energy consumption during drying/fixation to a considerable amount.

Heat recovery
With air/water heat exchanger up to 70% of the off-gas energy can be saved. Existing machinery can be re-constructed. Hot water can be used in dyeing. Optionally an electrostatic precipitator for off-gas cleaning can be installed downstream.

However, in textile finishing often a surplus on hot water is given. Therefore air/air heat exchanger can be installed in new installations. An advantage of air/air heat exchanger is that energy supply and energy demand is simultaneously given. Approx. 30% of off-gas energy can be reclaimed Heat recovery systems based on a one-step air/air heat recovery and two step systems (combination of two air/air devices or of an air/air and air/water system exist. Optionally an electrostatic precipitator can be installed downstream for off-gas cleaning. A flow chart for a system based on air/air heat exchanger, air/water heat exchanger and electrostatic precipitation is given in Figure 4.39.

Also systems which combines an air/air heat exchanger with an aqueous scrubber and an electrostatic precipitation are possible (flow chart see Figure 4.40)

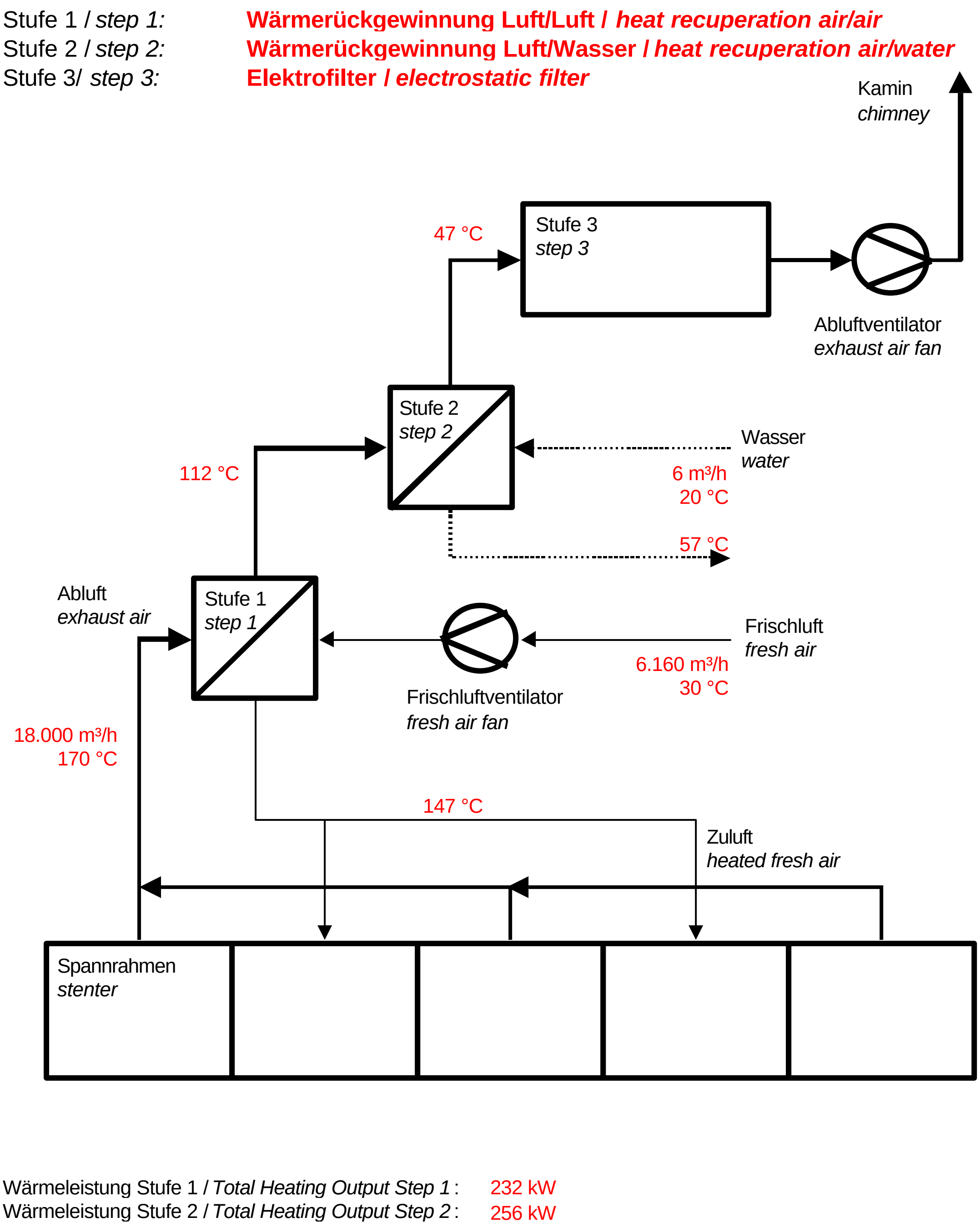


Figure 4.39: Heat recovery and exhaust gas cleaning by a combination of an air/air and air/water heat exchanger and an electrostatic precipitator [Brückner, 2001]

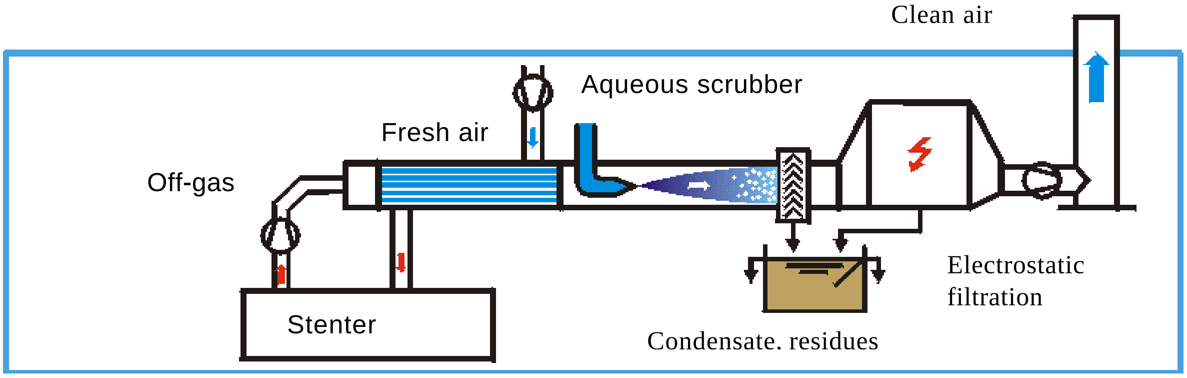


Figure 4.40: Heat recovery and exhaust gas cleaning by a combination of an air/air heat exchanger, aqueous scrubber and electrostatic precipitation [Koenig, 2000]

Thermal insulation

Proper thermal insulation of stenter encasement reduces heat losses to a considerable amount. Proper selection of the insulation material and a suitable thickness of the insulation can lead to energy savings. However it has to be kept in mind that heat losses due to radiation are only in a range of 2-4% of the total heat demand of the stenter.

Monitoring and control systems for temperature, air flow and moistness of textiles and air

If the air flow is controlled by means of monitoring moisture content in the off-gas respectively circulating air moisture contents in the exhaust air resp. circulation air can be adjusted as high as technically possible. I this way air/textile ratio can be minimized. An optimum for the moisture content in the exhaust air resp. circulation air is approx. in the range of 100 to 120 g water/kg (at temperatures between 160-180°C).

Control of temperature on the textile by means of pyrometers and adjusting of an optimized curing time and air temperature is an additional method to minimize the energy consumption

Moistness of incoming textiles should be minimized by means of vacuum techniques or optimized squeezing rollers. Energy consumption in a stenter can be reduced by 15% if moisture of incoming textiles is reduced from 60% to 50% [Fischer, 1992].

Burner technology

With optimized burner systems and sufficient maintenance of burners in direct heated stenters the methane emissions can be minimized.
A typical range for an optimized burner is [EnviroTex, 1998; EnviroTex, 2001]:
10-20 g methane (calculated as Organic-C)/h per burner. Assuming a fresh air consumption of 10.000 m^3/h and a stenter with 8 burners this mass flow is equivalent to 8-16 mg Organic-C/m^3.
However it has to be taken into account that methane emission of burners depend strongly on actual burner capacity.
Modern burner technology –implemented in German stenter technology - is supplied from

- Eclipse, USA
- Maxxon, USA

Main achieved environmental benefits

Savings in energy consumption and therefore minimization of off-gas loads caused by indirect or direct heating of the stenters (esp. carbondioxide and VOC (methane)) is the main ecological advantage using optimized stenter technologies.

Applicability

The described methods are applicable for all new installations. If existing equipment has to be re-build the applicability in some cases can be limited due to the fact that re-construction is too cost-intensive or a technological/logistic problem. If parameters like fresh air consumption or moistness of textiles will be changed in order to save energy it has to be regarded that quality of the textiles is not affected.

Cross-media effects

If off-gas abatement systems are installed the ventilator power and therefore energy consumption is higher. Condensed substances (mainly preparation oils) from heat recovery systems have to be collected separately. If aqueous scrubber systems are installed fresh water is needed and waste water is charged instead of off-gas. However compared to the total waste water load of a textile finishing plant the impact is negligible and abatement by means of a biological waste water treatment is in most cases efficient enough.

Reference plants

The described technologies are in use in German finishing mills and world-wide as well.

Operational data

Minimizing energy consumption at stenters especially if heat recovery systems are installed affords proper maintenance (cleaning of the heat exchanger and stenter machinery, checking of control/monitoring devices, adjusting of burners etc.). Cleaning of the heat recovery devices in some cases has to be done weekly.

Proper scheduling in finishing minimizes machine stops and heating-up/cooling down steps and is therefore a prerequisite for energy saving.

Economics

To underline the fact that economical efficiency of heat recovery systems strongly depends on the local situation two calculation examples for the pay-back periods are given below:

Example 1:Air/air or air/water heat recovery

Parameters:

Heat recovery sytem:	counter flow pipes
Drying temperature:	130°C
Heatsetting :	190°C
Off-gas volume flow:	15000 m^3/h
Off-gas moisture content „Drying“:	70 g/m^3
Off-gas moisture content „Heatsetting“:	40 g/m
Efficiency;	70%
Heating value for the gas	9.3 kWh/m^3
Costs for the gas:	0.25 EURO/m^3
Maintenance costs:	1.000 EURO/a
Interest:	6%

Calculation:

		1-shift		2-shift		3-shift	
	Process	**Savings [EURO]**	**Pay-back period [a]**	**Savings [EURO]**	**Pay-back period [a]**	**Savings [EURO]**	**Pay-back period [a]**
Air/water	Drying	32050	5.7	64150	2.6	96150	1.7
Fresh water temp.:15°C	Heatsetting	34450	5.4	68900	2.4	103350	1.5
Air/water	Drying	18050	12.6	36100	5.9	54150	3.3
Fresh water temp.:40°C	Heatsetting	23350	8.6	46700	3.7	70050	2.4
Air/air	Drying	8000	> 20	16000	15.6	24000	8.5
Fresh air temp.:20°C	Heatsetting	11000	> 20	22000	9.6	33000	6.6

Table 4.25: Return on investment assuming different proceses, heat recovery systems and working times [EnviroTex, 2000]

Example 2: Air/air heat recovery (air flow 18000 m^3/h; indirect heated stenter) [Babcock, 2001]
Parameters:
Heating output of the installation: 232 kW
Running time per year: 4800 h/a
Price of fuel: 0.031 EURO/kWh
Effectiveness of thermo oil heating device: 80%
Additional power for ventialtor: 8.05 kW
Price of electricity: 0.107 EURO/kWh
Interest: 6%
Economic life: 10 a
Invest costs: 60,000 EURO

Calculation:
Savings in heating costs per year: 43152 EURO
Additional energy costs for ventilators: 4135 EURO
Mainenance costs per year: 1800 EURO
Capital charges per year: 8152 EURO
Total savings per year: 29065 EURO
Pay back period: 1.6 a

Driving force for implementation

Minimization of energy consumption and therefore energy costs is the main reason to install optimized stenter technology respectively to re-built existing machinery.

Reference literature

[Babcock, 2000]
Babcock Textilmaschinen, D-Seevetal
Product information

[Brückner, 2001]
Brückner Trockentechnik GmbH, D-Leonberg
Product information and personal information

[Monforts, 2001]
Monforts Textilmaschinen GmbH, D-Mönchengladbach
Product information and personal information

[Fischer, 1992]
Fischer, R.
Zur Beurteilung von Thermomaschinen und den entsprechenden thermischen Prozessen. Part A and part B.
textil praxis international (1991) 468-472, 562-566; (1992) 744-746, 853-856, 1063-1071

[EnviroTex, 1998]
EnviroTex GmbH, D-Augsburg
Emissionen aus der Direktbefeuerung von Textilveredlungsanlagen. Teil 1: Emissionsverhalten von direktbefeuerten Spannrahmen
Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, D-München, 1998

[EnviroTex, 2000]
EnviroTex GmbH, D-Augsburg
CO_2 -Minderungspotenziale durch rationelle Energienutzung in der Textilveredlungsindustrie
Bayerisches Landesamt für Umweltschutz, D-Augsburg, 2000

[EnviroTex, 2001]
EnviroTex GmbH, D-Augsburg
Actual emission measurements (not published)

[Koenig, 2000]
Koenig AG, CH-Oberaach
Product information

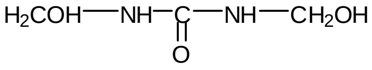
[Heck, 2001]
Heck Filtertechnische Anlagen GmbH, D-Köln
Product information

4.2.1.5.2 Formaldehyde-low easy-care finishing

Description

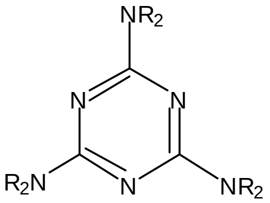
Easy-care finishing (in other words: non-creasing and non-shrinking finishing) is mainly carried out on cellulosic fibres and their blends with the intention to increase the crease recovery and/or dimensional stability of the fabrics.

Easy-care finishing agents are mainly compounds synthesized from urea, melamine, cyclic urea derivatives, and formaldehyde. Reactive (crosslinking) groups are composed of free or etherificated N-methylol groups (Figure 4.41).

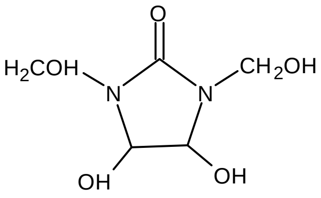


$H_2COH-NH-\underset{\underset{O}{\|}}{C}-NH-CH_2OH$

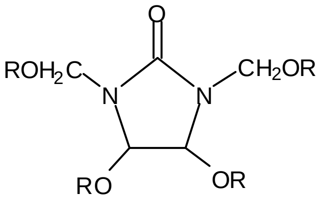
Dimethylol urea and Dimethylol urea derivatives



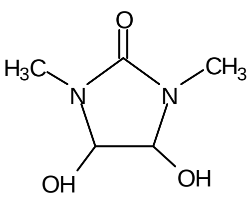
Melamine derivatives (R = H, CH_2OH, CH_2OCH_3



1,3-Dimethylol-4,5-dihydroxyethylene urea



1,3-Dimethylol-4,5-dihydroxyethylene urea derivatives (R= H, CH_3)



1,3-Dimethyl-4,5-dihydroxyethylene urea (DMeDHEU)
(1,3-Dimethyl-4,5-dihydroxyimidazolidinon-2; DMDHI)

Figure 4.41: Chemical structure of crosslinking agents

Catalysts mainly based on metal salts are used to accelerate the rate of cross-linking reactions. Formaldehyde-low or even (if required quality resp. non creasing effect is achieved) formaldehyde-free products are an alternative.

A rough overview on different product types and their potential to release formaldehyde is given in Table 4.26.

Type of crosslinking agent	Formaldehyde release
Dimethylol urea	High
Melamin formaldehyde condensation products	High
Dimethyloldihydroxyethene urea (DMDHEU)	High
Dimethyloldihydroxyethene urea (DMDHEU) derivatives (Mostly used)	Low
Modified Dimethyldihydroxyethene urea	Formaldehyde-free

Table 4.26: Overview on formaldehyde releasing capacity of the most important crosslinking agents

Main achieved environmental benefits

With formaldehyde-low or formaldehyde-free products a reduction of formaldehyde emissions in finishing is achieved. Formaldehyde residues on the textiles can be minimized (< 75 mg/kg textile). With optimised catalysts curing temperature and therefore energy consumption can be reduced.

Applicability

The products can be applied similar to conventional products. Kind and amount of catalysts as well as curing time and temperature has to be adjusted. Required quantity for formaldehyde-free products is approx. two times higher. When formaldehyde-free or formaldehyde-low products are applied it has to be taken into account that in case of direct heated stenters formaldehyde is also generated in a considerable amount by the burners.

Cross-media effects

All above mentioned crosslinking agents are hardly biodegradable. However, only small amounts (esp. residual liquors) of the products are introduced to the wastewater. Non optimised formaldehyde-free products can be smell intensive.

Reference plants

Auxiliaries for formaldehyde-free and formaldehyde-low easy-care finishing are supplied from various companies and are applied world-wide.

Operational data

Typical recipe for formaldehyde-low finishing of cotton (woven fabric):

- 40-60 g/l crosslinking agent
- 12-20 g/l catalyst
- liquor pick-up: 70%
- drying and condensation (150 °C, 3 min)

Typical recipe for a formaldehyde free finishing of cotton:

- 80-120 g/l crosslinking agent (integrated catalyst)
- liquor pick-up: 80%
- acidifying with acetic acid
- drying and condensation (130 °C, 1 min).

Crosslinking compounds are often applied in combination with wetting agents, softeners, products which increase ripping strength etc.

Economics

Prices for formaldehyde-free products are significant higher than for formaldehyde-low products.

Driving force for implementation

Regulations concerning formaldehyde in the off-gas and compliance to various codes of conducts concerning consumer health (eco-labels) are the main motivation for the use of the formaldehyde-free or formaldehyde-low products.

Reference literature

[BASF, 1999]
BASF AG, D-Ludwigshafen
Product information (1999)

[Ciba 2000]
Ciba Spezialitätenchemie Pfersee GmbH, D-Langweid
Personal information (2000)

[Thor, 2000]
Thor GmbH, D-Speyer
Product information (2000)

4.2.2 End-of-pipe techniques

4.2.2.1 Off-gas

4.2.2.1.1 Abatement of emissions to air

Description
In principle, the following off-gas abatement systems can be used in textile finishing (as single solutions as well as in a combination of two or more techniques)

- Oxidation techniques (thermal incineration, catalytic incineration)
- Condensation techniques
- Absorption techniques
- Electrostatic precipitation
- Adsorption techniques (seldom in use)
- Biological techniques (not in use)

Typical systems in textile finishing are
- Heat exchanger (condensation technique; primarily used for energy saving)
- Aqueous scrubber (absorption technique)
- Combination of aqueous scrubber and electrostatic precipitation
- Combination of heat exchanger and electrostatic precipitation

Oxidation techniques
Principally the oxidation technique is a transformation of combustible air pollutants into harmless substances by combustion/oxidation. In case of complete oxidation, all hydrocarbon compounds will be transformed to carbon dioxide (CO_2) and water (H_2O). If the oxidation is incomplete, carbon monoxide (CO), formaldehyde (CH_2O) and other partially oxidised substances are generated.
Two different oxidation techniques exist:

- thermal incineration and
- catalytic incineration.

Thermal incineration occurs at temperatures between 750 °C and 1000 °C. The off-gas arrived to a first heat exchanger by ventilation; there the heat content of the cleaned off-gas is exchanged to raw-gas. This preheated off-gas (approx. 500-600 °C) is subsequently heated by a burner, to get the ignition temperature. The clean-gas in turn passes a heat exchanger system. Normally nearly all pollutants are burned off (including odour intensive substances and low boiling solvents).

It is also possible to conduct off-gas to the boiler house where it is used as incineration air. Therefore a special burner which can work with a high air surplus and a high moisture content has to be installed.

Compared to thermal incineration, the advantage of catalytic incineration is the considerable low activation temperature which is between 300 °C and 450 °C. This is due to special catalysts, which reduce the ignition temperature at one hand and accelerate the reaction velocity between pollution substances and oxygen of the air at the other hand.

Condensation techniques
Besides energy recovery air/air and air/water heat exchanger cause partial condensation of the pollutants. Off-gas is cooled down in the heat exchangers to a temperature at which the pollutants form drops or a film. The condensed pollutants are already partly separated in the heat exchangers; the residual part can be separated in downstream filters.

Absorption techniques

The commonly used techniques are aqueous scrubbers. The exhaust-gas is brought into close contact with the washing liquid (water and partially additives like acids, alkali or oxidising agents)
Depending on the equipment producer there exist different types:

- nozzle vaporizers
- centrifugal systems
- systems based on turbulence of washing water.

This leads to
- cooling of the off-gas (condensation of the pollutants containing vapours)
- absorption of pollutants in the scrubber liquid (partially emulsions are generated with water-insoluble substances)
- dissolving of soluble substances in the water drops.

The pollutants get separated in the mist collector installed downstream. Wastewater from aqueous scrubbers can be treated with oil/water separators or other techniques. The scrubber liquid can be cycled or used in a continuous way.

Electrostatic precipitation

Electrostatic precipitation depends on the attraction of different charged particles. In electric precipitators, there are strong potential gradients between the sparkling electrodes and the precipitation electrodes with opposite polarity. The sparkling electrode has a small diameter like for example a wire or the point of a needle, the precipitation electrode has a big area like a plate for example. The off-gas has to pass the potential gradient between the electrodes. The solid and/or liquid particles of the off-gas are charged unipolar in the ionisation area.
The charged particles are attracted from the antipoles and precipitated at the precipitation electrodes. They loose their charge after getting in contact with the precipitation electrode and can then easily be removed by washing, vibration or gravity.
The electrostatic process exists of
- ionisation of the air
- charging of the pollutant particles
- transportation of the particles to the precipitation plate
- neutralisation of the particles
- cleaning of the precipitation plates from the waste.

Main achieved environmental benefits

Minimisation of volatile organic carbon (VOC) and special toxic substances in the off-gas as well as minimisation of odour nuisances are the main achieved environmental benefits of abatement systems for emissions to air.

Applicability

Oxidation techniques

The disadvantage of thermal incineration is the energy consumption for heating up the off-gas to at least 750 °C. After incineration the temperature of the cleaned off-gas is around 200 °C to 450 °C. Generally there are not sufficient heat consumers in the company, so most of the energy will be wasted. Another problem results from the gas-air-mixture typical for textile finishing. In textile industry, mostly there are high off-gas volume flows with comparable low charges, which has to be cleaned. Often there are changing amounts of off-gas, leading to inefficient thermal incineration. In case of catalytic incineration, phosphorous compounds, halogens, silicones and heavy metal compounds can react as catalytic poisons. These compounds are often found in textile industry, so special care has to be taken by using catalytic oxidation in this field.

Condensation techniques

Pollutants with a high volatility which are in most cases odour intensive substances are not removed.

Absorption techniques
The efficiency of aqueous scrubbers in textile finishing strongly depends on process specific parameters; normally the efficiency is in a range between 40 – 60%. Applicability for water-insoluble pollutants is limited.

Electrostatic precipitation
Electrostatic precipitators can precipitate dusts and aerosols with a size of 0.01 to 20 µm. Best efficiency will be reached at around 0.1 µm – 1.5 µm. Therefore, the producers recommend to install a mechanical filter before the electric filter, which precipitates most of the particles > 20 µm.
The efficiency for electrostatic precipitators for particle sized solid and liquid pollutants is in a range between 90% and 95%. Gaseous pollutants and at the same time odour relevant substances cannot be precipitated. Therefore, for best total efficiency it is important, that mostly all condensable substances, emitted as aerosols, are removed before reaching electrostatic precipitation . This can be achieved by heat exchangers or off-gas scrubbers.

Off-gas cleaning can be installed at both, new and existing installations. However if existing machinery has to be rebuilt, in some cases applicability is limited due to economical, technical and logistic factors. In each case, for installation of an off-gas cleaning system, a tailor-made solution regarding the above mentioned techniques has to be developed.

Cross-media effects
The high energy demand resp. high amounts of resulting CO_2 by thermal as well as catalytic incineration are questionable, because it is one of the greenhouse gases.

In aqueous scrubbers, the pollutants are redistributed from off-gas to the wastewater. Efficient wastewater treatment (oil/water separators, biological wastewater treatment) is required .

Reference plants
Off-gas cleaning systems which are delivered from various suppliers are installed in various German textile finishing industries. Systems based on heat exchangers, aqueous scrubbers and electrostatic precipitators dominate.

Operational data
To achieve a high operational reliability the adjustment of the appropriate operational conditions and proper maintenance (in some cases a weekly inspection and cleaning of the devices is needed) of the equipment is of crucial interest.

Economics
Installation and running costs have to be considered. Especially costs for the maintenance of the equipment and energy costs should be considered. Compared to the other above mentioned techniques oxidation techniques have by far highest investment cost and running cost.

Driving force for implementation
Improvement of the environmental performance, complaints about odour nuisances and compliance to national and local regulations are the main reasons to install off-gas abatement techniques.

Reference literature
[--]

4.2.2.2 Wastewater

4.2.2.2.1 Treatment of textile wastewater in activated sludge systems with low food-to-microorganisms ratio (F/M)

Description

Textile wastewater is a mixture of many different chemical compounds which can roughly be classified into easily biodegradable, heavily biodegradable (recalcitrant) and non-biodegradable compounds. Biological treatment is usually the most important part of textile wastewater treatment. In most cases, activated sludge systems are applied. In all activated sludge systems, easily biodegradable compounds are mineralised whereas heavily biodegradable compounds need certain conditions, such as low food-to-mass-ratios (F/M) (< 0.15 kg BOD_5/kg MLSS x d), adaptation (which is there if the concerned compounds are discharged very regularly) and temperature higher than 15°C (normally the case for textile wastewater). Before this background, F/M is the most relevant design parameter. When remaining under the mentioned F/M value, heavily degradable textile chemicals, such as nitrilotriacetate (NTA) [GDCh, 1984], m-nitrobenzene sulfonate and its corresponding amine [Kölbener, 1995], polyvinyl alcohol (PVA) [Schönberger, 1997] are degradaded and mineralised respectively. Today, many activated sludge systems meet these system conditions (see following examples) which also enable practically complete nitrification. In these cases, both easily and heavily biodegradable compounds can be discharged. Non-biodegradable compounds should be avoided or treated/pre-treated at source but this happens in a few cases only. Therefore, in many cases, in addition to activated sludge further treatment steps have been developed and implemented such as flocculation/precipitation, adsorption to activated carbon and ozonation. The plants, presented as follows meet the requirement of low F/M ratio, adaptation and temperature higher than 15°C. Most of them also have additional treatment steps to remove remaining dyestuffs (colour) and other non-biodegradable compounds.

Example 1:

The treatment plant receives the municipal wastewater and wastewater from four bigger textile finishing industries by different sewer lines. The textile wastewater is equalised and then mixed with primarily treated municipal wastewater. The hydraulic percentage of textile wastewater is about 45% and referring to COD-load about 60%. Subsequent to primary treatment and equalisation, there is biological treatment including nitrification/de-nitrification and flocculation with $FeCl_3$ as final step. The system can be seen from Figure 4.42.

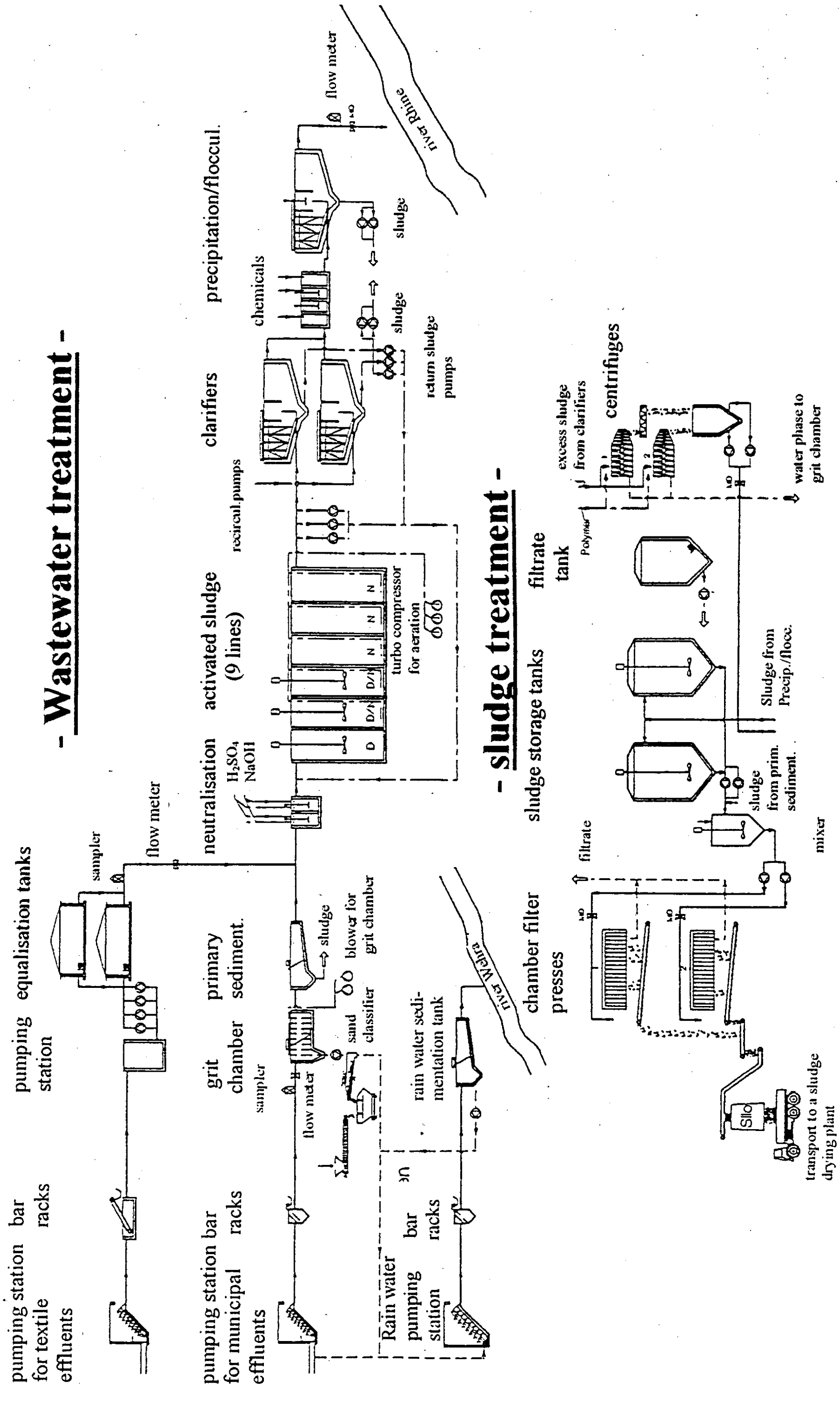


Figure 4.42: **Example 1- combined treatment of textile wastewater and municipal wastewater**

Figure 4.43 shows the daily determined COD concentration of the final effluent. Conspicuous is the range of varying values reflecting the weekly fluctuations, rainy days (because storm water enters the same sewer) and the very low values end of August which is the holiday time of the industries.

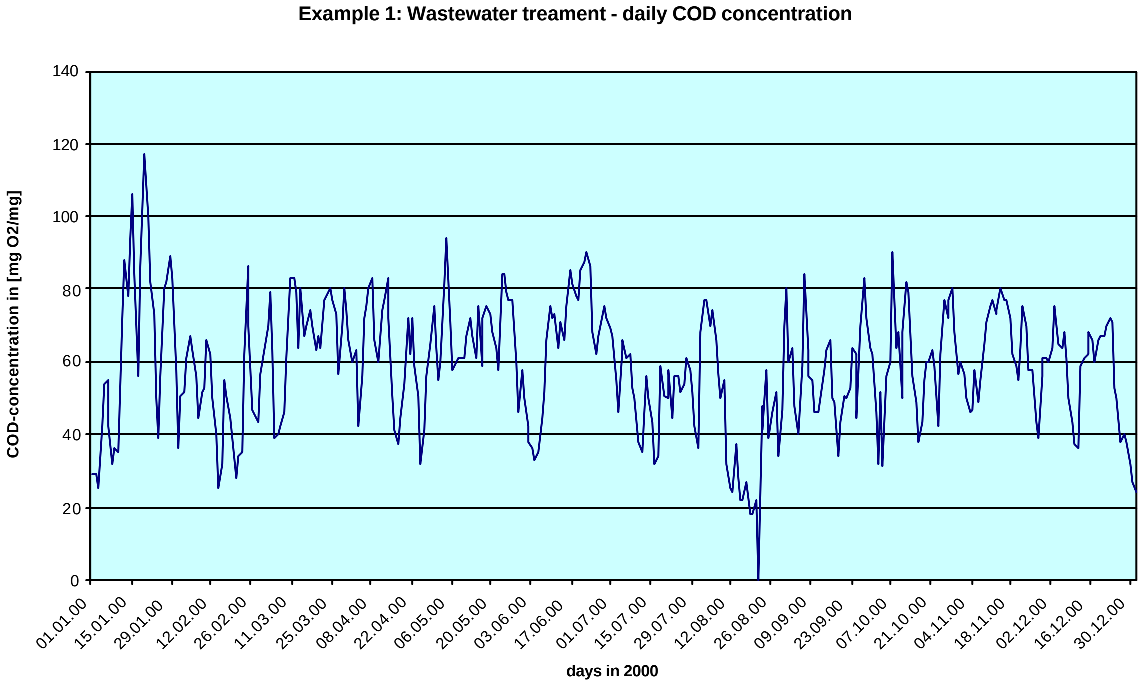


Figure 4.43: Daily COD concentration the final effluent of plant 1 for the year 2000

Example 2:

In this big plant, wastewater from two cities and some villages is treated together with textile wastewater from four big textile finishing industries having a hydraulic percentage of about 40% and referring to COD-load of 65%. Municipal wastewater and textile wastewater is already mixed in the public sewer line. Figure 4.45 shows the layout of the plant. The tanks for primary treatment are also used for equalisation of the influent. After the activated sludge stage there is no additional treatment for further reduction of organic compounds and colour. The daily COD-loads can be seen from Figure 4.44. There are predominant peaks which result from high flows of storm water. Thus the wastewater is diluted, retention time is reduced and removal efficiency is reduced. Like in the example of plant 1, during holiday of the industry end of August, residual COD-load is significantly lower.

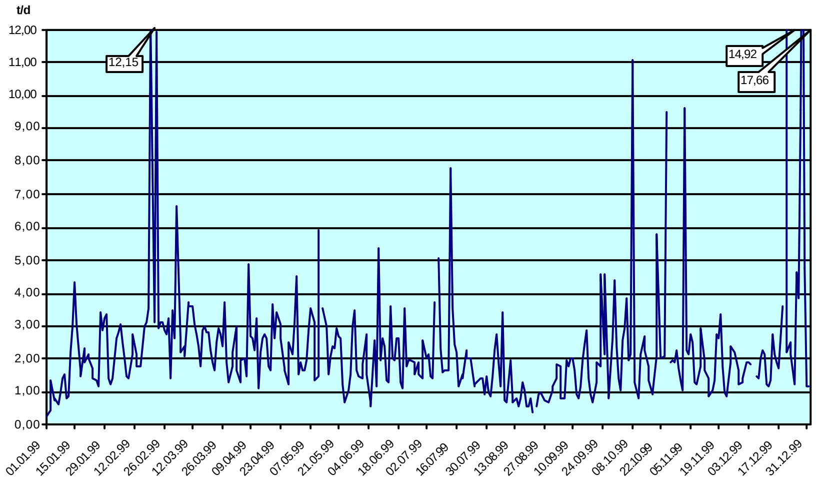


Figure 4.44: Combined treatment of municipal and textile wastewater - plant 2: daily COD-load in 1999

Legend:
1: Influent pumping station
2: Bar screen
3: Aerated grease and grit chamber
4: Venturi flow measurement
5: Primary treatment and equalisation
6: Intermediate pumping station
7: Activated sludge tanks
8: Clarifiers
9: Return sludge pumping station
10: Primary sludge pumping station
11: Pumping station for discharging the treated effluent
12: Sludge thickener
13: Anaerobic digesters
14: Gas holding tank
15: Operation and administration building
16: Machinery building
17: Blower house
18: Gas motors building
19: Sludge container hall
20: Bunker for fatty wastes
21: Overflow in case of emergency

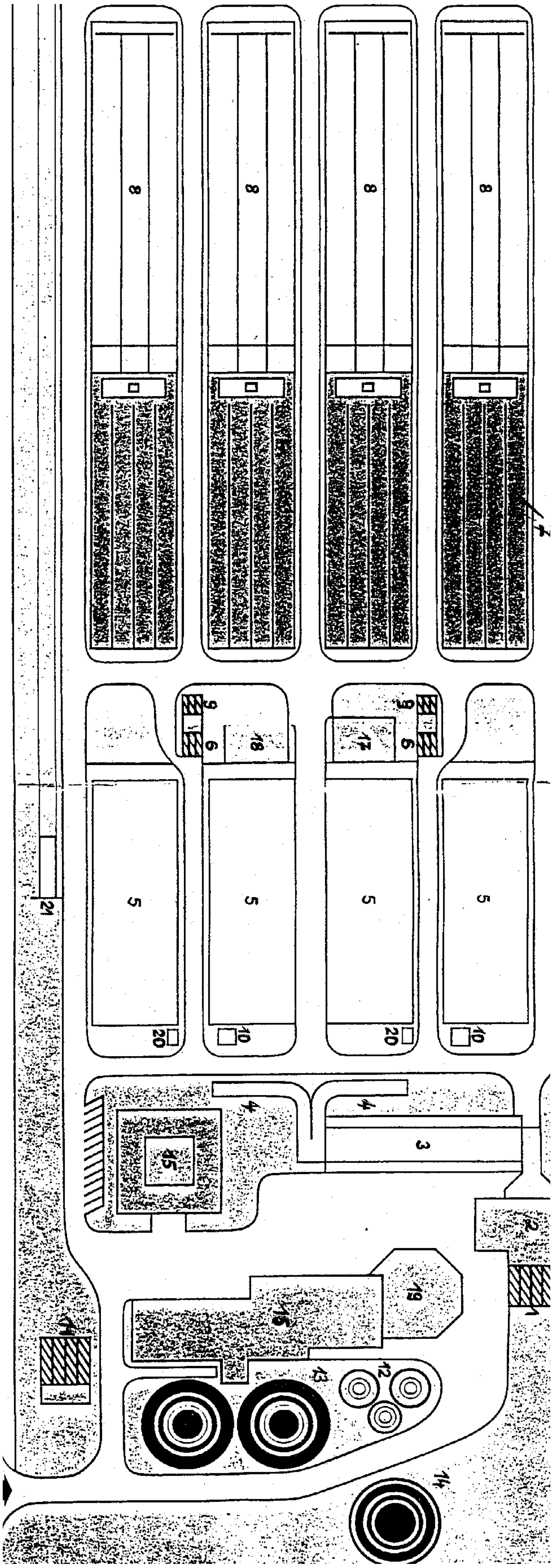


Figure 4.45: Plant 2- combined treatment of textile wastewater and municipal wastewater

Example 3:

This example is another one for the combined treatment of municipal and textile wastewater. The layout of the plant shows Figure 4.46. The neutralised and equalised wastewater of a big textile industry is discharged to the plant by a separate sewer line. It is specially pre-treated in a high-loaded activated sludge system with F/M 1.1 kg BOD_5/kg MLSS x d. Under these conditions, PVA which is present at high concentration in the textile wastewater is not degraded at all but in the subsequent second activated sludge stage having F/M 0.05 kg BOD_5/kg MLSS x d which allows PVA removal to more than 90%. Ozonation of textile wastewater reduces colour significantly but COD only little (< 10%) because of low ozone dosage (about 50 g/m^3); however it is postulated that biodegradability is increased. Activated carbon is added in case of exceeding the standards only, which has not been the case the past three years. Flocculation filtration as a polishing step reduces COD to 10-20% and some colour as well.

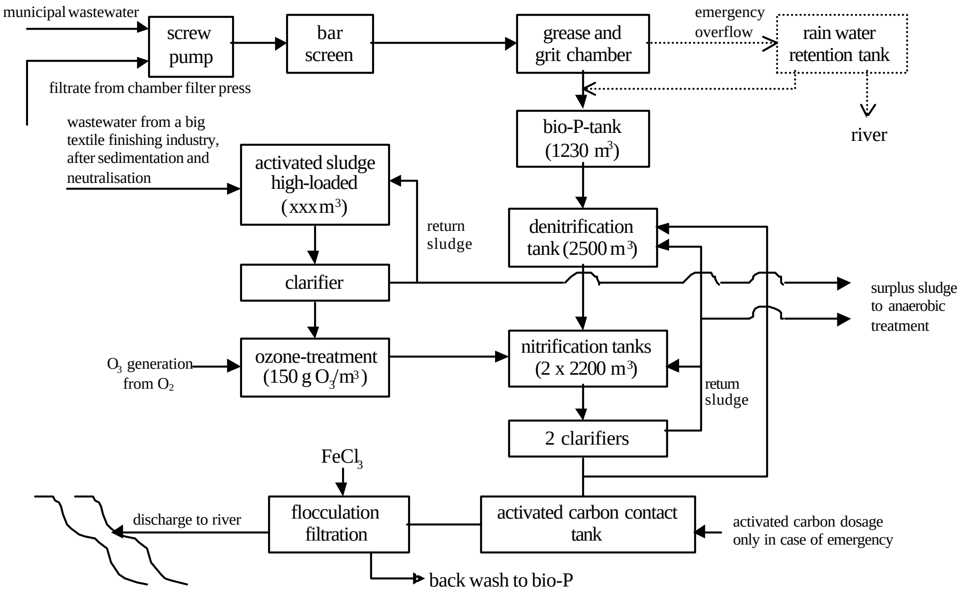


Figure 4.46: Plant 3- combined treatment of textile wastewater and municipal wastewater

Example 4:

This big plant is for the treatment of wastewater from about 150 textile units. The hydraulic percentage of textile wastewater is about 55%, of municipal wastewater of about 23% and the residual part is infiltration and storm water. The layout of the plant is shown in Figure 4.47. After biological treatment including nitrification/de-nitrification the mixed wastewater is precipitated/flocculated for further COD reduction. Subsequently, it is treated with ozone in order to remove colour and recalcitrant surfactants. The F/M ratio is higher than 0.15 kg BOD_5/kg MLSS x d and thus, practically complete nitrification can not be achieved and heavily degradable compounds may not be removed to an extend which may be reached with a lower F/M ratio.

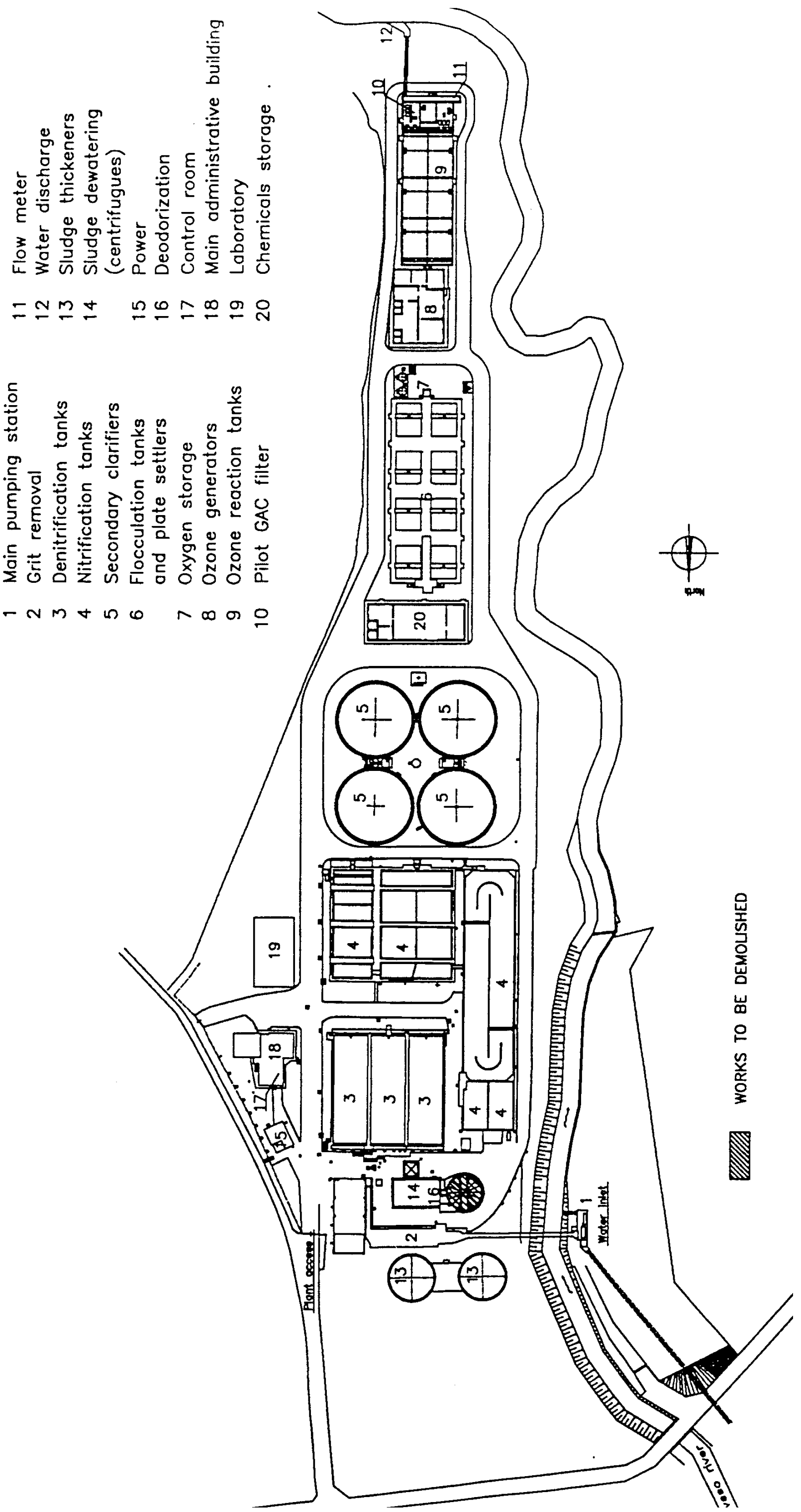


Figure 4.47: Plant 4 - combined treatment of mainly textile wastewater and some municipal wastewater

Example 5:

In plant 5, the wastewater is treated from one textile finishing industry. The company is mainly finishing cotton fabric, which is pre-treatment (de-sizing, scouring, bleaching), dyeing (cold pad batch and exhaust dyeing), printing (mainly with pigment printing pastes) and finishing. About 5% of the treated wastewater is recycled for washing and cleaning operations (floor washing, cleaning of printing equipment like pumps, pipes, squeegees and screens). Retention time in the activated sludge system is very high which corresponds with low F/M. Subsequent de-colourisation is achieved by reductive cleavage of azo groups of dyestuffs by an iron(II)-salt. Figure 4.48 shows the flow sheet of the plant.

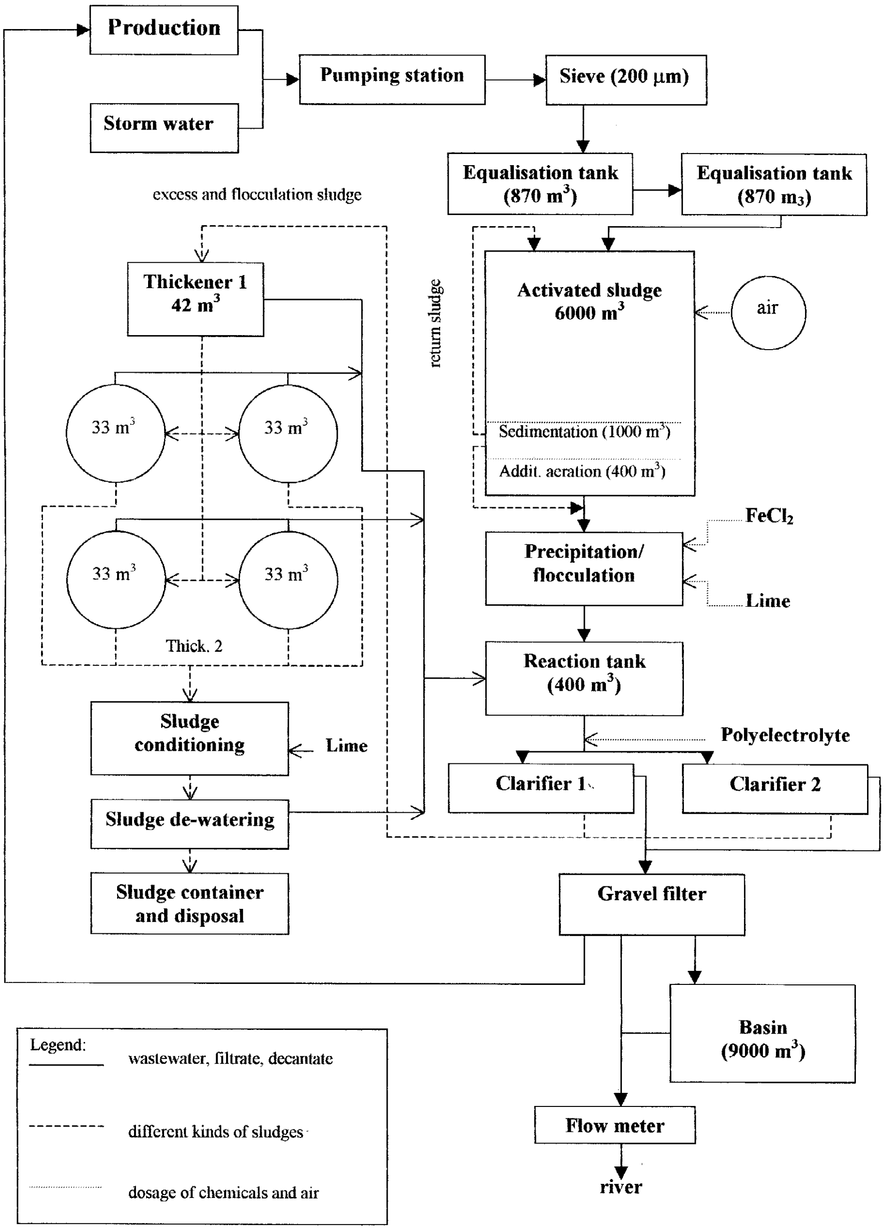


Figure 4.48: Plant 5 - wastewater from one textile finishing industry with a 5%-recycling

Example 6:

In the plant, shown in Figure 4.49, wastewater from about 30 textile finishing units is treated together with municipal wastewater. The hydraulic percentage of textile wastewater is about 30%, referring to COD, the percentage is about 40%. The textile finishing industries discharge their wastewater to the public sewer after neutralisation. Various industries have pre-treatment plants, especially pigment printing units which treat the wastewater from cleaning the printing equipment by flocculation/precipitation. The layout of the plant is typical, considering bar screen, aerated grit and grease chamber, primary clarifier, de-nitrification and nitrification but is exceptional for additional treatment with activated carbon powder in order to minimise COD and colour in the final effluent (Figure 4.49). The dosage of activated carbon powder is about 30 g/m^3 and about 3 g/m^3 alum sulfate and polyelectrolyte for complete removal of residual suspended carbon particles. Back wash water, containing activated carbon is fed to the activated sludge system which has a significant stabilising effect. Residual COD are very low (below 20 mg O_2/l, the annual average is 11 mg O_2/l). The final effluent is colourless.

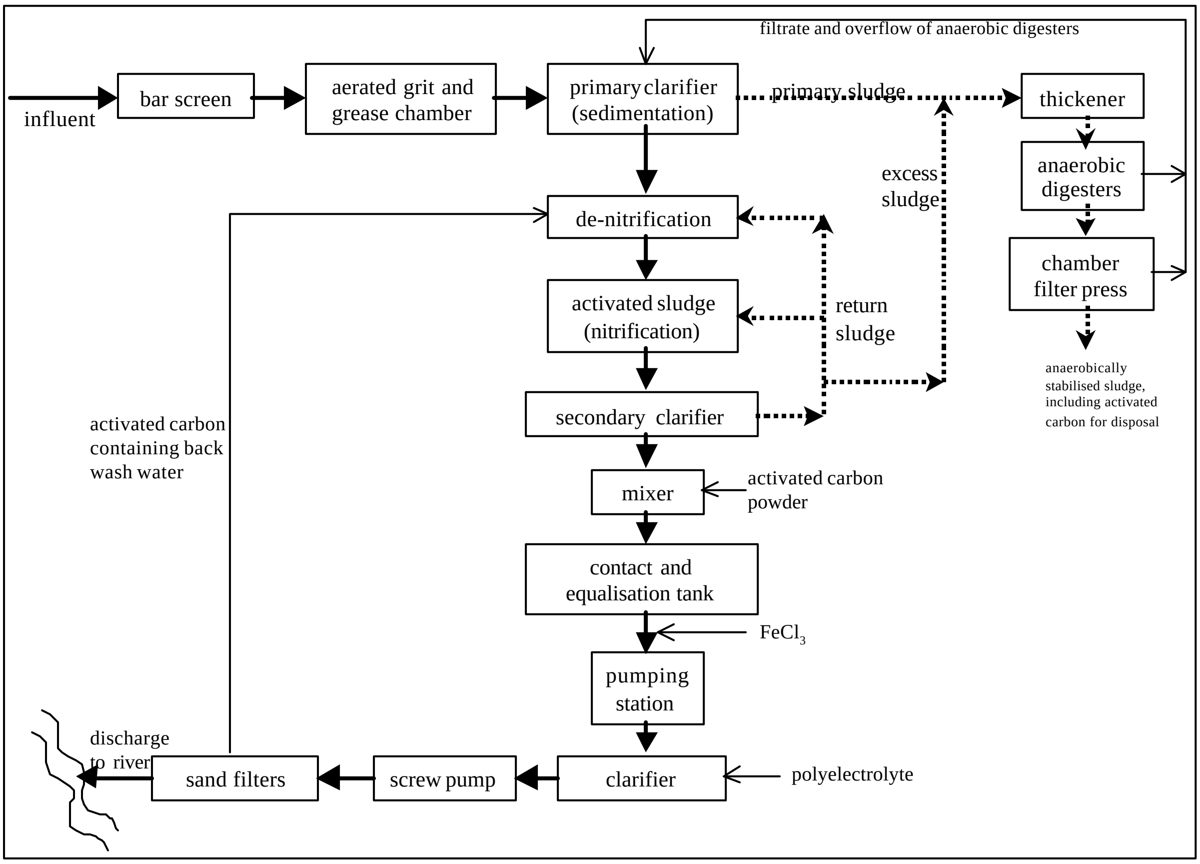


Figure 4.49: Plant 6 - combined treatment of textile wastewater and municipal wastewater

Main achieved environmental benefits

In Table 4.27, the influent and effluent values along with F/M-ratios of the six described treatment plants are compiled. F/M-ratios below 0.15 kg BOD_5/kg MLSS x d enable practically complete nitrification (residual ammonia concentrations lower than 0.5 mg/l). In some cases of combined treatment, textile wastewater and municipal wastewater is discharged to the plant via different sewer lines. For these plants, the influent values are presented separately. In case of mixing textile and municipal wastewater in the sewer already, the influent values are given under "influent (textile ww)".
Plant 4 has a F/M ratio of 0.2 resulting in higher ammonia concentrations and lower BOD_5 removal efficiency.

Aspect/component	unit	Plant 1 ann. average values for 2000	Plant 2 ann. average values for 1999	Plant 3 ann. average values for 2000	Plant 4 ann. average values for 1998	Plant 5 ann. average values for 2000	Plant 6 ann. average values for 2000
Total flow	$[m^3/d]$	8377+-1431	47770+-24500	6690	25000	2070	38750+-16790
Municipal ww flow	$[m^3/d]$	4562+-2018		4865			
Textile ww flow	$[m^3/d]$	3685+-1431		1825			
Food-to-microorga-nisms ratio (F/M)	kg BOD_5/kg MLSS x d	0.1	0.1	1.1 and 0.05	0.2	0.1	0.1
Influent (municipal ww)							
pH		8+-0.4		8.1			
COD	[mg O_2/l]	443+-200		336			278+-86
BOD_5	[mg O_2/l]	114+-50		144			138+-49
NH_4-N	[mg N/l]	30+-14		31			12.5+-4.8
Norg	[mg N/l]	18+-7		15.9			n.a.
Ptotal	[mg P/l]	6+-2		6.2			3.7+-1.2
Influent (textile ww)							
pH		9.2+-0.8	8.4+-0.4	8.7	n.a.	9-9.5	
COD	[mg O_2/l]	791+-281	349+-129	967	950	1200-1500	
BOD_5	[mg O_2/l]	157+-57	145+-49	336	400	400-500	
NH_4-N	[mg N/l]	2.6+-2.0	26+-8	5.6	n.a.	11-25	
Norg	[mg N/l]	19.5+-7.0	6+-3	9.5	50	30-40	
Ptotal	[mg P/l]	3.8+-1.2	5+-2	2.2	n.a.	10-25	
PVA	[mg/l]	28-138	n.a.	53	n.a.	n.a.	
Effluent							
pH		7.2+-0.2	8.2+-0.3	7.4	n.a.	7.8-8.6	6.8-7.5
COD	[mg O_2/l]	59+-16	46+-23	54	60-110	90-110	11+-1.3
BOD_5	[mg O_2/l]	3+-2	4.4+-3.8	3	10-40	<5	3+-0.7
NH_4-N	[mg N/l]	0.1+-0.2	0.2+-0.9	0.12	5-15	0.3-1.6	0.4+-0.3
NO_3-N	[mg N/l]	2.9+-1.9	3.6+-1.1	5.4	1-10	<2	6.8+-1.0
Norg	[mg N/l]	1.7+-0.5	n.a.	n.a.	8-15	5-10	n.a.
Ptotal	[mg P/l]	0.2+-0.2	0.9+-0.7	0.6	n.a.	1-2.5	0.15+-0.015
AOX	[mg Cl/l]	0.06 - 0.08	0.06 - 0.1	n.a.	n.a.	<0.04-0.15	n.a.
PVA	[mg/l]	0.6 - 7.8	n.a.	3	n.a.	n.a.	n.a.
SAC (435 nm)	[1/m]	8.3+-3	n.a.	2.4	0.02	5-7	0.42+-0.08
SAC (525 nm)	[1/m]	6.8+-2.9	n.a.	0.9	n.a.	1.5-5	0.31+-0.08
SAC (620 nm)	[1/m]	2.9+-1.4	n.a.	0.9	n.a.	1-3.5	0.18+-0.05
Removal efficiencies							
COD	[%]	90+-4	84.4	89	91	92.5	96
BOD_5	[%]	97+-2	96.2	98	93.5	99	98
nitrogen	[%]	88+-6	88	78	77	82	47
phosphorous	[%]	96+-3	79	88	n.a.	90	96

Table 4.27: Compilation of parameters of influent and effluent of six plants for the separate and combined treatment of textile wastewater

Applicability

Activated sludge systems with low F/M ratios and additional treatment steps to remove non-biodegradable compounds are applicable both to new and existing plants for all kinds of textile wastewater. It can also be applied to municipal wastewater treatment plants with low and high percentages of textile wastewater as well as to pure industrial plants in which the wastewater of one or more TFI is treated.

Cross media effects

The treatment of wastewater at low F/M-ratios, retention time and aeration energy is higher; however significant lower residual COD and ammonia concentrations justifies the additional energy consumption.

Economics

Lower F/M-ratios require bigger aeration tanks resulting in higher investment costs. At first order, size of activated sludge systems is directly proportional with F/M. Precise data on investment costs is not available. Additional cost for additional aeration is about 0.30 EURO/m^3.

Reference literature:

[GDCh, 1984]
Fachgruppe Wasserchemie in der Gesellschaft Deutscher Chemiker (Hrsg.),
NTA-Studie über die aquatische Umweltverträglichkeit von Nitrilotriacetat (NTA),
Verlag H. Richarz, St. Augustin (1984)

[Kölbener, 1995]
Kölbener, P.J.
Biodegradation of aromatic sulfonates - especially linear alkylbenzenesulfonates (LAS)- in a laboratory trickling filter
Dissertation ETH Zürich, No. 11'145 (1995)

[Schönberger, 1997]
Schönberger,H.; Baumann, U.; Keller, W.
Study of Microbial Degradation of Polyvinyl Alcohol (PVA) in Wastewater Treatment Plants
American Dyestuff Reporter 86 (1997) 9-17

4.2.2.2.2 Treatment of mixed wastewater and recycling of about 60%

Description

Non-segregated, mixed wastewater is treated in a more-step treatment process. The flow sheet is shown in Figure 4.50. However, before treatment the hot streams (> 40°C) are heat exchanged with fresh water to recover heat. After heat exchange, the mixed wastewater is equalised (about 20-h-equalisation) and neutralised. Then the biodegradable compounds are completely removed in a special activated sludge system consisting of loop reactors and clarifiers. Biodegradation efficiency is improved and stabilised by lignite coke powder which acts as temporary adsorbens both for organic compounds and oxygen (buffer function); in addition sessile microorganisms, growing on lignite powder can be enriched in the system. The content of dry matter in the reactors is about 35 g dry matter/l. BOD_5 is practically completely removed (< 5 mg O_2/l). In the following adsorption stage, lignite coke powder (with a specific surface of 300 m^2/g) is added with a dosage of about 0.8-1 kg/m^3 in order to remove dyestuffs and other heavily or non-biodegradable compounds. The content of dry mater in the reactors is about 40 g/l. After sedimentation, lignite coke powder is recycled to adsorbers as well to activated sludge loop reactors. However, because of small particles the removal of lignite powder is incomplete which makes further removal necessary which is carried out by precipitation and flocculation and removal of the sludge by flotation. As flocculants (dosage is about 180 g/m^3), alum sulfate and an anionic polyelectrolyte is added. In addition, in case of exceeding internal limits especially for red colour, an organic cationic flocculant (forming water-insoluble ion pairs with the sulfo groups of the dyestuffs) is dispensed. Subsequently, suspended solids and some organic are removed by filtration in a fixed bed gravel filter. Then about one third of the flow is discharged to a river and two third are treated in an activated carbon filter in order to remove residual traces of organic compounds. Finally, the latter two third of the flow are desalinated in a reverse osmosis plant (10 moduls containing 4 spiral moduls each) whereas the permeate is mixed with fresh water and is used for all finishing processes. The treated wastewater is stored in a tank and conditioned with ozone (about 2 g/m^3) in order to avoid any biological activities. It is colourless and inorganic and organic load is very low. The salty concentrate is reused for the preparation of the brine solution needed for reactive dyeing.

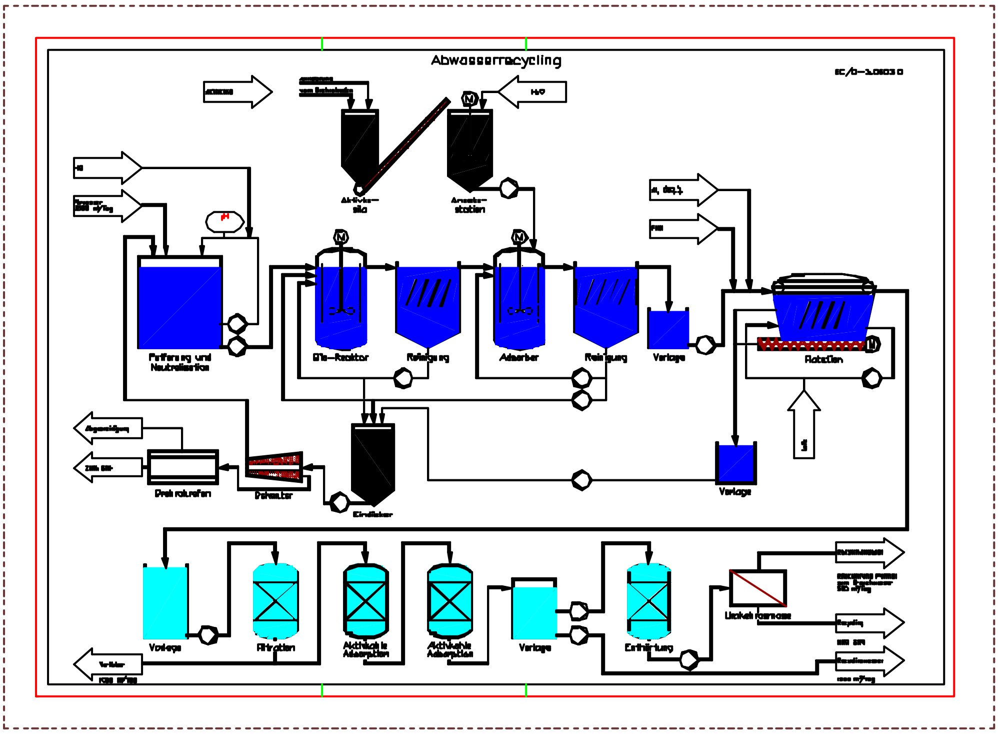


Figure 4.50: **Plant for the treatment and recycling (about 60%) of non-segregated, mixed wastewater from a textile finishing industry finishing cotton knit fabric (nearly exclusively reactive exhaust dyeing)**

Along with excess sludge from activated sludge, the sludge from flotation is de-watered in a thickener and decanter and then is thermally regenerated in a rotary kiln (Figure 4.51). The off-gas temperature after the kiln is about 450°C, after post-combustion about 850°C and after heat exchange about 120°C.

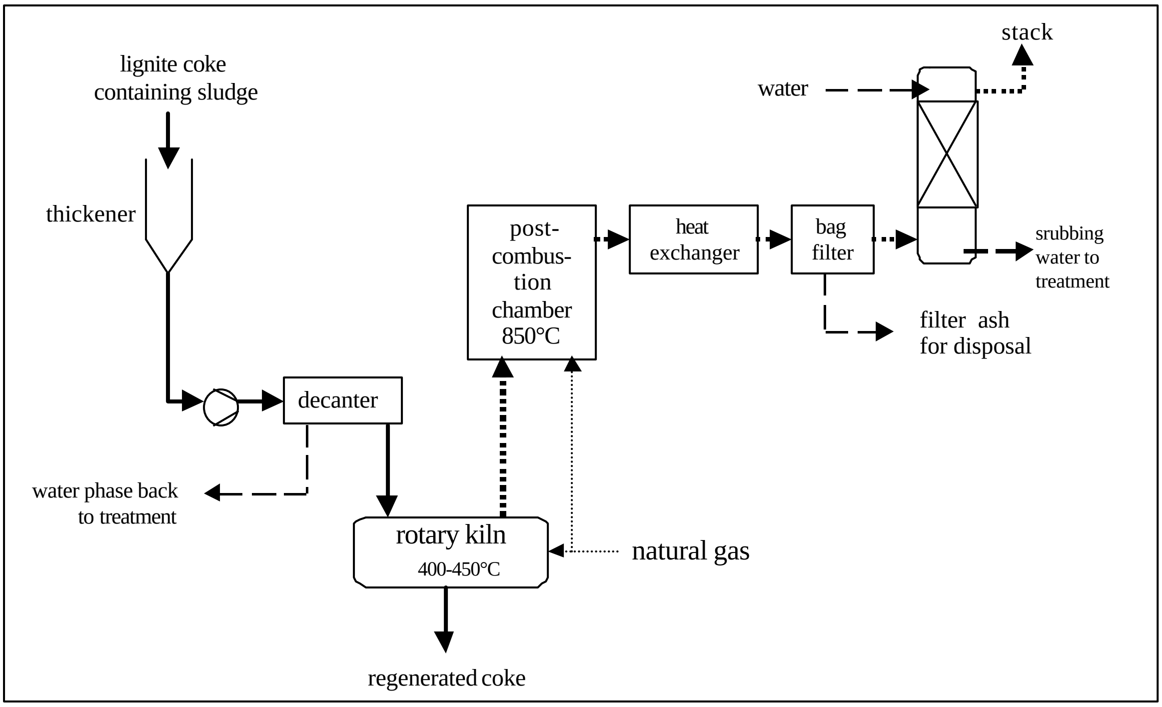


Figure 4.51: **Thermal regeneration of excess sludge from activated sludge treatment and sludge from flotation (containing lignite coke) including post-combustion of off-gas, heat recovery and purification of flue gas**

Main achieved environmental benefits

The described treatment enables significant reduction of wastewater flow corresponding with about 60% recycling. In addition, about 50% of neutral salt is recovered and reused for exhaust dyeing. The non-recycled is discharged with very low residual contents of organic compounds.

Applicability

The described technique is applicable to all types of textile wastewater. It has been approved at pilot plant scale (1 m^3/h) for wastewater from textile finishing industries finishing yarn, woven fabric and knit fabric having or without having a relevant printing section (ITV, 1982-1992)

Cross-media effects

The treatment requires considerable amounts of energy which is 1.5 kWh/m^3 electricity (mainly for the reverse osmosis plant).

Reference plants

There is a plant for the treatment and recycling of wastewater at Schiesser, D-09243 Niederfrohna (in operation since 1995) for a design wastewater flow 2500 m^3/d. This company is finishing cotton knit fabric and is dyeing nearly exclusively with reactive dyestuffs. The present wastewater flow is about 1300 m^3/d. Because there are two lines for activated sludge treatment and adsorption, only one line is in operation, the second is stand-by in case of increasing flow.

A second plant is in operation since 1999 at Palla Creativ Textiltechnik GmbH, D-09356 St. Egidien which is designed for a flow of 3000 m^3/d and a 60% recycling rate. This company is mainly finishing woolen woven fabric.

Operational data

The performance of the Schiesser plant is illustrated in Table 4.28. The very low values for COD, BOD_5, TOC, detergents, colour and heavy metals indicate that there are no limitations for recycling. However, salt and hardness (introduced to wastewater by extraction especially of calcium from cotton) have to be removed by additional treatment (ion exchange and reverse osmosis).

Parameter	unit	Influent	Effluent after filtration, before adsorption	Effluent after reverse osmosis
pH		7.3	7.2	7.0
Conductivity	[mS/cm]	5.9	6.2	0.8
Temperature	[°C]	26.2	22.9	
COD	[mg O_2/l]	515	20	10
BOD_5	[mg O_2/l]	140	< 0.1	< 0.1
TOC	[mg C/l]	135	4.8	3
AOX	[mg Cl/l]	0.56	0.2	
Anionic detergents	[mg/l]		0.02	
Cationic detergents	[mg/l]		0.02	
Hardness	[°dH]	2.5	13.6	
Ammonia	[mg N/l]	0.3	< 0.01	
Nitrate	[mg N/l]	2.5	0.9	
Total Iron	[mg/l]		< 0.01	
Total aluminium	[mg/l]		< 0.01	
Chloride	[mg/l]	1750	1710	
Sulfate	[mg/l]	163	188	
o-Phosphate	[mg/l]	0.7	< 0.01	
SAC at 436 nm	[1/m]	13	0.04	0
SAC at 525 nm	[1/m]	16.2	0.04	0
SAC at 620 nm	[1/m]	24.5	0.04	0

Table 4.28: Typical influent and effluent values (mean values) for the treatment plant at Schiesser, D-Niederfrohna

Regarding the regeneration of lignite coke in the sludge, following emission values are achieved (Table 4.29):

Parameter	**unit**	**Achieved value**	**Emission limit value**
		Related to 11 Vol% O_2	
Total particulate matter (dust)	[mg/Nm^3]	9.2	10
Carbon monoxide	[mg/Nm^3]	9.3	50
Total organic carbon	[mg/Nm^3]	< 3.0	10
Gaseous inorganic chlorine compounds	[mg/Nm^3]	< 1.0	10
Sulfur dioxide	[mg/Nm^3]	< 1.4	50
Nitrogen oxides (as NO_2)	[mg/Nm^3]	190	200
PCDD/PCDF	[ng I-TEQ/Nm^3]	0.004	0.1

Table 4.29: Measured representative emission values for the off-gas from the thermal regeneration plant - [UBA, 1996]

The composition of fresh and regenerated lignite coke is compiled in Table 4.30. The carbon content of regenerated coke is slightly higher but ash content is about 30% lower. Thus, recycling is possible without limitations. Also size distribution of regenerated coke is very similar to fresh one.

Parameter	Fresh lignite coke [weight-%]	Regenerated (at 450°C) lignite coke [weight-%]
C	88.5	90.5
H	0.4	0.3
N	0.4	0.28
Total Si	0.5	0.59
ash	9.0	6.63

Table 4.30: Elementary analysis of fresh and regenerated lignite coke - [UBA, 1996]

Ash removed from off-gas after heat recovery (Figure 4.51) has to be disposed on a landfill for hazardous waste. The specific quantity is 5 g/m^3 treated effluent.

It has to be noted that Schiesser had to face and to tackle substantial corrosion problems in the plant. The biological reactors had been manufactured out of stainless steel; however corrosion problems occurred. There is the assumption that lignite coke powder formed a layer on the surface and high chloride concentrations lead to corrosion. Meanwhile the reactors are coated with polyurethane and corrosion is avoided now. Corrosion also occurred in the pipes, especially at welding seams. Meanwhile most of the stainless steel pipes have been replaced by plastic pipes. Thus, corrosion problems could be solved.

Since summer 1998, the reverse osmosis plant is no more in operation because of high operation cost and the fact, that the company does not need a 60% recycling rate because the actual flow is far below the designed one. Thus, a recycling rate of 25% is sufficient at the moment.

Data on the plant at Palla Creativ Textiltechnik GmbH are not available.

Economics

Investment cost for such a plant are very high, for the plant at Schiesser it was 10.1 million EURO, thereof 2.0 million Euro for building construction, 7.4 million Euro for technical equipment and 0.7 million Euro for planning, scientific investigations etc. The plant has been highly subsidised by the federal and state government (about 80%). Ignoring the subsidies, which means to take capital cost into account, the cost per year and flow specific cost respectively, are compiled in Table 4.31.

Cost factor	Cost per year [EURO/a]	Flow specific cost [EURO/m^3]
Capital cost (10 a-depreciation at an interest rate of 6.88%)	876,260	1.46
Personal cost	78,000	0.13
Maintenance cost	63,000	0.105
Operation cost		
• Lignite coke	60,000	0.1
• Acetic acid	9,000	0.015
• Polyelectrolyte	6,000	0.01
• Alum sulfate	30,000	0.05
• Cationic organic flocculant	15,000	0.025
• Wetting agent	15,000	0.025
• Cleaning agent for membranes (acidic)	3,000	0.005
• Cleaning agent for membranes (alkaline)	3,000	0.005
• Electricity (1.51 kWh/m^3)	63,000	0.105
• Natural gas for coke regeneration	57,000	0.095
• Disposal of ash from flue gas purification	1,150	0.0019
Fee for wastewater discharge	18,000	0.03
total	1297,410	2.16
Pay back from heat recovery	538,200	0.9
Total cost	**759,210**	**1.27**

Table 4.31: Capital and operation cost of the Schiesser plant - [UBA, 1996]; the flow specific cost are calculated for the design flow of 2500 m^3/d and 600,000 m^3/a respectively, however the actual flow is about 1300 m^3/d only which leads to higher specific cost

The total flow specific cost has to be compared with cost to cover in case the wastewater is discharged to the municipal wastewater treatment plant. In addition, as the company is only allowed to use 1000 m^3/d ground water, to cover the design consumption (2500 m^3/d), 1500 m3/d would have been purchased from public water supply. Thus, the company would have had to pay 2.90 EURO/m^3. Thus, 1.63 EURO/m^3 could be saved respectively nearly one million EURO per year.

Data on the plant at Palla Creativ Textiltechnik GmbH are not available.

Driving force for implementation

Ground water supply is limited. This was an important reason to go for a wastewater recycling technique. The very high investment costs could be accepted because of the generous granted subsidies.

Reference literature

[UBA, 1996]
Janitza, J.; Koscielski, S.
Abwasserreinigung und -recycling einschließlich Wärmerückgewinnung in einem textilherstellenden Betrieb
Abschlussbericht zum UBA-Vorhaben-Nr. Z. II.1.1 - 20 441-14/6 (1996)

[Braun, 1997]
Braun, G.; Felgener, G.W.
Betriebserfahrungen einer Großanlage zur Abwasserreinigung und -recycling aus einer Maschenveredlung und neue Entwicklungen für eine Tuchfabrik
Technische Universität Berlin, Schriftenreihe Biologische Abwasserreinigung 9
Behandlung von Abwässern der Textilveredlung, Kolloquim an der TU Berlin, 17--18. 11.1997 (1997) 79-100

4.2.2.2.3 Recycling of textile wastewater by treatment of selected wastewater streams with membrane techniques

Description

The technique is described by hand of an example (van Clewe GmbH, D-Dingden) – see Figure 4.52. There, the main textile processes are following: woven fabric, mainly consisting of cotton is pre-treated (cold pad batch bleaching with hydrogen peroxide including subsequent rinsing as well as hydrogen peroxide bleaching in discontinuously operated jet machines), dyed (cold pad batch) or coated with pigment pastes and finished (application of softeners or fluorocarbon resins on a stenters). Most of the wastewater is caused from rinsing operations. The single streams have been carefully analysed and segregated in order to protect the membranes. For instance no pigment paste containing stream is directed to the plant because the binders would lead to irreversible scaling. In addition, processes have been changed. Cold pad batch dyeing is no more carried out with water glass because silicates also would bloc the membranes. Figure 4.53 shows the flow sheet of the plant consisting of a series of different filtration techniques. It is important to remove fibres and particles (dust from sengeing or teasing) as far as possible. The first membrane step is an ultrafiltration tubular ceramic modul (Figure 4.53) in order to remove all residual particles and polymers. About 90% of the feed can be recycled for most of the processes. Also the reuse has to be specific; e.g. for the preparation of bleaching, dyeing and finishing liquors, fresh water is used.

Figure 4.52: Ultrafiltration tubular moduls as part of the described plant for treatment and recycling of textile wastewater

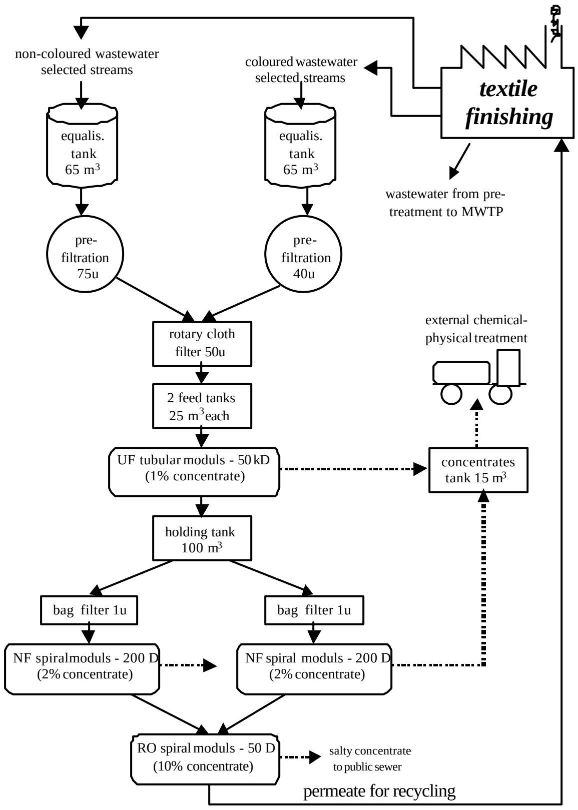


Figure 4.53: Treatment of selected segregated wastewater streams a series of membrane techniques for the UF, NF and RO membranes, the cut-offs are mentioned in Daltons (D)

Main achieved environmental benefits

Water consumption and wastewater discharge could be reduced to about 60%. The COD-load is reduced to about 50%.

Applicability

The technique is applicable to all textile finishing industries provided proper wastewater segregation and membrane-compatible selection of single wastewater streams. Recipes have to be checked in terms of membrane compatibility and have to be changed if necessary. For instance the use of water glass has to be avoided for dyeing padding liquors (see description above). Wastewater streams containing non-avoidable compounds which can create irreversible scaling of membranes may not be treated in the membrane plant (e.g. pigment paste containing streams - see description above, or reactive resins from finishing).

Additional pipe system for wastewater segregation and recycling of permeate is needed. To this purpose, also additional tanks for interim storage have to be installed.

Cross-media effects

The energy consumption of the plant is about 20 kWh/m^3 treated wastewater which is not negligible. Regarding the fact that membrane techniques are separation techniques, proper disposal of the concentrate is a crucial point.

Reference plants

Plant at van Clewe GmbH & Co.KG, D-46499 Dingden (http://www.van-clewe.de) with a design flow of 10 m^3/h.

Operational data

The plant went into operation end of 1995. Many problems had to be tackled, especially the removal of fibres and particles and the identification of chemicals causing scaling of the membranes. The ultrafiltration step had to be changed from spiral moduls to ceramic tubular moduls which are much less sensitive to scaling.

The permeate fluxes are:

- Ultrafiltration (UF): 85-130 l/m^2 x h
- Nanofiltration (NF): 12 - 17 l/m^2 x h
- reverse osmosis (RO): 11 - 17 l/m^2 x h

Wastewater from pre-treatment (scouring and bleaching) and finishing (residual padding liquors from stenters) are not treated in the membrane plant but is discharged, after neutralisation, to the municipal wastewater treatment plant.

The plant treats about 900 m^3/week wastewater (which is about 70% of the overall wastewater flow) and recovers about 800 m^3/week water which can be used for all washing/rinsing operations.

The plant is operated batch-wise. The concentrate is physical-chemically treated in an external plant. For further optimisation, the concentrate will be concentrated to 15% water by evaporation and will be incinerated in an incineration plant according to state to the art.

Economics

The investment for the 10 m^3/h plant (Figure 4.53) is about 1 million EURO. Taking into account capital cost and operation cost (personal, energy, chemicals for membrane cleaning, maintenance and concentrate disposal) the specific costs are 4.5 EURO/m^3 recycled water (capital cost: 1.3 EURO/m^3, operation cost: 3.2 EURO/m^3).

Driving force for implementation

The company is discharging the wastewater to a municipal wastewater treatment plant and is facing strong limitations in terms of flow and COD load.

Reference literature

[Marzinkowski, 1998]
Marzinkowski, J.M.; van Clewe, B.
Wasserkreislaufführung durch Membranfiltration der farbigen Abwässer
Melliand Textilberichte 79 (1998) 174-177

[van Clewe, 1999]
Innerbetriebliche Abwasserteilstrombehandlung zur Schließung von Wasserkreisläufen
Abschlussbericht über ein Innovationsprojekt unter dem Az: 07711 von der Deutschen Bundesstiftung Umwelt (1999)

4.2.2.2.4 Treatment and recovery of wastewater containing pigment paste

Description

In the following, the treatment of wastewater from a station for the preparation of pigment pastes is described. Wastewater is mainly resulting from cleaning operations of stirrers and drums. The pigment pastes are applied for coating of woven fabric. They mainly contain organic dye pigments, organic thickeners (usually polyacrylates), organic binders (co-polymerisates), fixation agents (organic resins), catalysts and softening agents. The treatment (flow sheet in Figure 4.54) consists of coagulation first in order to de-activate the organic dyes, binders and fixation agents. Therefore, polyaluminium chloride sulfate is added. Subsequently, the formed coagulates are precipitated with bentonite at pH 6. The formed precipitate then is removed by microfiltration. The applied membranes consist of polypropylene and have a cut off of 0.2 µm. Suspended solids of the concentrate are removed in a tube settler by dosage of a flocculant. The formed sludge is sent to external disposal which is physical-chemical treatment at the moment but will be incineration in the near future. Permeate is totally free of suspended solids and can be reused for cleaning operations again.

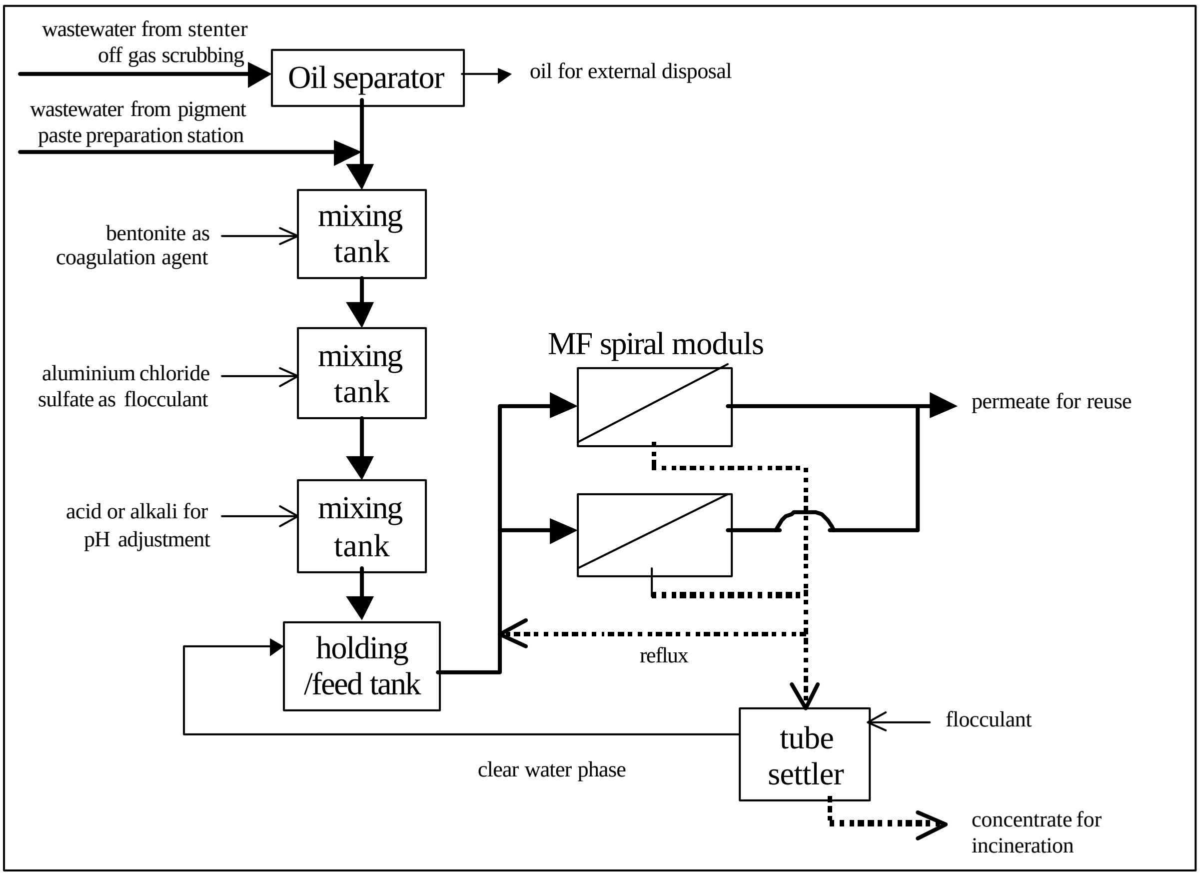


Figure 4.54: Flow sheet of a plant for treatment and recycling of wastewater from a pigment paste preparation system; in addition scrubbing water from stenters off gas purification is treated in the same plant

Figure 4.54 also indicates, that there is combined treatment of wastewater from a pigment paste preparation station with scrubbing water from purification of off gases of three stenter frames. The core of the plant are two micro filtration moduls consisting of 400 spiral membrane tubes each (Figure 4.55).

Figure 4.55: Microfiltration modul for the treatment and recycling of wastewater from a pigment paste preparation station

Main achieved environmental benefits

Wastewater is recycled to more than 90%. Biologically non-biodegradable compounds, such as organic thickeners, binders and fixation agents are completely removed and are (in the near future) mineralised in an external incineration plant according to state of the art. In biological treatment plants, these water-insoluble compounds could not be degradaded but would just adsorb to sludge to a high extend

Applicability

The technique is applicable to existing and new installations preparing pigment pastes for coating and printing respectively.

Cross-media effects

Energy is required for wastewater treatment and recycling.

Reference plants

The plant for 1.25 m^3/h is in operation since 2001 at van Clewe GmbH, D-46495 Dingden; there, combined treatment with scrubbing water from stenter off-gas purification takes place (additional 1.25 m^3/h).

Operational data

Influent COD of wastewater varies between 4000 to 10000 mg O_2/l. COD in the permeate is about 600 mg O_2/l which means a removal efficiency of about 90%. Coagulation has to be carried out and controlled very carefully because of organic binders and fixation agents. In case of incomplete de-activation of these compounds, they would lead to scaling of the membrane and would block it within short time.

The pressure difference of microfiltration is about 1 bar.

Economics

The described plant with a flow of 2.5 m^3/h (the two mentioned wastewater streams) needed investment of 180,000 EURO. Operation cost including external disposal of the concentrate (which is the major part) is about 4 EURO/m^3.

Driving force for implementation

The company is discharging the wastewater to a municipal wastewater treatment plant is facing strong limitations in terms of flow and COD.

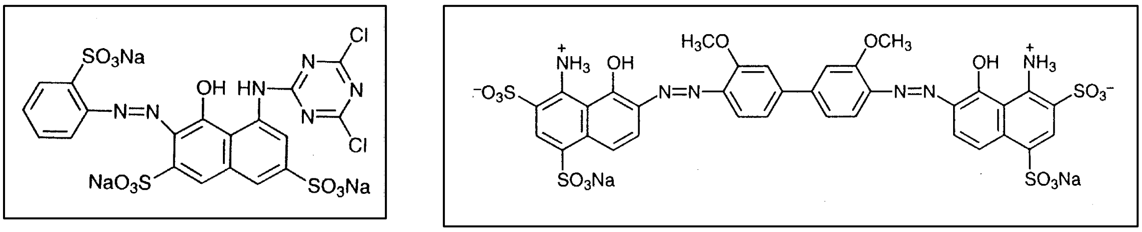
Reference literature

[Not available yet]

4.2.2.2.5 Anaerobic colour removal of residual dyestuff padding liquors and printing pastes

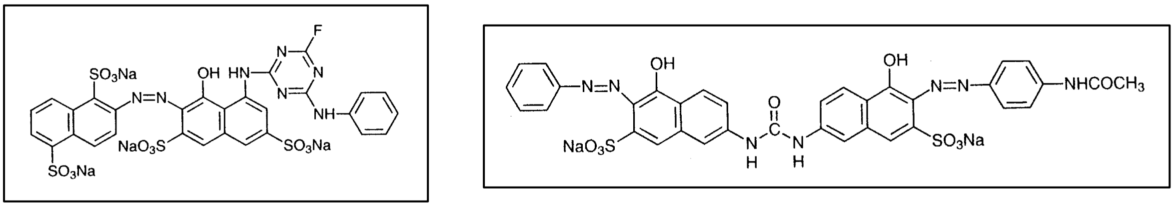
Description

Padding liquors for the continuous and semi-continuous (cold pad batch) dyeing and printing pastes contain high concentrations of dyestuffs. First, residual padding liquors for dyeing and residual printing pastes should be minimised by process- and production-integrated techniques (see the concerned described techniques). The dyestuffs of certain unavoidable residual padding liquors and printing pastes can be treated in anaerobic digesters, preferably in co-fermentation with primary and excess sludge from biological treatment. This means, the residues are fed into anaerobic digesters of municipal wastewater treatment plants. Azo dyestuffs are the most important dyestuffs which are applied today. The decisive part of their chromophores are one or more azo groups (see some examples in Figure 4.56).



Reactive Red 1

Direct Blue 1



Reactive dyestuff with mono-fluorine triazine reactive group

Direct Red 23

Figure 4.56: Examples for azo dyestuffs containing azo groups (-N=N-) - two examples for reactive azo dyestuffs and two examples for direct azo dyestuffs

Under anaerobic conditions, these azo groups can be irreversibly cleaved and thus, the dyestuffs loose their colour. However, the remaining aromatic systems still absorb light. So, often some slight yellowish colour remains. The water-soluble (the ones with sulfo groups) cleavage products are present in the water phase and reach the activated sludge stage by overflow of the anaerobic digesters and filtrate from sludge de-watering. The more-substituted naphthalene derivatives are heavily biodegradable and may be still present in the final effluent. Nevertheless, the anaerobic colour removal represents a significant improvement compared to untreated discharge of residual padding liquors for dyeing and printing pastes.

Main achieved environmental benefits

The targeted removal of colour with an efficiency of more than 90% (determined as reduction of spectral absorption coefficients at the wave lengths 436, 525 and 620 nm) is the most important benefit. In case of printing pastes containing natural thickeners, such as alginates or galactomannans, there is also a conversion to biogas because of degradation of these biopolymers.

Although the quantity of the mentioned concentrates is small (only a few tonnes per week even for big TFI), there are cases in which the residual colour in the effluent of treatment plants could be reduced to about 50%.

Applicability
The technique can be applied both to new and existing installations. It concentrates on azo dyestuffs. Other chromophoric systems can not be treated substantially. Vat dyes are reduced to the colourless form but this process is reversible. In addition, padding liquors and printing pastes with heavy metal containing dyestuffs should be separated unless the sludge is incinerated according to the state of the art. Pigment printing pastes can not be treated in anaerobic digesters because all components are non-biodegradable; in addition scaling problems occur because of polymer binders.

Cross-media effects
The reductive cleavage of the azo bonds leads to aromatic amines which may course cancerogenic/carcinogenic effects. However, investigations carried out so far did not confirm this fear [Kolb, 1988].

Reference plants
In Germany, residual printing pastes are treated in the anaerobic digesters of the municipal wastewater plants of Ravensburg, D-Ravensburg and Bändlegrund, D-Weil. Residual padding liquors for dyeing are treated in the anaerobic digester of the municipal wastewater treatment plant of Heidenheim, D-Heidenheim-Mergelstetten.

Operational data
It is important to separate the unavoidable padding liquors at source from other streams in order to keep them concentrated. Even in bigger TFI, the quantity is only about a few tonnes per week. In addition, it may be necessary (depending on the final fate of the anaerobically treated sludge) to segregate heavy metal containing padding liquors and printing pastes for separated disposal. At the anaerobic digesters, for feeding the residual padding liquors and printing pastes, a separate tank or containment should be available; it is also possible to add the residues to the primary sludge bunker. The dosage of reactive printing paste should not exceed 10 g/kg sludge because of possible inhibition effects of the anaerobic process.

Economics
The known cost for anaerobic treatment in municipal anaerobic digesters vary between 30 and 110 EURO/t padding liquor or printing paste.

Driving force for implementation
The reduction of colour in the effluent of TFI because of non-compliance with existing standards at the discharge point of treatment plants (in Germany mainly of municipal wastewater treatment plants) have been the main driving forces.

Reference literature

[Minke, 1997]
Minke, R.; Rott, U.
Innerbetriebliche anaerobe Behandlung organisch hoch belasteter und stark farbiger Teilstromabwässer der Textilveredlungsindustrie
Preprints zum Colloquium "Produktionsintergrierter Umweltschutz - Abwasserreinigung" vom 15.-17.09.1997 (1997) B53 - B 75

[Minke, 1998]
Untersuchung zur anaeroben mikrobiologischen Abbaubarkeit farbstoffhaltiger Teilstromabwässer aus der Textilveredlungsindustrie unter Berücksichtigung der Wirkung von Co-Substraten und einer nasschemischen oxidativen Vorbehandlung
Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft der Universtät Stuttgart
Abschlussbericht zum Forschungsvorhaben der Willy-Hager-Stiftung (1998)

[Kolb, 1988]
Kolb, M.; Blädel, H.; Funke, B.
Untersuchungen zur Toxizität von entfärbtem Textilabwasser
Gwf Wasser-Abwasser 129 (1988) 764-766

4.2.2.2.6 Treatment of selected and segregated, non-biodegradable wastewater streams by chemical oxidation

Description

From various processes in the textile finishing industry, high loaded wastewater streams result, such as desizing baths and exhaust dye baths for exhaust dyeing. Depending on the efficiency of washing machines and water consumption respectively and on the load of sizing agents on the fabric, COD-concentrations of desizing baths up to 20,000 mg O_2/l can result (3.3.2.1). Depending on the class of dyestuffs, exhausted dye baths have COD-concentrations between 1,000 – 15,000 mg O_2/l (3.1.2 and 3.2.2.3.1). Residual padding liquor from e.g. cold pad batch dyeing and finishing as well as residual printing pastes have even higher COD-concentrations.

Desizing baths with non-biodegradable sizing agents as well as exhausted dye baths can be treated by oxidation in a special reactor at 100-130°C and about 3 bars (max. 5 bars) pressure. Thereby, the main oxidising agent is molecular oxygen. Hydrogen peroxide is only initiating the oxidation reaction and keeps it running. As a catalyst, a iron(II)-salt is added. With COD of the feed of more than 2500 mg/l, the reaction is exothermic. Figure 4.57 shows the principle scheme and a picture of such a reactor. In addition, segregation of the selected streams (preferably automatically), concerned pipe-work and equalisation tanks are required. Required space for oxidation reactor, equalisation tanks and feed tanks of chemicals is small.

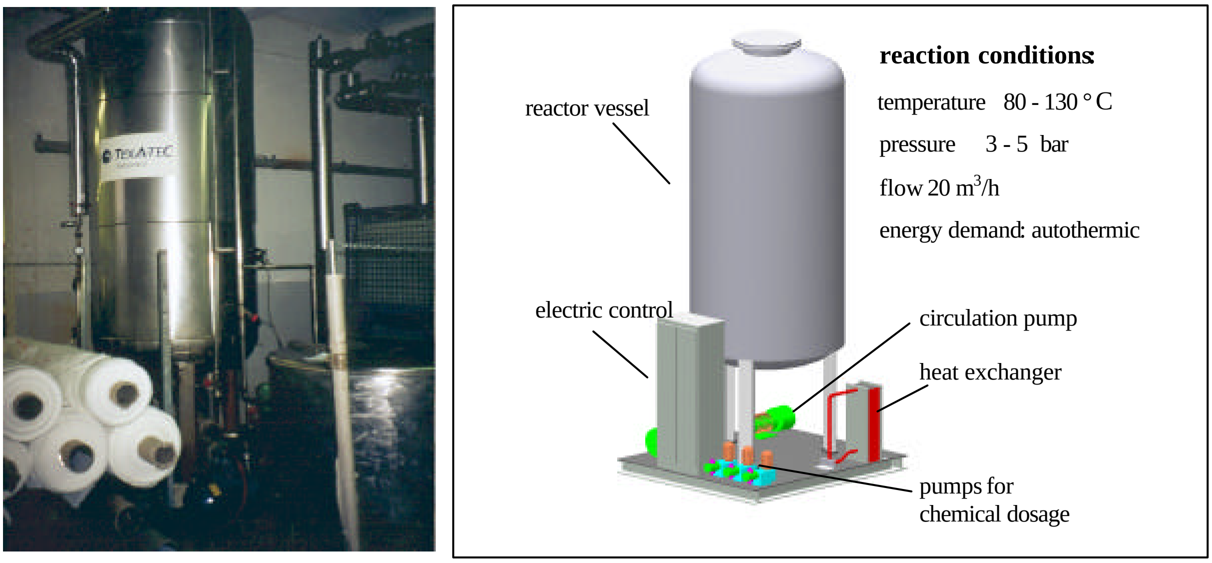


Figure 4.57: **Picture and principle scheme for treatment of selected, segregated high-loaded textile wastewater streams by catalytic oxidation with O_2/H_2O_2 and picture of the reactor at Schoeller AG, CH-Sevelen which is in operation since 1996**

Main achieved environmental benefits

Depending on retention time, applied temperature and pressure as well as on the chemical properties of the wastewater compounds, COD removal efficiencies of 70-85% are achieved. However, residual COD is biodegradable to a high extend (because of modification of the compounds during the oxidation process). Thus, taking subsequent biological treatment (normally in the municipal wastewater treatment plant) in to account, high COD removal efficiencies (≥ 95%) are achieved. This removal is real mineralisation and complete break-down of organic compounds respectively. De-colouration is more than 90% and treated exhaust dye baths are practically colourless.

Applicability

The oxidation technique is applicable both to new and existing installations.

Cross-media effects

The operation of the oxidation reactor requires electricity; however this is not of significant relevance.

Reference plants

There is one plant in operation at Schoeller Textil AG, CH-9475 Sevelen since 1996; the flow is 4-5 m^3/h.. A second and third plant are under construction (August 2001) for Tintoria di Stabio SA, CH-6855 Stabio and Givaudan Vernier SA, CH-1214 Vernier.

Operational data

Wastewater streams from different processes (different compounds and concentrations) are treated in sequence to minimise running costs. The treatment is performed continuously and is fully automated. It needs low man-power for operation. The iron catalyst can be recycled but in many cases, it may not be needed in case of subsequent treatment in a municipal wastewater treatment plant where iron may be used for phosphate removal or at least for sludge de-watering.

Typical dosage of chemicals for the oxidation process is (e.g. COD = 8500 mg O_2/l)

- 13 l H_2O_2-solution (35%)/m^3 wastewater (1.53 l H_2O_2-solution/m^3 and 1000 mg O_2/l COD)
- 35 ml H_2SO_4 (30%)/m^3 wastewater
- 120 g Fe^{2+}/ m^3 wastewater

Economics

Investment cost for a reactor with a flow of 4-5 m^3/h (reactor, dosing of hydrogen peroxide and of the catalyst, heat exchanger, catalyst preparation unit, automated control and pipe-work) is about 230,000 EURO. Operation cost, including above mentioned dosage of chemicals, maintenance, man-power and electricity, is about 3 EURO/m^3. It should be emphasized that this number is for the treatment of the selected high loaded wastewater streams and not for whole mixed wastewater.

Driving force for implementation

Wastewater problems is the main driving force for the implementation of this technique; e.g. the COD-load to be discharged to a municipal wastewater treatment plant is limited or exceeding existing standards or the wastewater is non-biodegradable or toxic.

References

[Marte, 1997]
Marte, W.; Meyer, U.; Waeber, P.
<<Faktor vier>> in der Textilveredlungsindustrie – eine überrissene Forderung?
Textilveredlung 32 (1997) 167-173

[Böhringer, 1997]
Böhringer, A.
Innovation und ökologische Verantwortung trotz wirtschaftlich schwieriger Zeiten
ITB Färberei/Druckerei/Ausrüstung (1997), Nr. 2, 43-45

4.2.2.2.7 Wastewater treatment by flocculation/precipitation and incineration of sludge

Description

Treatment of textile wastewater by precipitation/flocculation in order to reduce organic load and especially colour is performed since more than 100 years. However, today there are techniques to minimise the quantity of sludge and disposal of sludge by incineration according to state of the art. Thus, the problem of organic compounds is not just shifted from one media to another. In modern plants, the precipitate is separated from aqueous phase not just by sedimentation but by dissolved air flotation. Flocculation agents are specifically selected in order to maximise COD and colour removal, and to minimise sludge formation. In most cases, a combination of aluminium sulfate, cationic organic flocculant and very low amounts of an anionic polyelectrolyte gives best results. Figure 4.58 shows three pictures of a typical treatment plant for precipitation/flocculation of textile wastewater.

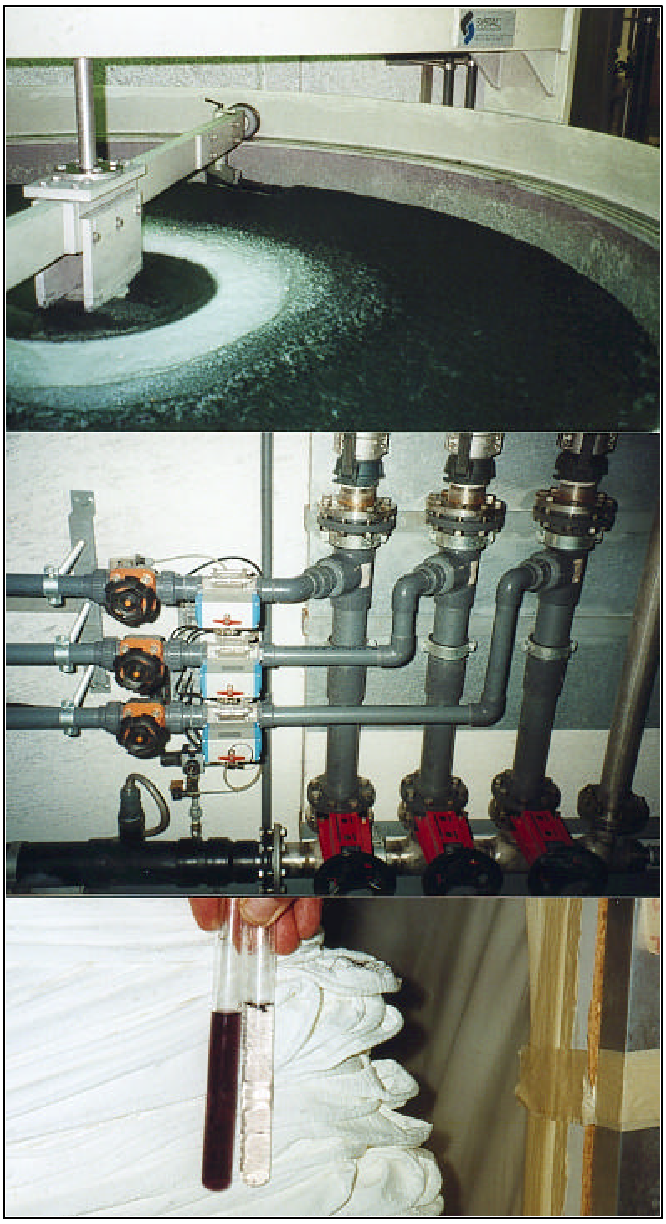


Figure 4.58: Three pictures of a typical plant for the treatment of textile wastewater by flocculation/precipitation with incineration of formed sludge in an incineration plant according to state of the art; the first picture shows the flotated sludge which is removed from surface by skimming; the second picture shows the pipes for compressed air; the third pictures shows a sample before and after treatment

Main achieved environmental benefits

In most cases, COD removal is about 40-50% and de-colouration more than 90%. In case, there is a high content of water-insoluble compounds (e.g. in case of wastewater from pigment printing sections), COD-removal is even higher. The sludge is completely mineralised in an incineration plant.

Applicability

The technique is applicable both to new and existing installations.

Cross-media effects

A considerable amount of organic compounds are shifted from the aqueous phase to sludge. However, the sludge is incinerated and thus mineralised not causing any adverse effect. Thereby, carbon dioxide generation is neglected because of very small quantity.

Reference plants

There are many plants in operation in Europe; however, sludge is incinerated in a few cases only; e.g. at Schellenberg AG, CH-Fehraltorf

Relevant suppliers are:

- Systac GmbH, D-72764 Reutlingen
- Krofta Apparatebau GmbH, D-76185 Karlsruhe

Operational data

Before precipitation/flocculation, the textile wastewater is equalised. However, compared to biological treatment, equalisation time can be shorter (about 12-h-equalisation). Fibres are removed by a sieve. The dosage of flocculants is about (in case of treatment of mixed wastewater with COD of about 1000 mg O_2/l):

- aluminium sulfate: 400 – 600 mg/l
- cationic organic flocculant: 50 - 200 mg/l
- anionic polyelectrolyte : 1 – 2 mg/l

The quantity of sludge is about 0.7-1 kg dry matter/m^3 treated wastewater. Usually, it is de-watered in a chamber filter press. Content of dry matter of 35-40% is normally achieved.

Economics

Investment cost for a plant for 20 m^3/h wastewater (including sieve for fibre removal, reactor, sludge container, chamber filter press, compressed air supply, pipes and control instruments) vary between 200,000 and 300,000 EURO. Operation cost vary from 0.25 – 1.50 Euro/m^3.

Cost for incineration in plants according to state of the art vary from 70 – 250 EURO/t.

Driving force for implementation

In most cases, wastewater problems (e.g. wastewater can not be de-colourised in municipal wastewater treatment plants or prescribed COD standard is exceeded) are the decisive driving force.

References

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduktion der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

5 BEST AVAILABLE TECHNIQUES

5.1 Introduction

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface which is unique for all BREFs and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission *(and consumption)* levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in Germany;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission *(and consumption)* levels for this sector in a general sense all according to Annex IV of the Directive.

Expert judgement has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission *(and consumption)* levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels are appropriate in this sector and represent the environmental performance that could be anticipated as a result of the application of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of “BAT”. However, they are not emission *(and consumption)* limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but they are not considered to be justified, unless there are special local driving forces, because of economic and/or cross-media considerations.

Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well designed, well maintained and well operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in chapter 4. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general “BAT” in this chapter could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate “BAT” – based conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general “BAT” levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general “BAT” levels or do better.

While the BREFs do not have a legal status, they are meant to give orientation/guidance to the industry and competent authorities on achievable emission levels when using specified techniques. The appropriate emission limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

For textile finishing industries, the following techniques or combination of techniques are considered as BAT. The order of priority and the selection of the techniques will differ according to local circumstances. Any other technique or combination of techniques achieving the same or better performance or efficiency can also be considered; such techniques may be under development, an emerging technique or a technique which is already available but not mentioned or described in this document.

It has to be kept in mind that selection of BAT in particular in textile finishing mills depends on various site specific parameters; therefore, the decision for each production site may be unique.

The principal site specific characteristics, which define the selection and priority of BAT are summarised below:

- Size and structure of the plant (integrated mills or commission finisher, number of shifts, number and size of batches per day, workload of machines etc.).
- Infrastructure of the textile finishing plant (buildings, space, existing transport systems, energy generation, fresh water supply etc.).
- Manufactured products (textile materials, textile constructions, kind of dyeing methods, and finishing procedures etc.) and their application field resp. quality standards.
- Process logistic (e.g. existing batch and continuous processes, existing pre-treatment methods (wet processes, heat setting, or dry cleaning), existing machinery (e.g. dyeing machines with low or high liquor ratio)).
- Neighbourhood situation of the company (esp. in case of possible odour nuisances).
- Local situation regarding effluent treatment (discharge of waste water into the river or into municipal waste water treatment, efficiency of municipal waste water treatment, existing on-site treatment etc.).

Because of individuality of every textile finishing industry, it has been recognised to be an appropriate approach to identify and to implement BAT on the strategy, illustrated in Figure 5.1.

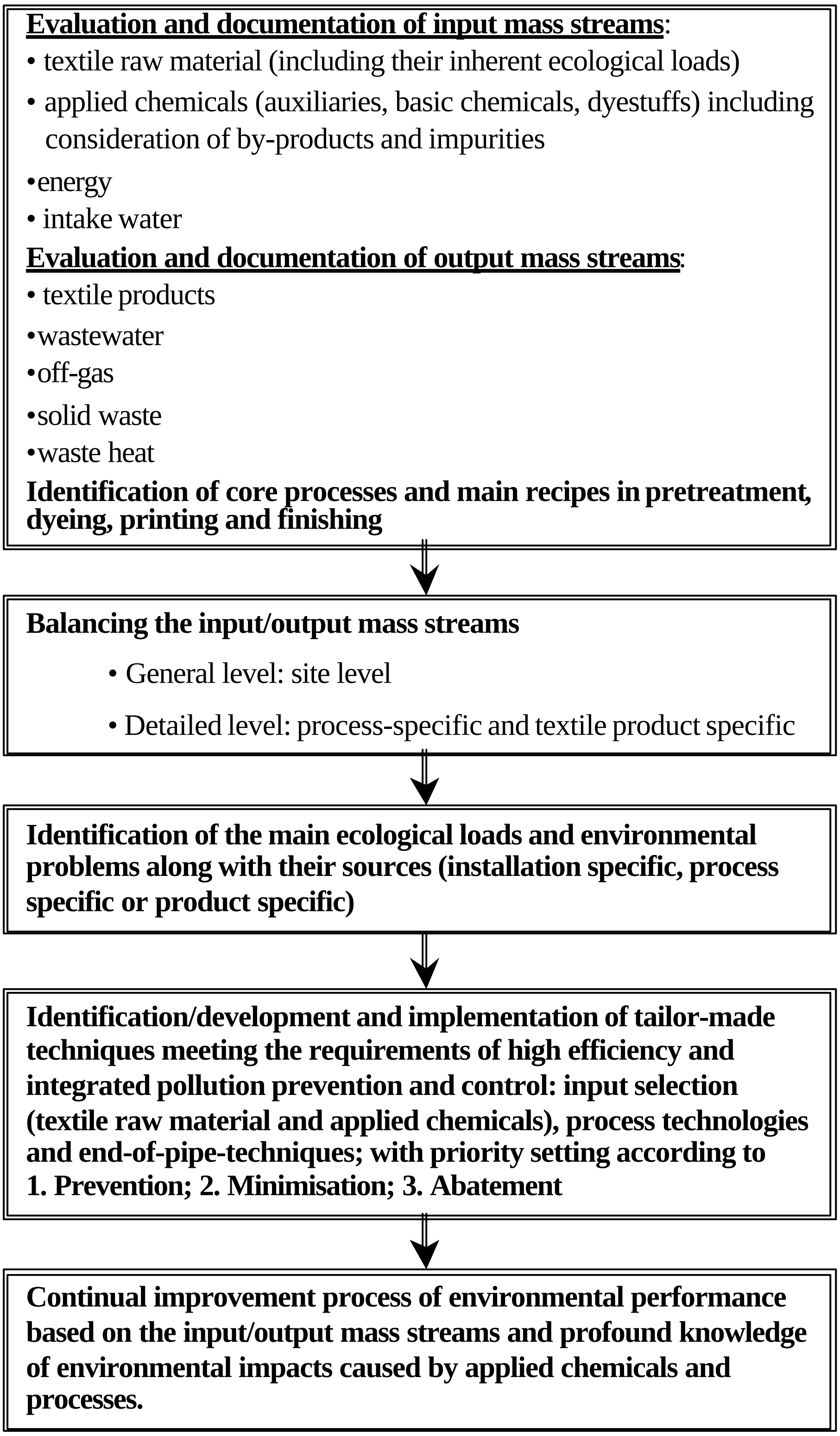


Figure 5.1: Approach for the process of selecting BAT for a certain TFI

5.2 BAT for the textile sector

Concerning applicability and limitations to apply a technique, reference is given to chapter 4 where the techniques are described in detail.

5.2.1 Best management practice

Best management practice is for all kind of textile finishing industries whereas in the following chapters, techniques which may be specific for different kind of TFI are mentioned.

		Description in chapter
5.2.1.1	**System measures and good housekeeping for the minimisation of emissions**	4.1.1
5.2.1.2	**Input/output mass streams evaluation/inventory**	4.1.2
5.2.1.3	**Automated liquor bath preparation**	4.1.3
5.2.1.4	**Measures for rational energy using**	4.1.5
5.2.1.5	**Management tool to minimise odour nuisances**	4.1.6

5.2.2 BAT for raw material selection

Considering the high environmental relevance of up-stream processes of textile finishing, such as fibre manufacture, yarn manufacture and fabric manufacturer, it is of substantial importance to apply pollution prevention measures at these stages of the textile chain. Therefore, BAT is defined for these stages. In addition, other techniques, concerning raw material selection are mentioned.

		Description in chapter
5.2.2.1	**Method for the classification of textile auxiliaries according to their wastewater relevance**	4.2.1.1.1
5.2.2.2	**Emission factor concept**	4.2.1.1.2
5.2.2.3	**Application of low emission preparation agents**	4.2.1.1.3
5.2.2.4	**Application of biologically degradable/eliminable sizing agents**	4.2.1.1.4
5.2.2.5	**Minimisation of add-on of sizing agents by selecting more efficient products**	4.2.1.1.5
5.2.2.6	**Minimisation of add-on of sizing agents by prewetting the warp yarns**	4.2.1.1.6
5.2.2.7	**Application of environmental-friendly surfactants**	4.2.1.1.7
5.2.2.8	**Application of biodegradable/bioeliminable complexing agents for pre-treatment and dyeing processes**	4.2.1.1.8
5.2.2.9	**Application of dispersing agents with higher bioelimination**	4.2.1.1.9
5.2.2.10	**Compact spinning**	4.2.1.1.12

5.2.3 BAT for TFI finishing floc and yarn

		Description in chapter
5.2.3.1	**Application of the method for the classification of textile auxiliaries according to their wastewater relevance**	4.2.1.1.1
5.2.3.2	**Application of low emission preparation agents**	4.2.1.1.3
5.2.3.3	**Application of environmental-friendly surfactants**	4.2.1.1.7
5.2.3.4	**Application of biodegradable/bioeliminable complexing agents for pre-treatment and dyeing processes**	4.2.1.1.8
5.2.3.5	**Application of dispersing agents with higher bioelimination**	4.2.1.1.9
5.2.3.6	**Substitution of hypochlorite**	4.2.1.2.1
5.2.3.7	**Enzymatic scouring**	4.2.1.2.4
5.2.3.8	**Enzymatic removal of residual hydrogen peroxide after bleaching**	4.2.1.2.5
5.2.3.9	**Optimisation of pre-treatment of cotton warp yarn**	4.2.1.2.6

5.2.3.10	**Exhaust dyeing of cellulosic fibres with polyfunctional reactive dyestuffs**	4.2.1.3.4
5.2.3.11	**Exhaust dyeing of cellulosic fibres with low salt reactive dyestuffs**	4.2.1.3.5
5.2.3.12	**Enzymatic aftersoaping in reactive dyeing**	4.2.1.3.6
5.2.3.13	**Exhaust dyeing of PES and PES blends - carrier-free or use of ecologically optimised carriers**	4.2.1.3.7
5.2.3.14	**More environment-friendly reductive aftertreatment in PES dyeing**	4.2.1.3.8
5.2.3.15	**Substitution of afterchrome dyestuffs for dyeing of wool**	4.2.1.3.9
5.2.3.16	**Dyeing of loose WO and PES in standing bath**	4.2.1.3.10
5.2.3.17	**Dyeing of loose wool fibre and combed tops - minimisation of emissions**	4.2.1.3.11
5.2.3.18	**Treatment of textile wastewater in activated sludge systems with low food-to-microorganisms ratio (F/M)**	4.2.2.2.1

5.2.4 BAT for TFI finishing knit fabric

		Description in chapter
5.2.4.1	**Application of the method for the classification of textile auxiliaries according to their wastewater relevance**	4.2.1.1.1
5.2.4.2	**Application of emission factor concept**	4.2.1.1.2
5.2.4.3	**Application of low emission preparation agents**	4.2.1.1.3
5.2.4.4	**Application of environmental-friendly surfactants**	4.2.1.1.7
5.2.4.5	**Application of biodegradable/bioeliminable complexing agents for pre-treatment and dyeing processes**	4.2.1.1.8
5.2.4.6	**Application of dispersing agents with higher bioelimination**	4.2.1.1.9
5.2.4.7	**Substitution of hypochlorite for bleaching**	4.2.1.2.1
5.2.4.8	**Recovery of caustic soda from mercerisation process**	4.2.1.2.3
5.2.4.9	**Enzymatic scouring**	4.2.1.2.4
5.2.4.10	**Enzymatic removal of residual hydrogen peroxide after bleaching**	4.2.1.2.5
5.2.4.11	**Discontinuous dyeing with airflow dyeing machines**	4.2.1.3.1
5.2.4.12	**Minimisation of dyeing liquor losses in cold pad batch dyeing**	4.2.1.3.2
5.2.4.13	**Silicate free fixation method for cold pad batch (cpb) dyeing**	4.2.1.3.3
5.2.4.14	**Exhaust dyeing of cellulosic fibres with polyfunctional reactive dyestuffs**	4.2.1.3.4
5.2.4.15	**Exhaust dyeing of cellulosic fibres with low salt reactive dyestuffs**	4.2.1.3.5
5.2.4.16	**Enzymatic aftersoaping in reactive dyeing**	4.2.1.3.6
5.2.4.17	**Exhaust dyeing of PES and PES blends - carrier-free or use of ecologically optimised carriers**	4.2.1.3.7
5.2.4.18	**More environment-friendly reductive aftertreatment in PES dyeing**	4.2.1.3.8
5.2.4.19	**Substitution of afterchrome dyestuffs for dyeing of wool**	4.2.1.3.9
5.2.4.20	**Pigment printing with low emissions to air**	4.2.1.4.2
5.2.4.21	**Volume minimisation of printing paste supplying systems of rotary screen printing machines**	4.2.1.4.3
5.2.4.22	**Recovery of printing paste from supplying system of rotary screen printing machines**	4.2.1.4.4
5.2.4.23	**Recycling of residual printing pastes**	4.2.1.4.5
5.2.4.24	**Reactive 2-phase printing**	4.2.1.4.6
5.2.4.25	**Stenter with optimised energy consumption**	4.2.1.5.1

5.2.4.26	**Formaldehyde-low easy-care finishing**	4.2.1.5.2
5.2.4.27	**Abatement of emissions to air**	4.2.2.1.1
5.2.4.28	**Treatment of textile wastewater in activated sludge systems with low food-to-microorganisms ratio (F/M)**	4.2.2.2.1
5.2.4.29	**Anaerobic colour removal of residual dyestuff padding liquors**	4.2.2.2.5

5.2.5 BAT for TFI finishing woven fabric

		Description in chapter
5.2.5.1	**Application of the method for the classification of textile auxiliaries according to their wastewater relevance**	4.2.1.1.1
5.2.5.2	**Application of emission factor concept**	4.2.1.1.2
5.2.5.3	**Application of low emission preparation agents**	4.2.1.1.3
5.2.5.4	**Application of biologically degradable/eliminable sizing agents**	4.2.1.1.4
5.2.5.5	**Minimisation of add-on of sizing agents by selection of more efficient products**	4.2.1.1.5
5.2.5.6	**Minimisation of add-on of sizing agents by prewetting the warp yarns**	4.2.1.1.6
5.2.5.7	**Application of environmental-friendly surfactants**	4.2.1.1.7
5.2.5.8	**Application of biodegradable/bioeliminable complexing agents for pre-treatment and dyeing processes**	4.2.1.1.8
5.2.5.9	**Application of dispersing agents with higher bioelimination**	4.2.1.1.9
5.2.5.10	**Substitution of hypochlorite for blaching**	4.2.1.2.1
5.2.5.11	**Recovery of sizing agents by ultrafiltration**	4.2.1.2.2
5.2.5.12	**Recovery of caustic soda from mercerisation process**	4.2.1.2.3
5.2.5.13	**Enzymatic scouring**	4.2.1.2.4
5.2.5.14	**Enzymatic removal of residual hydrogen peroxide after bleaching**	4.2.1.2.5
5.2.5.15	**Discontinuous dyeing with airflow dyeing machines**	4.2.1.3.1
5.2.5.16	**Minimisation of dyeing liquor losses in cold pad batch dyeing**	4.2.1.3.2
5.2.5.17	**Silicate free fixation method for cold pad batch (cpb) dyeing**	4.2.1.3.3
5.2.5.18	**Exhaust dyeing of cellulosic fibres with polyfunctional reactive dyestuffs**	4.2.1.3.4
5.2.5.19	**Exhaust dyeing of cellulosic fibres with low salt reactive dyestuffs**	4.2.1.3.5
5.2.5.20	**Enzymatic aftersoaping in reactive dyeing**	4.2.1.3.6
5.2.5.21	**Exhaust dyeing of PES and PES blends - carrier-free or use of ecologically optimised carriers**	4.2.1.3.7
5.2.5.22	**More environment-friendly reductive aftertreatment in PES dyeing**	4.2.1.3.8
5.2.5.23	**Substitution of afterchrome dyestuffs for dyeing of wool**	4.2.1.3.9
5.2.5.24	**Environment-friendly dyeing with sulphur dyestuffs**	4.2.1.3.12
5.2.5.25	**One-step continuous vat dyeing in pastel to pale shades**	4.2.1.3.13
5.2.5.26	**Substitution of urea in reactive printing pastes**	4.2.1.4.1
5.2.5.27	**Pigment printing with low emissions to air**	4.2.1.4.2
5.2.5.28	**Volume minimisation of printing paste supplying systems of rotary screen printing machines**	4.2.1.4.3
5.2.5.29	**Recovery of printing paste from supplying system of rotary screen printing machines**	4.2.1.4.4
5.2.5.30	**Recycling of residual printing pastes**	4.2.1.4.5
5.2.5.31	**Reactive 2-phase printing**	4.2.1.4.6
5.2.5.32	**Stenter with optimised energy consumption**	4.2.1.5.1
5.2.5.33	**Formaldehyde-low easy-care finishing**	4.2.1.5.2

5.2.5.34	**Abatement of emissions to air**	4.2.2.1.1
5.2.5.35	**Treatment of textile wastewater in activated sludge systems with low food-to-microorganisms ratio (F/M)**	4.2.2.2.1
5.2.5.36	**Anaerobic colour removal of residual dyestuff padding liquors and printing pastes**	4.2.2.2.5

6 EMERGING TECHNIQUES

6.1 Introduction

Chapter 6 addresses an overview on pollution prevention and control techniques that are under research. In reading this chapter the following items concerning information on emerging techniques have to be mentioned:

- assessment on the current status of development (resp. evaluation of time scales before the techniques might be commercially available) are in most cases not on-hand
- cost estimation of the techniques is hardly possible
- literature on public sponsored research projects is widespread; information on industries in-house developments is restricted

6.2 Novel textile finishing techniques

6.2.1 Enzyme catalysed finishing processes

Description
Enzymes are proteins which as a biocatalyst activate and accelerate chemical reactions, which normally need more energy. Enzymes can be generated in bacteria, yeasts and fungi. In textile finishing enzymes such as

- amylases, catalyse the hydrolysis of starch
- lipases, catalyse the hydrolysis of fats
- pectinases, catalyse the hydrolysis of pectins
- cellulases, catalyse the hydrolysis of cellulose
- proteases, catalyse the hydrolysis of proteins
- oxidoreductases (esp. catalases, laccases), catalyse the oxidation or reduction of various chemical compounds
- xylanases (hemicellulases), catalyse the hydrolysis of xylanes (hemi-cellulose)

can be used.

In Table 6.1 the main enzymatic processes (yet available or in emerging state) are listed.

Fibre	Treatment	Enzymes	Substrates	Technical state
Cotton	Desizing	Amylases,amyloglucosidases	Starch	State of the art
	Scouring	Pektinases	Cotton by-products	Available [Kahle, 2000]
	Scouring	Enzymatic mixture	Cotton by-products	Emerging
	Bleaching	Laccases, glucoseoxidases	Lignin, dyestuffs, glucose	Emerging
	Degradation of residual H_2O_2 after bleaching	Peroxidases	H_2O_2	Available
	Bio-polishing	Cellulases	Cellulose	Available
	Bio-stoning	Cellulases	Cellulose	Available
Wool	Scouring	Lipases	Lanolin	Emerging
	Carbonising	Cellulases	Cellulose	Emerging
	Antifelting	Special enzymes [Breier, 2000]	Wool	Emerging
Silk	Degumming	Sericinases	Sericin	Emerging
Flax	Softening	Pektinesterases	Flax by-products	Emerging
Jute	Bleaching, softening	Cellulases, xylanases	Jute by-products	Emerging

Table 6.1: Enzyme processes in textile finishing [Quand, 2000]

Some enzyme applications for cotton are state of the art such as enzymatic desizing. With the aid of cellulases some finishing objectives such as elimination of surface hairiness, lowering the pilling tendency, soft handle, lustre and smoothness can be achieved. Stonewashed effects are achieved with cellulases. Bioscouring and biobleaching are still objects of investigations [Opwis, 2000]. For enzymatic scouring a mixture of cellulases, lipases, proteases, xylanases, pectinases, and oxidoreductases is proposed.

Especially for wool enzyme based finishing processes are in work. Compared to cotton the problem is here, that the enzymes diffuse into the fibre. So the work focuses on the development of enzyme systems to be used for surface specific modification of wool fibres with special emphasis on shrink-resistance, handle, softness and dyeability [GROWTH, 2000; AiF, 1997; DWI, 2001; DBU, 2000]. Special interest is given also on antifelt finishing. First results are obtained with special enzymes and optimisation of the process with yarns and combed slivers (Lanazym-process) [Breier, 2000; DBU, 1998]. But the effects have to be optimised concerning demands on washability.

An other focus is given on extremophile enzymes which are stable against low and high pH, high salt and surfactant concentrations, and temperatures between 0 °C and 100 °C. As for example

- divers proteases for silk and wool to inhibit felt and knot formation and to improve the dyeability
- alkaline stable pectinases for cotton pre-treatment
- temperature and alkaline stable catalases for optimising the peroxide removal process with the advantage that the amount of rinsing bathes can be reduced which leads to savings in water consumption [Quand, 2000].

Enzymes immobilised onto a suitable carrier material lead to advantages in higher stability against processing parameters (pH and temperature), as well as inhibiting substances as surfactants, and variations in substrate concentration. They can be used several times and for a much longer period than free enzymes. Continuous and stable processing is possible, additional separation of enzymes and textile is not necessary [Quand, 2000]. On site water treatment (degradation of H_2O_2 residues after bleaching and recycling of the bleaching bathes) by means of immobilised enzymes is under research [BRITE/EURAM, 2001].

Another field of interest is the combination of enzymatic processes in pre-treatment. As for example starch can be converted with amylases into oligosaccharides and further with amyloglucosidases into glucose. In a second step glucoseoxidases transform the glucose to gluconic acid, which can be used as complexing agent, and to hydrogen peroxide, which can be used as oxidising agent in bleaching [Opwis, 1999].

Nowadays used cellulases are crude mixtures; they can cause unacceptable fabric strength loss. Advances in biotechnology lead to the development of tailor made gen modified cellulases. With this enzyme types the process control is improved and new finishing effects are possible [BRITE/EURAM, 1998].

A new field of interest is the application of enzymes as crosslinking catalysts for the reaction between cellulose and various crosslinking agents (easy care finishing) [Etters,1998].

The use of enzymes for man-made fibres is not mentioned explicit in the literature. However, possibilities for process optimisations are immense. Bacteria have been discovered which are capable of breaking down polyester and polyamide by polyesterases and polyamidases respectively [Stöhr, 1995].

Main achieved environmental benefits
Compared with conventional techniques, enzymatic methods are advantageous in terms of ecology and economy. Lower processing temperatures (energy saving) and lower water consumption (reduction of rinsing steps and cooling water) are advantages of enzymatic processes. Substitution and minimisation of ecological critical substances is possible. Another benefit of enzymes is their biodegradability. Enzymes can be used in catalytic amounts and the excellent substrate selectivity allows more gentle conditions compared to commonly used techniques. As a biocatalyst enzymes can be recycled.

Cross media effects:
Considering wastewater and consumer safety a complete degradation of the enzymes after their use should be proofed.

Reference literature:

[AiF, 1997]
Photobleiche von Wolle durch Kombination von Corona-, Plasma- und Enzymbehandlungen
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF 9703)
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (1996/1997)

[Breier, 2000]
Breier, R.
Rein enzymatische Antifilzausrüstung von Wolle nach dem Lanazym-Verfahren
Melliand Textilberichte 81 (2000) 298-302

[BRITE/EURAM, 1998]
Biofinishing of Cotton Fabrics with Cellulases
http://dbs.cordis.lu. EU-Project: BRITE/EURAM 3, BRPR 950009 (1998)

[BRITE/EURAM, 2001]
Catalases for low water textile processes
http://dbs.cordis.lu. EU-Project: BRITE/EURAM 3, BRPR 988004 (2001)

[DBU, 2000]
Biotechnologische Produkte für die Wollveredlung
Deutsches Wollforschungsinstitut, D-Aachen
Project: Deutsche Bundesstiftung Umwelt, D-Osnabrück, DBU 13003 (2000)
http://www.dbu.de

[DBU, 1998]
Filzfreiausrüstung von Wolle durch enzymatische Behandlung anstelle der klassischen Chlorierung und Harzbehandlung
Textilforschungsinstitut Thüringen-Vogtland, D-Greiz
Project: Deutsche Bundesstiftung Umwelt, D-Osnabrück, DBU 02509 (1998)
http://www.dbu.de

[DWI, 2001]
http://www.dwi.rwth-aachen.de/gruppen/heine/enzym.html (2001)

[Etters, 1998]
Etters, J.N.; Annis, P.A.
Textile Enzyme Use: A Developing Technology
American Dyestuff Reporter (1998) no. 5, 18-23

[GROWTH, 2000]
Enzymatic modification of wool
http://dbs.cordis.lu. EU-Project: G1RD-00131 (2000-2003)

[Kahle, 2000]
Kahle, V.
Bioscouring mit Baylase EVO
Product information, Bayer AG, D-Leverkusen (2000)

[Opwis, 1999]
Opwis, K.; Knittel, D.; Kele, A.; Schollmeyer, E.
Enzymatic recycling of starch-containing desizing liquors
Starch/Stärke, 51 (1999) 348-353

[Opwis, 2000]
Opwis, K.; Knittel, D.; Schollmeyer, E.
Aspekte zu enzymatischen Verfahren in der Textilveredlung
Internationales avantex-Symposium, D-Frankfurt, November 2000

[Quand, 2000]
Quand, C.; Kühl, B.
Einsatzmöglichkeiten und Optimierung enzymatischer Prozesse in der Textilveredlung
Melliand Textilberichte, 81 (2000) 834-836

[Stöhr, 1995]
Stöhr, R.
Enzyme – Biokatalysatoren in der Textilveredlung
Melliand Textilberichte 76 (1995) 1010-1013

6.2.2 Plasma technology

Description

A plasma can be characterised as a mixture of partially ionised gases. In other words a plasma (also indicated as “fourth state of matter”) contains gases which are decomposed due to the high electrical energy induced. Atoms, radicals, ions and electrons can be found in the plasma. Characteristic for low temperature plasmas normally used for surface treatment is the high kinetic energy (resp. temperature) of the electrons compared to the temperature of the gas. The electrons in the plasma are able to cleave covalent chemical bondings. Therefore, physical and chemical modification of surfaces of various substrates is possible. More in detail, the following plasma reaction types can be carried out:

- plasma etching (removing of parts from the plasma treated substrate)
- plasma modification (modification of functionality, e.g. oxidation of the substrate surface)
- plasma polymerisation/grafting (coating processes).
-

Two types of plasmas are generally used (see also Table 6.2):

- corona plasma
- low pressure plasma.

	Corona plasma	**Low pressure plasma**
Generation of the plasma	High voltage (20 kV; 20-40 kHz) between dieletrically Coated electrodes	Direct current or high-frequency (up to microwave area)
Pressure	Atmospheric pressure	Low pressure (1 mbar)
Expansion of the plasma	30 µm (micro discharge)	Electrode diameters
Lifetime	1-10 ns	Permanent
Continuous production	Easy	Sumptuary/expensive

Table 6.2: Comparison between corona technology and low pressure technology

Plasma treatment can be performed on natural as well as on man-made fibres. Plasma treatment for apparel and industrial textiles covers the following possible application fields:

- pre-treatment (degreasing of wool, desizing)
- changes in wettability (hydrophilic, hydrophobic properties)
- pre-treatment for dyeing and printing (increasing dyestuff affinity, better levelling properties, better bath exhaustion)
- shrinkage and antifelt finishing (wool)
- sterilisation (antibactericidal finish)
- increase of the stability of the textile against aggressive gases and fluids
- improvement of the fibre matrix adhesion (for the use in composites).

Improved antifelt finishing effects of wool after plasma treatment is one of the most interesting cases, especially in comparison with the conventional used chlorination, because the plasma treatment causes less degradation of the wool fibre and avoids AOX impact to wastewater. Work in this area is very promising and pushed from industry [BMBF, 2000a; AiF, 2001; BRITE/EURAM, 1999; Rakowski, 1989; VDI, 1995].

Improved wetting and swelling properties, dyeing kinetics, and finishing effects for wool, cotton and other cellulosic fibres after plasma pre-treatment lead to considerable savings of dyestuffs and finishing auxiliaries [Ganssauge, 2000; AiF, 2001; Fuchs, 1999; BMBF, 2000b; BMBF, 2000c]. Plasma treatment of woolen fabrics results in a considerable improvement of wool prints [Radetic, 2000; AiF, 1998].

Another focus is given to the generation of a diffusion blocking coating and advanced adhesive properties between fibre and matrix in composites by plasma induced technique [AiF, 2001; INCO, 1999; G1RD, 2000; BMBF, 2000d].

Two industrial plants for plasma treatment exist: Plant KPR 180 from Russia and plasma plant in D-Flöha with included infrared drying [VDI, 1999] (Figure 6.1).

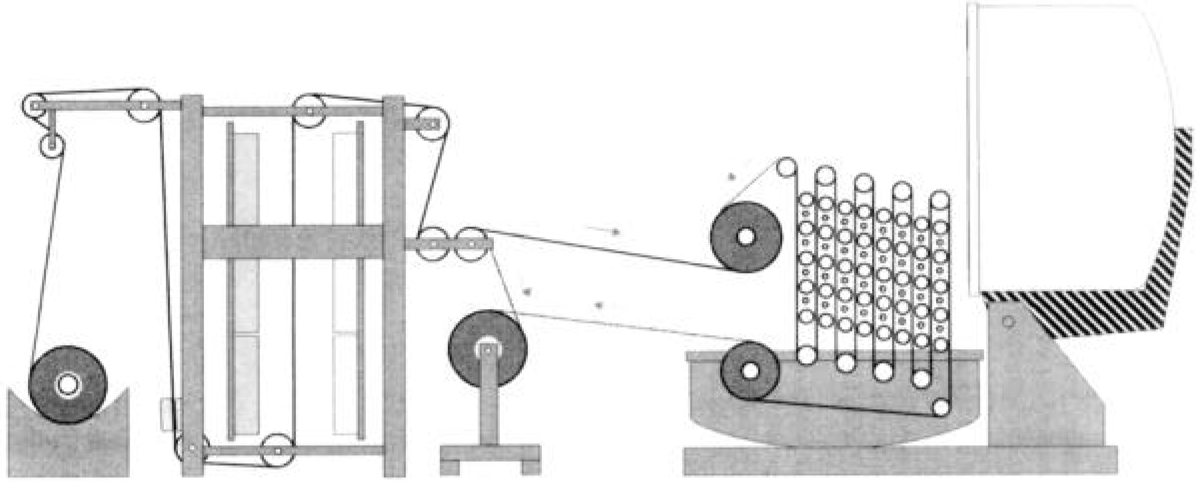


Figure 6.1: Equipment for plasma treatment at Flöha (IR-dryer and plasma chamber)

Main achieved environmental benefits

The main advantages of plasma treatment are the extremely short treatment time and low application temperatures; water or solvents resp. drying steps after plasma finishing can be avoided. Chemical and physical modification of surfaces can be achieved with the advantage that no or less auxiliaries/chemicals have to be added.

Economics

From a technical point of view corona technology shows advantages regarding easy construction and easy handling. One fundamental reason why low pressure plasma technology is not realised is that a vacuum is needed and that therefore the textiles have to be dried carefully. The high volume of fabrics, humidity of the textiles (esp. in case of natural fibers), and presence of residual auxiliaries lead to high operating costs.

Reference literature

[AiF, 1998]
Niederdruckplasmatechnologie in der Textilvorbehandlung
Deutsches Textilforschungszentrum Nord-West, D-Krefeld
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 8928
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (1997/1998)

[AiF, 2001]
Verbesserte Gebrauchseigenschaften von Synthesefasern durch plasmagestüzte Polymerisation
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen, AiF 11298 (2001)
http://www.dwi.rwth-aachen.de/publica/

[AiF, 2001]
Veredlung von textilen Flächengebilden – Einfluss der Plasmabehandlung auf Prozessführung und Warenausfall
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen, AiF 10664 (2001)
http://www.dwi.rwth-aachen.de/publica/

[AiF, 2001]
Umweltfreundliche Antifilzausrüstung durch strahlenchemische Fixierung von Kollagenhydrolysaten auf plasmamodifizierter Wolle
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen, AiF 10189 (2001)
http://www.dwi.rwth-aachen.de/publica/

[BMBF, 2000a]
Einfluss von Plasma und Harzbehandlung auf die Eigenschaften von Wolle
Deutsches Wollforschungsinstitut, D-Aachen
Project: Bundesministerium für Bildung und Forschung, D-Berlin
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[BMBF, 2000b]
Grundlagenuntersuchung zur Plasmabehandlung von Baumwoll-, Regeneratfaser- und Mischgeweben
Institut für Textilchemie, D-Denkendorf
Project: Bundesministerium für Bildung und Forschung D-Berlin,BMBF 13N6894
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[BMBF, 2000c]
Plasmabehandlung cellulosischer Fasermaterialien
Sächsisches Textilforschungsinstitut e.V., Chemnitz, Germany,
Project: Bundesministerium für Bildung und Forschung D-Berlin, BMBF 13N6964/9
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[BMBF, 2000d]
Plasmabehandlung technischer Textilien bei Atmosphärendruck
Institut für Textil- und Verfahrenstechnik, D-Denkendorf
Project: Bundsministerium für Bildung und Forschung, D-Berlin, BMBF 13N7275/3
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[BRITE/EURAM, 1999]
Friendly environmental treatments textiles finishing – integration plasma technology productive system
http://dbs.cordis.lu. EU-Project: BRPR 960336 (1999)

[Fuchs, 1999]
Fuchs, H; Bochmann, R.; Poll, H.U.; Schreiter, S.
Plasmabehandlung cellulosischer Fasermaterialien
Textilveredlung 5,6 (1999) 23-27

[Ganssauge, 2000]
Ganssauge, D.; Thomas, H.
Auswirkungen der Plasmabehandlung auf die Eigenschaften von Schurwollgeweben
Melliand Textilberichte (2000) 634-639

[G1RD, 2000]
Development of high-performance fabrics based on industrial cold plasma technology
http://dbs.cordis.lu. EU-Project: G1RD-00234 (2000)

[INCO, 1999]
Combined chemical/cold plasma treatment for optimising nonwoven textile filter materials applied on gaseous and aqueous effluents
http://dbs.cordis.lu. EU-Project, INCO 35528 (1999)

[Radetic, 2000]
Radetic, M; Jociæ, D.; Jovanèiæ, P.;Trajkoviæ, R.
The effect of low-temperature plasma pre-treatment on wool printing
Textile Chemist and Colorist & American Dyestuff Reporter 32 (2000) 55-59

[Rakowski, 1989]
Rakowski, W.
Melliand Textilberichte (1989) 780-785

[VDI, 1995]
Strategischer Dialog zur Plasmatechnologie, St. Augustin, 1995
ed.: VDI-Technologiezentrum Physikalische Technologien, D-Düsseldorf

[VDI, 1999]
Workshop: Plasmaanwendungen in der Textilindustrie, Stuttgart, 4. März 1999
ed.: VDI-Technologiezentrum Physikalische Technologien, D-Düsseldorf

6.2.2 Electron-ray treatment

Description

Electron ray treatment can be used for the production of coatings and lamination and for graft co-polymerisation reactions on textiles pre-coated with monomers and pre-polymers. Electron rays starts radically initialised polymerisation. Electron ray is generated by usage of high voltage (up to 180 kV) with a glow cathode (tungsten wire).

Main achieved environmental benefits

In comparison to thermal curing solvent free formulations can be used; this reduces off-gas loads and costs for drying operations.

Economics

The investment costs can be estimated to 0.5 –0.75 Mio. € . The implementation of this technique can be realised in the next five years, because it is well established in other areas [Clauß, 2001].

Reference literature

[AiF, 1998]
Herstellung mikroporöser Textilbeschichtungen durch strahleninduzierte Härtung von Präpolymeren
Institut für Textil- und Verfahrenstechnik, D-Stuttgart
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF10555 (1998)
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[AiF, 2001]
Institut für Textil- und Verfahrenstechnik, D-Denkendorf
Einfluss der Herstellungsbedingungen auf die Struktur und Funktionalität neuartiger Textilbeschichtungen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 11927 (2001)
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2001)

[Clauß, 2001]
Clauß, B.
Personal information (2001)

6.2.3 Supercritical Carbondioxide

Description

Systems consisting of gases under high pressure and temperature (super critical fluids (SCF)) show interesting properties for dissolving organic molecules of low to medium polarity. They are used in a large scale for the extraction of natural products. By exceeding the critical point pressure and temperature a liquid can be transformed into a SCF. In a closed system when the liquid is heated a state is achieved where there is no boundary between the liquid and gaseous state. Further increase in pressure will increase the density and the dielectric constant of the system. In this way (at last when CO_2 is used) a dissolving power will be established for hydrophobic molecules like e.g. disperse dyes used in dyeing of polyester [Knittel, 1993].

CO_2 is a non-flammable, non-explosive, non-toxic gas. The critical point (p-T phase diagram) of CO_2 (p = 7,3858 MPa; T = 304,20 °K) enhance chances on a industrial application.
Advanced development works on dyeing of PES in supercritical carbondioxide are known.

The CO_2 dyeing process of e.g polyethylenterephthalate and polypropylene is carried out under isothermal and isobaric conditions at 120 °C and 300 bar. The dyeing time is max. 1 h (dyeing of yarn bobbins). To get good washing and rubbing fastness properties excess dye, which is dissolved in the dyeing medium, should be extracted with supercritical CO_2 at the end of the dyeing cycle. During the cleaning process, the CO_2 is completely exchanged by fresh gas [Bach, 1998].

Some of the auxiliaries e.g. dispersing agents, oils and antidusting materials in the conventional dye formulations strongly influence the dye release in supercritical CO_2. Therefore only dyes formulated with certain special additives should be used.

Hydrophobic substances such as preparation agents are highly soluble in supercritical CO_2 and are extracted during dyeing of man-made fibres. When dyeing is finished these substances precipitate as oily droplets. To overcome this problem the textile material should be extracted in supercritical CO_2 prior to dyeing.

Dye uptake and the fastness properties of textile dyed in supercritical CO_2 are very similar to water dyeing [Bach, 1998].

Dyeing in an industrial way is already possible (but not applied in technical scale) for PES and PP [Bach, 1996a; Bach, 1996b]. Technical equipment for dyeing in supercritical CO_2 is available [Uhde, 2001; DBU, 1998].

Problems are still existing for the dyeing of wool, PA, and cotton, because, due to the polar character of the dyestuffs, the dissolution in the apolar media is insufficient [Liao, 2000; BRITE/EURAM, 2000; Giessmann, 1999; AiF, 2000].

Main achieved environmental benefits

The following aspects are important:

- nearly water free process
- nearly no emissions to off-gas
- no downstream drying step necessary
- no levelling and dispersing agents (esp. in PES-dyeing carriers can be avoided) necessary (and, if necessary, only in small amounts)
- concentrated dyestuff residues in powder form which can be recycled can be used
- recycling of the media (CO_2-dyeing liquors) is possible (minimal CO_2-losses).

Economics

Disadvantages in an economic way of view are the high investment costs for the new dyeing equipment esp. considering dyeing of PES textiles which are normally low-price products.

Reference literature

[AiF, 2000]
Färben von Wolle und PES/Wolle-Mischungen aus überkritischem CO_2
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 10187
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[Bach, 1996a]
Bach, E.; Cleve, E.; Schollmeyer, E.
Textilveredlung in überkritischen Medien
17. IFVTCC Kongress, Wien, 05. – 07.06.(1996) 206-207

[Bach, 1996b]
Bach, E.; Cleve, E.; Schollmeyer, E.
Dyeing of Polyethyleneterephthalate fibers in Supercritical Carbon Dioxide
High pressure Chem. Engineering (ed.: Rohr, P.R.; Trepp, C.) Elsevier (1996) 581-586

[Bach, 1998]
Bach, E.; Cleve, E.; Schollmeyer, E.; Bork, M.; Körner, P.
Experience with the Uhde CO_2-dyeing plant on technical scale, Part 1:
Optimization steps of the pilot plant and first dyeing results
Melliand Textilberichte 79 (1998) 192-194

[BRITE/EURAM, 2000]
New clean process for textile dyeing – supercritical fluid dyeing system avoiding effluents and leading to energy and water savings
http://dbs.cordis.lu. EU-Project: BRITE/EURAM 3 BRPR 960252

[DBU, 1998]
Anlagen zur Färbung von Flächengebilden aus Synthesefasern in Stück-, Strang- und anderen Aufmachungsformen in überkritischem Kohlendioxid
Jasper Maschinen und Apparatebau, D-Velen
Project: Deutsche Bundesstiftung Umwelt, D-Osnabrück, DBU 00649 (1998)
http://www.dbu.de

[Giessmann, 1999]
Giessmann, D.; Schäfer, K.; Höcker,H.
Färben aus überkritischem CO_2 von Wolle und PES/Wolle-Mischungen
Textilveredlung 11, 12 (1999) 12-19

[Knittel, 1993]
Knittel, D.; Saus, W.; Schollmeyer, E.
Application of Supercritical Carbon Dioxide in Textile Finishing
J. Text. Inst. 84 (1993) 534-552

[Liao, 2000]
Liao, S.K.; Ho, Y.C.; Chang, P.S.
Dyeing of nylon 6.6 with a disperse-reactive dye using supercritical carbon dioxide as the transport medium
J. Soc. Dyers and Colorists 116 (2000) 403-407

[Uhde, 2001]
Uhde Hochdrucktechnik, D-Hagen
Personal information (2001)

6.2.4 Ultrasonic treatment

Description
Ultrasonic waves are characterised by a frequency above 16000 kHz. Ultrasound is generated using piezoelectricity of e.g. quartz crystals. If ultrasonic treatment is carried out on liquids, diffusion rate and relative velocity of particles increases and cavitation occurs.

Energy caused by ultrasound enhances the dispersability of dyestuffs and auxiliaries and stimulates the emulsifying ability and solubility of dyestuffs leading to higher homogenisation of the auxiliaries and dyestuffs. In addition the degasing (deaeration) of the liquor and the fabrics normally carried out with the help of deaeration agents increases. Dyeing of wool, CO, PA, PAC, wool/PES blends show higher bath exhaustion and levelling properties. Although for bleaching higher efficiencies are observed. Furthermore ultrasonic pre-treatment leads to a higher removal of fats and minerals from the textiles [AiF, 2000a; AiF, 200b; AiF, 1999]. The implementation in existing machinery is possible.

Main achieved environmental benefits
The main ecological benefits of ultrasonic treatment in finishing are

- lower process temperatures (energy savings)
- shorter running times (energy savings)
- minimisation of auxiliary consumption.

Reference literature
[AiF, 1999]
Ultraschall in der Wollfärbung
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 10187
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (1998/1999)

[AiF, 2000a]
Einsatz von Ultraschall in der oxidativen Bleiche von Wolle
Deutsches Wollforschungsinstitut, D-Aachen
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 11299
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

[AiF, 2000b]
Minimierung des Restbegleitstoffgehaltes technischer Textilien durch die ultraschallgestützte Industriewäsche
Institut für Textil- und Verfahrenstechnik, D-Denkendorf
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 11081
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (2000)

6.2.5 Printing technology

6.2.5.1 Ink jet printing

Description
In a simplified way the application of ink jet printing works like an office printer. This contactless digital printing technology enables quick response and high flexibility especially in patterning.

In ink jet printing design information, this means colour-type and colour-position on the textile are digitally recorded and digitally supplied to the printing system. The transformation of the sample on the substrate takes place by a contactless way by innumerable ink drops (drop volume 1 x 10^{-12} litres) pressed out of the printing nozzles. Several drops of one colour generate one „dot“ (dpi). A raster program put these drops one upon another or side by side by an organising principle generating on this base shade, tinctorial power, and pattern.

Two technologies exist in ink jet printing: Continuous flow and drop on demand as shown in Figure 6.2.

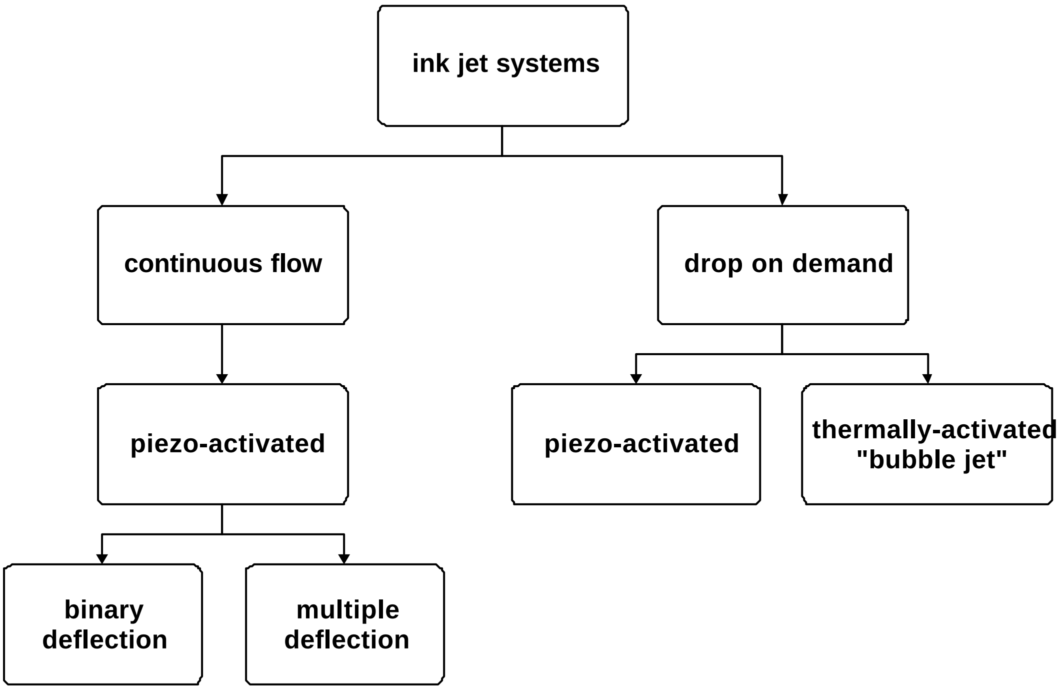


Figure 6.2: Inkjet techniques

Continuous flow (Figure 6.3**)**

The drops are generated continuously. The ink is pressed through fine nozzles, the stream is fractionalised into micro drops with help of piezo crystals and then the drops are electrostatically charged and deflected in an electric field. Selective drop control is done by binary deflection (electrical charged drops are used) or multiple deflection (only uncharged drops are used).

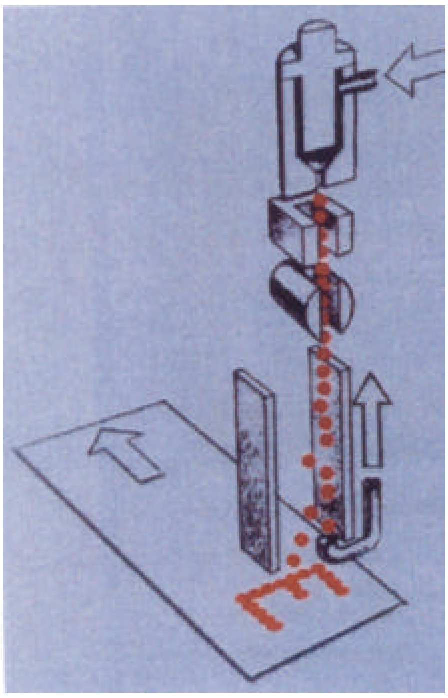


Figure 6.3: Continuous ink jet techniques [Blanck, 2001]

Drop on demand

Drops are only generated on demand by electromechanical impulse (piezo crystals) or thermally by bubble jet technology.

Typical process steps in ink jet printing are summarised in Figure 6.4.

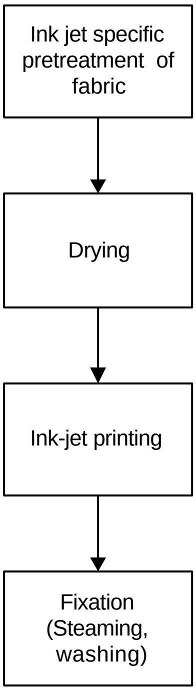


Figure 6.4: Typical process steps in ink jet printing

A lot of work is done and still going on the development of advanced inks [Winckelbeiner, 1998; Ciba, 2001; Siegel, 1998; Mheidle, 1998].

Reactive, acid, and disperse dyestuffs, as well as pigments can be used. The requests on the dyestuffs used in ink jet printing are high due to sensible micro technology. The following items have to be considered:

- purity
- drop size
- viscosity
- surface tension
- conductibility
- chemical/physical stability
- thermophysical properties
- pH
- non-foaming behaviour
- degree of fastness
- tinctorial power.

At time ink jet methods are only used for carpet printing, patterning, production of small lots (up to 100-200 m esp. in printing of flags). For carpets high resolution and velocity are not required. The systems work with 10 – 20 dpi. Equipment is available from:

- Milliken (Millitron, USA)
- Zimmer (Chromotronic- and Chromojet, Austria)
- and Godfrey Hirst (Titan MK IV Printer, Australia).

The newest development comes from the British Textile Technology Group and is taken under licence by the American carpet producer Durkan, Dalton/Georgia [Stefanini, 1997].

For other applications a higher resolution (100 – 700 dpi) and a higher production velocity is necessary. Therefore applicability is limited to small lots and patterning.

On the ITMA trade show 1999 in Paris the following machine manufacturers exhibit jet printing devices and supplies:

- Arioli, I-Gerenzano
- Mitter MMB, D-Hövelhof
- Optotex, D-Wolfegg
- Perfecta Schmid, CH-Rorschach
- Shima Seiki, J-Wakayama
- Sophis Systems, B-Wevelgem
- Stork, NL-Boxmeer
- Tecnorama, I-Prato
- Zimmer, A-Kufstein

Main achieved environmental benefits

Main environmental advantages are:

- Indirect printing system (no requirements on printing screens etc.)
- No (or less amount of) thickeners
- Only a small dyestuff palette is needed
- Reduction in water consumption (washing of printing equipment is not necessary)
- In comparison to conventional printing where residual printing pastes have to be handled nearly no dyestuff surplus occurs
- Savings in energy

Economics
Economical advantages arise mainly from the quick response, high flexibility and the screen-less printing system.

Reference literature

[Blank, 2001]
Blank,K.H.
Werk Höchst, Business Unit Spezialfarbstoffe, Frankfurt
Product information (2001)

[Ciba, 2001]
Anonymous (Ciba Spezialitätenchemie, CH-Basel
Neues „Soft" Pigment Drucktintensortiment
Melliand Textilberichte (2001) 77

[Mheidle, 1998]
Mheidle, M.
Integration of ink jet textile printing technology
American Dyestuff Reporter (1998) 22-23

[Siegel, 1998]
Siegel, B.; Siemensmeyer, K.; Dorer, M.
Digitaler Druck – Der nächste Schritt im Transferdruckverfahren
International Textile Bulletin, 44/2, (1998) 85-87

[Stefanini, 1997]
Stefanini, J.P.
Ink-Jet Technologie im Textildruck
Melliand Textilberichte (1997) 168-174

[Winckelbeiner, 1998]
Winckelbeiner, S.
Digitalisierung und Automation des Textildruckes – die Chance für die Branche
International Textile Bulletin Vol. 44/6 (1998) 74-76

6.2.6 Electrochemical Dyeing

Description
Vat dyes (including indigo) and sulfur dyes hold a large part of the dyestuff market for cellulosic fibres. Besides their well-known advantages, both vat and sulfur dyes have a complicated application procedure, involving a reduction step (sulfur containing reducing agents with environmental disadvantages concerning water toxicity, storage safety and work place atmosphere are used) to attain a water soluble form of the dye molecule with substantivity to the cellulosic fibre. Fixation (re-oxidation) of the dyestuffs is carried out with oxidation agents.

The exchange of chemical reducing agents by electrolysis is a suitable way to prevent ecological charges. Direct and indirect electrolysis is possible. In contrast to direct electrolysis, where the dye itself must be reduced at the surface of the cathode, in indirect electrolysis the reducing power of the cathode is transferred to the solution by a soluble reversible redox system (mediators e.g based on anthraquinone chemistry and iron complexes). This reversible redox system is continuously regenerated at the cathode so that a renewal of the reducing agent is achieved. This technique offers the possibility of full dyebath recycling, including the reuse of the reducing agents. A further advantage of indirect dye reduction is that the reducing conditions of the dyebath can be controlled by electrochemical methods. Direct cathodic reduction in an electrochemical cell is possible for sulfur dyes [Schrott, 2000]. Vat dyes and indigo can be reduced by mediators [Bechtold, 1991; Bechtold, 1994; Bechtold, 1997a; Bechtold, 1997b].

Main achieved environmental benefits
Compared to conventional dyeing, where a surplus of sulfur containing reducing chemicals is necessary to ensure that the vat dyes remain in their reduced form during the whole dyeing process, the electrolysis works with a defined amount of electrons. In addition, recycling of the mediator system and dyeing liquors is possible. Therefore, compared to common vat dyeing wastewater charges are reduced to a considerable amount. Furthermore problems concerning working place atmosphere and odour nuisances caused by the sulfur containing reducing agents are minimised.

Economics
Significant reductions in the consumption of chemicals and water and improvement in process reliability lead to cost savings.

Reference literature

[Bechtold, 1991]
Bechtold, T.; Burtscher, E.; Gmeiner, D.; Bobleter, O.
Untersuchungen zur elektrochemischen Reduktion von Farbstoffen
Melliand Textilberichte (1991) 50-54

[Bechtold, 1994]
Bechtold, T.; Burtscher, E.; Turcanu, A.; Bobleter, O.
The reduction of vat dyes by indirect electrolysis
J. Soc. Dyers and Colorists 110 (1994) 14-19

[Bechtold, 1997a]
Bechtold, T.; Burtscher, E.; Kühnel, G.; Bobleter, O.
Electrochemical reduction process in indigo dyeing
J. Soc. Dyers and Colorists 113 (1997) 12-21

[Bechtold, 1997b]
Bechtold, T.; Turcanu, A.; Burtscher, E.;. Bobleter,O.
Schwefelfarbstoffe in der Ausziehfärberei – Reduktion durch indirekte Elektrolyse
Textilveredlung 32 (1997) 204-209

[Schrott, 2000]
Schrott, W.
Innovationen bei Textilfarbstoffen auf Basis des integrierten Umweltschutzes
20. Fortbildungsseminar – VTCC und VdF, D-Bad-Säckingen, March 2000

6.3 Alternative textile auxiliaries

As a substitute for common complexing agents polyasparaginic acid is under research. The product is biodegradable and does not have any potential to remobilise toxic heavy metals [Knittel, 1998].

Polycarbonic acids are an alternative for formaldehyde emitting crosslinking agents based on N-methylol-components [Schramm, 2000]. Best results are achieved with 1, 2, 3, 4-butane-tetracarboxylic acid and natriumphosphinate as catalyst. To reduce costs substitution of butantetracarboxylic acid by small amounts of citric acid are tested. Due to ecological reasons the development of a phosphor-free catalyst is in work.

The permanent fixation of so-called supramolecular components such as cyclodextrin and aza crown ether derivatives on cotton and blends with man-made fibres is very promising with regard to functionability by surface modification [Denter, 1998; AiF, 1998]. Both substances are harmless with regard to toxicology and ecology. The cavities fixed on the fibre surface can also be loaded with various substances. Finishing efects can be produced with environmental friendly chemicals.

Reference literature

[AiF, 1998]
Funktionelle Polymere durch Oberflächenmodifikation mit supramolekularen Verbindungen
Deutsches Textilforschungszentrum Nord-West, D-Krefeld
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 9696 and 10955
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (1997/1998)

[Denter, 1998]
Denter, U.; Buschmann, H.J; Schollmeyer, E.
Modifizierung von Faseroberflächen durch permanente Fixierung supramolekularer Komponenten, Teil 3: Azakronenether
Angew. Makromol. Chem. 258 (1998) 87-91

[Knittel, 1998]
Knittel, D.; Schollmeyer, E.
Polyasparaginsäure (PAS) – Phosphonatersatz und Dispergiermittel?
Melliand Textilberichte (1998) 732-736

[Schramm, 2000]
Schramm, C.
Formaldehydfreie Hochveredlung mit Polycarbonsäuren
Textilveredlung (2000) 16-21

6.3.1 Biopolymers – Chitosan

Description

Besides cellulose, chitin, the main structural component of crustaceans shells (crabs, lobster, etc.) and insects, is the second main biopolymer. Increased importance is given to its deacetylated derivative chitosan, which is easier to handle due to a better solubility. The potential applications of the biopolymer chitosan or its derivatives in fibre and textile treatments are widespread due to its healing stimulating, hygienic and complexing properties. In addition chitosans are non allergenic, non toxic and biodegradable.

- An antimicrobial effect on textiles can be obtained by blending 10% of chitosan fibres with cotton fibres to produce a mixed fibre yarn. It is a permanent effect and of special interest for fabrics in close contact to the skin [Knobelsdorf, 2000]. The antimicrobial effect can also be obtained by spraying of chitosan solutions on nonwovens. Compared to other commonly used antimicrobiotics chitosan is harmless with regard to aquatic and human toxicity.

- Cationic modified derivatives of chitosan can be used in aftertretment of direct dyeing improving the fastness properties [Knittel, 1999].

- Furthermore chitosan increases the dyestuff uptake, acts as softening agent and binding agent for nonwovens and can be used as additive in printing pastes and sizing agents. It is also of interest in wastewater treatment (Chapter 6.5) [Knittel, 1998]. With chitosan additives in printing pastes the amount of urea can be minimized [Bhamani, 2000; DBU, 1998; Knittel, 1996]

- The permanent fixation of chitosan and other biopolymers as dextrins, alginates, or pectines on fibres by derivatisation is under development. For man-made fibres increased hydrophilic properties, for natural fibres antimicrobial effects could be achieved [Knittel, 2000].

Main achieved environmental benefits
The main advantages of using chitosan and other biopolymers is their biodegradability and sustainability.

Reference literature

[Bahmani, 2000]
Bahmani, S.A.; East, C.; Holme, I.
The application of chitosan in pigment printing
Journal Soc. Dyers and Colorists 116 (2000) 94-99

[DBU, 1998]
Entwicklung einer Textildruckpaste auf der Basis nachwachsender Rohstoffe
KATALYSE, Institut für angewandte Umweltforschung D- Köln
Project: Deutsche Bundesstiftung Umwelt, D-Osnabrück, DBU 07327/01 (2000)
http://www.dbu.de

[Knittel, 1996]
Knittel, D.; Schollmeyer, E.
Beiträge zum Reaktivdruck – Substitution von Harnstoff
Textilveredlung 31 (1996) 153-157

[Knittel, 1998]
Knittel,D.; Schollmeyer, E.
Chitosan und seine Derivate für die Textilveredlung. Teil1: Ausgangsposition
Textilveredlung 3,4 (1999) 67-71

[Knittel, 1999]
Knittel, D.; Schollmeyer, E.
Chitin und seine Derivate für die Textilveredlung
Textilveredlung 3,4 (1999) 19-21

[Knittel, 2000]
Knittel, D.; Schollmeyer, E.
Funktionalisierung von Fasern mit dünnen Schichten aus Biopolymeren 3. Teil
Textilveredlung 11,12 (2000) 29-30

[Knobelsdorf, 2000]
Knobelsdorf, C.; Mieck, K.P.
Hygienisch wirkende Garne durch den Einsatz von Chitosanfasern
Textilveredlung 7,8 (2000) 10-14

6.4 Process control

6.4.1 Fuzzy logic

Description

Significant improvements regarding process reliability arise by the use of fuzzy logic and neural networks. Expert systems based on self-learning software systems, which enlarge their knowledge themselves by algorithms, are under development. Considerable increase in productivity, quick response for innovations and pollution prevention due to a better process control can be achieved. A problem for implementation of software based expert systems is in some cases the availability of a reliable data base.

The following research activities are known:

Sizing process

An expert system, which includes all information about the sizing parameters was investigated. By selection of the most suitable sizing agents, setting the required size add-on level and setting data of the sizing machine environmental charges and energy consumption are reduced, and the following weaving process is optimised. This leads to reduced costs and higher quality of the produced warp yarns [BRITE/EURAM, 2000].

Condensation of crosslinking agents

The decisive point in wet crosslinking processes is the determination of the residual water content of the fabric after condensation. This depends on various process parameters. Automatic control by fuzzy logic provides a definite and constant residual moisture content resulting in optimised processing times, higher product quality and possible savings in energy [Zschenderlein, 1999].

Reference literature

[BRITE/EURAM 2000]
Development of a self-learning expert system to increase flexibility, weaving efficiency and to reduce water pollution in textile industry
http:///dbs.cordis.lu. EU-Project:BRITE-EURAM 3 BRST 985163 (1998-2000)

[Zschenderlein, 1999]
Zschenderlein, D.; Mensak, B.
Optimierung der Hochveredlung auf Spann-Trocken-Fixiermaschinen mit der Fuzzy-Regelung
Melliand Textilberichte (1999) 944-949

6.4.2 On-line monitoring

Description

Currently, the general commercial approach to textile process control is to follow a predetermined specification, determined by experience, and then either accept product variations or make corrections at the end of the process. Process control by on-line monitoring enhances operation reliability, so right in first run production is possible.

Investigations on the following items are known:

Coating

Control of coating process by determination of the crosslinking/gelling behaviour with photothermal infrared radiometry is under research. The determination of the actual degree of condensation resp.

crosslinking of the coating agents is possible. In fact the heat conductivity - which depends on solvent content and crosslinking degree - of the coated substrate is measured on-line. Using this parameter process control and optimistion of running times, curing temperature etc. resp. energy saving is possible [Bahners, 1999].

Dyeing

The COD concentration (and therefore in a indirect way the dyestuff concentration) in washing and rinsing bathes of discontinuous dyeing processes is measured on-line with specific sensors. When a quasi stationary condition, where the dyestuff concentration in the rinsing bath is negligible, is achieved the rinsing process is stopped automatically. This leads to considerable savings of water and energy [Rieker, 1999].

Dyeing and bleaching

With a specific amperometric sensor the residual concentration of reducing or oxidising agents on fabrics can be controlled on-line. E.g. the completeness of H_2O_2 removal after bleaching or the concentration of reducing agents in vat dyeing can be monitored. Surplus of chemicals can be avoided [AIF, 1999].

Dyeing with vat dyes

With a well controlled dyeing by means of monitoring the redox-potential the point, when the reducing agent is completely rinsed off can be detected exactly. Rinsing can be stopped in time. Water consumption can be adjusted depending on the depth of shade [Schrott, 2000].

Dyestuff uptake

The constant concentration of the dye liquor in continuous dyeing resp. control of the degree of exhaustion in exhaust dyeing are very important for equal and true shade dyeing. By means of pulsed, direct photo acoustic the dyestuff concentration for water soluble or water insoluble (dispersed) dyestuffs can be controlled on-line. Re-works and bad-works can be avoided [Schloßer, 1997].

Reference literature

[AIF, 1999]
Sensorentwicklung zur Messung von redoxaktiven Substanzen an laufenden Warenbahnen
Deutsches Textilforschungszentrum Nord-West, D-Krefeld
Project: Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF 10564
Textilforschung, Bericht des Forschungskuratoriums Textil e.V., D-Eschborn (1998/1999)

[Bahners, 1999]
Bahners, T.; Schlosser, U.; Gebert, B.; Schollmeyer, E.
Beschichtungspolymere – Charakterisierung ihrer thermischen Stabilisierung mittels photothermischer Infrarot-Radiometrie
Textilveredlung ½ (1999) 35-40

[Rieker, 1999]
Rieker, J.; Guschlbauer, T.
Wasch- und Spülprozesse – Automatische Steuerung mittels neuer Sensorik
Textilveredlung 9,10 (1999) 4-12

[Schloßer, 1997]
Schloßer, U.; Bahners, T.; Schollmeyer, E.
Konzentrationsmessung an lichtstreuenden Färbeflotten mit der direkten, gepulsten Photoakustik
Melliand Textilberichte (1997) 622-625

[Schrott, 2000]
W. Schrott, BASF AG
Redox-potential controlled dyeing with proVat plus
20. Fortbildungsseminar – VTCC und VdF, D-Bad-Säckingen, March 2000

6.5 End of pipe techniques for wastewater

Description

Dyestuff elimination based on Cucurbituril

Cucurbituril, precipitated on a carrier material, leads to decolorization of solutions containing different dyes [Buschmann, 1998]. The macrocyclic molecule contains cavities, where hydrophobic molecules or parts of them can be incorporated. Elimination rates between 75 – 99% for different kinds of dyestuffs can be achieved [Buschmann, 1996]. Reuse of the decolorized water as processing water is possible, also the recycling of cucurbituril. The described process is a concentration process. As a next step degradation or further concentration with recycling or elimination techniques of the dyestuffs must follow. Surfactants can reduce the elimination rate, since they are also encapsulated by cucurbituril.

Adsorption

Dissolved substances can be chemically or physically bonded on the surface of solid adsorption agents. Activated carbon as adsorbent is well known. Regeneration of the expensive activated charcoal and sludge deposition are strong disadvantages. Chitosan, as a bio-polymer, has the ability to adsorb substantial quantities of dyestuffs allowing recovery of the dyestuffs in concentrated form [Bhavani, 1999]. Investigations about optimal pH and adsorption time for direct and reactive dyes, and pigments lead to decolorization rates up to 95%. The regeneration of the adsorbent is possible. On the other hand deposition is no problem, because chitosan is biodegradable.

Reference literature

[Bhavani, 1999]
Bhavani, K.D.; Dutta, P.K.
Physico-Chemical Adsorption Properties on Chitosan for Dyehouse Effluent
American Dyestuff Reporter (1999) 53-58

[Buschmann, 1996]
Buschmann, H.J.; Schollmeyer, E.
The selective removal of dyes from wastewater
European Water Pollution Control 6 (1996) 21

[Buschmann, 1998]
Buschmann, H.J.; Schollmeyer, E.
Die Entfärbung von textilem Abwasser durch Bildung von Farbstoffeinschlussverbindungen
Textilveredlung 33 (1998) 44-47

6.6 System measures

Description

Nowadays more and more so-called soft skills such as material and energy flow management as well as management tools for information, communication, and supply chain management are demanded to improve economical and ecological performance.

Research to increase and improve environmentally friendly product development by close co-operation along the whole textile chain using modern information and communication techniques is represented in the VIRTEX-project [BRITE/EURAM, 2001]. On the base of ecobalancing according to ISO 14040 environmental relevant processes are identified and quantified. The data base provides the developer with product and processing specifications as well as with information concerning environmental and health aspects.

Besides quality and environmental management systems such as EN ISO 9000 ff, EN ISO 14001, EMAS, and labelling systems (Ökotex 100, EU ecolabel) a new concept is emerging. The bluesign-concept is a holistic, interdisciplinary and global network system [bluesign, 2001; Hübner, 2001]. The system is based on a co-operation along the whole textile chain including the chemical industry. The aim of the system is a sustainable production along the textile chain and the prevention or minimizing of polluting substances. Consumer health is also considered to a great extent.

Reference literature

[bluesign, 2001]
www.bluesign-tech.ch

[BRITE/EURAM, 2001]
EU-Project, BRITE EURAM, BE 96 3470
Institut für Textil- und Verfahrenstechnik, D-Denkendorf. Personal information on VIRTEX (2001)

[Hübner, 2001]
Hübner, H.J.
Hochtechnologie-Stoffe: Innovationen mit Dominoeffekt für die ganze Textilbranche
Textilveredlung (2001) 4-7

ANNEX I Kind and quality of chemicals applied to textile fibres prior to textile finishing

1 Preliminary remarks

This Annex submits information on those auxiliaries and chemicals which are applied to man-made fibres during their processing, yarn processing and fabric formation such as primary preparation agents (spin finishes), secondary preparation agents such as coning oils, warping oils, batching oils, and twisting oils and sizes. For yarn formation of natural fibres or blends preparation agents can be used (not necessarily, depending on the spinning process and former treatment of the fibres/yarns), as well as twisting oils. Special reference is given to such auxiliaries which are removed during textile pre-treatment causing emissions to water and to air.

The names of the agents and chemicals respectively are according to TEGEWA nomenclature [TEGEWA nomenclature, 1987].
The following information base on [UBA, 1994] which have been updated.

2 Spinning solution additives, spinning additives and spinning bath additives

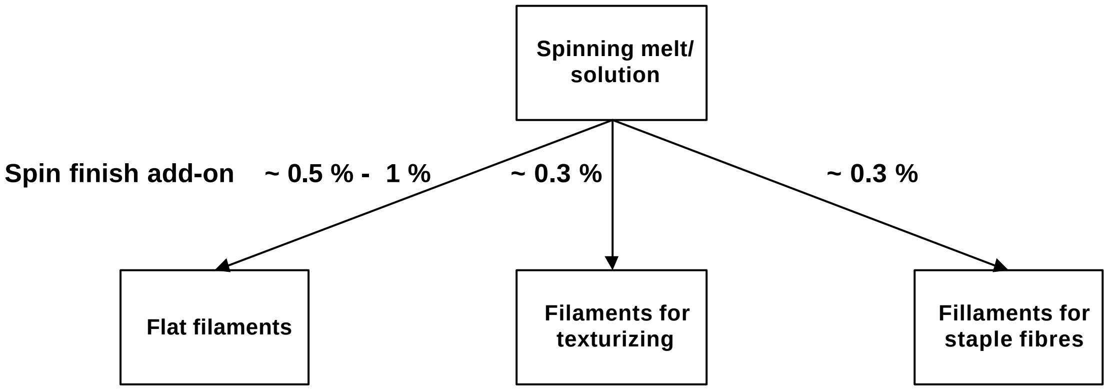
Here only chemicals are mentioned which can be washed off during textile pre-treatment. Regarding this limitation the so-called “modifier” are most relevant. They are only applied for special viscose qualities but normally not for common qualities and CV staple fibres. The load of the modifiers is 5 mg/kg fibres. They mainly consist of ethoxilated fatty amines or polyethylene glycol ethers with molecular weights of about 1500. During pre-treatment, both groups of chemicals are washed off to an extend of more than 90%.

3 Spin-finishes – primary preparation agents

Spin finishes are chemical products which are applied during the production and processing of man-made fibres - directly after the spinning process (primary spinning process). The preparation agents give the man-made fibres the necessary slippery properties (optimum friction properties, avoidance of electrostatic charging, cohesion in case of multifilament yarns) amongst and between the fibres as well as for the guide elements of the machines. Depending on the different requirements of the textile substrates, spinning techniques etc. the preparation agents usually contain following components:

- lubricants (40 – 70%)
- emulsifiers
- anti-electrostatic agents
- additives (e.g. wetting agents, biocides, corrosion inhibitors, antioxidants).

The main distinction has to be made between preparation agents for flat filaments, filaments for texturizing, and such for staple fibres as shown in the following diagram (fibres for carpets and elastane fibres not considered):



Lubricants mostly consist of

- Fatty acid triglycerides (refined natural oils)
- Ester oils (e.g. octyl stearate, tridecyl stearate, trimethylolpropane trinonaoate) and
- EO/PO-adducts.

Usually, as **emulsifiers**, non-ionic detergents such as fatty alcohol ethoxilates, fatty acid ethoxilates, partial glycerides and triglyceride ethoxilates and anionic detergents are used such as sulfonated and sulfated vegetable oils. The anionic detergents also have anti-electrostatic properties. As special **anti-electrostatic** agents mono and diesters of phosphorus pentoxides (mainly their potassium salts) are in use and also amphoteric detergents, sarcosides, amine oxides and sulfo succinates.

For stabilising emulsions of spinning preparations **biocides** are applied, such as heterocyclic compounds (isothiazolinones, imidazoles) with a load of about 2 mg/kg fibres.

Corrosion inhibitors consist of fatty acid soaps, sarcosides, fatty acid alkanolamides, and phosphoric esters.

3.1 Flat filament fibres

The load of preparation agents for the different flat filaments are compiled in Table 3.1.

Textile substrate	Load [g /kg textile substrate]	Explanations
PES	5 – 10	The content of lubricants is 40 - 70%.
PA	8 – 12	Same composition as above
CA CV	20 10	The content of lubricants is higher (60-85%).
PP	5 – 15	Here preparation agents consist of surfactants to 100%, typically 90% fatty acid and fatty alcohol ethoxilates and 10% phosphoric esters as anti-electrostatic agents
EL	30 - 70	Preparation agents mainly consist of dimethyl siloxanes

Table 3.1: Load of preparation agents on flat filaments

3.2 Filament fibres for texturizing

The load of preparation agents for the different filaments for texturizing are compiled in Table 3.2.

Textile substrate	Load [g /kg textile substrate]	Explanations
PES	3 - 5	Spinning preparation agents consist of 90% EO/PO-adducts.
PA	3.5 – 5.5 7 - 12	Preparation agents on basis of EO/PO-adducts as well as on basis of esters. In case of yarns for carpets; in former times preparation agents consisted of emulsified mineral oil but today they are very rarely in use. Normally they have been substituted by ester oils (trimethyl propane ester and pentaerythrit ester) and non-ionic surfactants
PP	8 – 12 8 - 15	The preparation agents consist of 100% surfactants (Table 3.1) Load in case of yarns for carpets

Table 3.2: Load of preparation agents on filaments for texturizing

3.3 Filaments for staple fibres

Textile substrate	Load [g /kg textile substrate]	Explanations
PES ❖ CO-types ❖ WO-types	 1 – 1.8 2 – 2.5	They consist of 50 – 80% phosphoric esters and their salts and of 20 – 50% non-ionic surfactants such as fatty acid ethoxilates and fatty alcohol ethoxilates.
PA	4 – 6	PA stable fibres are normally used for forming yarns for carpets. The preparation agents have similar compositions like for PES. Ester oils can also be part of the recipes.
CV	3 – 6	Non-ionic surfactants (fatty acid ethoxilates) are used; fatty acid soaps and phosphoric ester salts are typical ingredients.
PP	5 – 10	Preparation agents have the same composition like the ones for filament yarns (Table 3.1).
PAC	3 - 8	Different preparation agents are used; the chemistry mainly is similar to nitrogen-containing softening agents (polyamine fatty condensates, short chain quaternary ammonia compounds). They cannot be washed off. Also anionic systems like for PES are applied as well as non-ionic systems.

Table 3.3: Load of preparation agents on man-made filaments for staple fibres

3.4 Secondary preparation agents

Secondary preparation agents summarize all auxiliaries which are needed for further yarn processing and fabric formation. Differences to the primary preparation agents are their lower viscosity and the higher ad-on.

3.5 Preparation agents for secondary spinning and twisting

For these agents there is no clear definition. In the following, preparation agents for secondary spinning of synthetic staple fibres, cotton, and their blends are called conditioning agents. For wool the term spinning lubricants is used.

During secondary spinning of synthetic staple fibres including viscose staple fibres the application of conditioning agents is needed, provided that the fibres have lost their preparation agents during upstream processes such as bleaching or dyeing. Also the spinning of bleached or dyed cotton floc material needs the application of conditioning agents. However, as mentioned before, the preparation agents for secondary spinning of washed or dyed wool are called spinning lubricants.

The chemical composition of conditioning agents for synthetic fibres correspond to the one for staple fibres (Table 3.1). The load varies between 1 and 5 g/kg fibres.

The loads for cotton, viscose stable fibres and wool are compiled in Table 3.4.

Textile substrate	Load [g /kg textile substrate]	Explanations
WO and CO-wool-type; means stable fibre length is > 60 mm	30	During "spinning in the fat" of carded yarns this load is applied. The used lubricants consist of technical white oils (ca. 80%) and non-ionic surfactants as well as of EO/PO-adducts of fatty alcohols, fatty acids or polyoles.
	8 – 10	This load is applied during "dry spinning" of carded yarns without subsequent dyeing.
CO or CV	4	For spinning many recipes are in use mostly containing white oils and ester oils (30 – 40%) and non-ionic surfactants. Also oil-free systems are available.
If further processing of dyed yarns or flocs is foreseen the textile finishing industries apply conditioning agents with a load of 3 – 5 g/kg, normally discontinuously by bath exhaustion. Thereby the exhaustion rates for PES and PA can be very low (10 – 30%), but are relatively high for CO and PAC (> 80%).		
WO and CV	5	Lubricant agents are emulsions of mineral oil and ester oil.

Table 3.4: Load of conditioning agents and lubricants on cotton, viscose (staple fibres) and wool

For the **twisting process** so-called twisting oils are often applicated. They consist of mineral oils or ester oils and the add-on varies from 0,1 – 2%.

3.6 Coning, warping and batching oils

For processes such as coning and warping texturized and flat filament yarns auxiliaries have to be applied. Only in exceptional cases solid paraffines are used. Normally liquid formulations are applied, e.g. coning or warping oils.

Between texturizing and spooling **coning oils** are applicated on the man-made filament yarns in order to increase smoothness, slippery and anti-electrostatic properties. The load of coning oils depends on the further processing and the volume of the yarn. It varies for PES between 15 – 30 g/kg (20 g/kg average). For common PA the load is 5 g/kg and in case of highly elastic PA 15 – 20 g/kg. Also loads up to 30 g/kg are applied, but such values are assessed to be too high. It is reported that imported fabrics can have loads of coning oils more than 50 g/kg.

For warping around 0.2 – 1% **warping oils** are applied on flat filament yarns

After dyeing or bleaching of filament yarns **batching oils** (conditioning agents) are applied to the last rinsing bath. The load on the filament is about 5 - 10 g/kg. For dyed or bleached staple fibres and natural fibres see 3.1.

Oils for coning and warping consist of

- highly refined mineral oils, so-called white oils (mixture of hydrocarbons with C_{12} – C_{50} chain length having a range of boiling points between 220°C and 450°C); their use is strongly declining
- ester oils; common ones or new, emission low components
- special polyolesters
- polyester-/polyetherpolycarbonates
- EO/PO-adducts.

Due to new legislative regulations the add-on of these auxiliaries is reduced and more and more emission low products come on the market.

4 Knitting machine oils

The needles of knitting machines have to be lubricated with so-called knitting machine oils (loss lubrication). They consist of highly refined mineral oils with high pressure additives. On the knit fabric up to 10 g/kg remain.

5 Sizing agents

Woven fabrics are formed by weaving. In the weaving operation, the length-wise yarns are called the warp and the crosswise are called weft. While the weft yarns undergo little strain in the weaving process, warp yarns undergo much strain and must be processed to prepare them to withstand the strain. Therefore the warp yarns are protected by a viscous, elastic, friction resistant and adhesive film. For this purpose sizing agents are applied. After the weaving process the sizing agents have done their job. For subsequent textile finishing they have to be removed completely (practically at least to more than 90%) in order to guarantee undisturbed textile finishing, e.g. even dyeing. This desizing process results in high wastewater loads. In case of finishing woven fabric sizing agents can represent 30 – 70% of the total COD load in wastewater. The lower percentage is for finishing of woven fabric mainly consisting of flat filament yarns and the higher for stable fibres, especially for cotton and in case of native sizing agents. The add-ons of sizing agents depending on the different substrates are presented in Table 1.1. The add-on depends on various factors such as the density of warp yarns, the kind of sizing agents, the sizing machine (one or two chassis), the air conditioning in the weaving hall, the type of weaving machine, the weft insertion rate etc.. Usually, applied sizing agents mass consists not of the sizing agents only but also of lubricants (waxes, fats) and (in some cases) of urea and even oxidizing agents for the desizing process. In addition paraffin is added on the sizing machine directly after the application of sizing agents.

In Germany the ratio of synthetic sizing agents to native sizing agents is about 1:3.
The relevant sizing agents can be grouped into two classes:

a) Sizing agents on base of native polysaccharides:

  - starch
  - starch derivates such as carboximethylstarch or hydroxiethylstarch ether
  - cellulose derivates, especially carboximethylcellulose (CMC)
  - galactomannans

b) Fully synthetic polymers

- polyvinyl alcohols (PVA)
- polyacrylates (acrylic acid based and ester based)
- polyvinyl acetate
- polyester
- copolymerisates

Textile substrate	Add-on [g /kg warp yarn]	Explanations
Stable fibres		
- CO and CO/PES	80 – 200	As sizing agents starch and starch derivates, very often in combination with PVA, CMC or polyacrylates are applied. Thereby the ratio of starch/starch derivates to synthetic sizing agents mostly is 3 : 1, for air jet weaving machines 1 : 1. The add-on for starch/starch derivates is significantly higher (150 – 200 g/kg) than for synthetic sizing agents.
- CV	40 – 120	The add-on is 60 g/kg average. Normally combinations of all available sizing agents are applied, e.g. polyacrylates in combination with CMC and/or starch derivates
- WO	0 – 20	Woven fabric consisting of wool is usually produced with twisted yarn. Then for the weaving process the warp yarns have not to be sized. In case of simple yarns (in practice not very relevant) up to 200 g/kg starch/starch derivate in combination with synthetic sizing agents are applied.
Filament yarns		
- PES	40 – 60	For 90% of PES flat yarns polyester sizing agents (which can be dispersed) are applied; the rest is sized with modified PVA and polyacrylate.
	80 – 120	This the add-on for texturised yarns; about 80 g/kg for polyester sizing agents, about 120 g/kg for PVA and about 100 g/kg for polyacrylates
- PA	20 – 50	Polyacrylic acid is used as sizing agents; 50 g/kg in applied in case of very thin fabric only
- CV	15 – 30	Mostly in case of linings for which polyacrylates as sizing agents are used
- CA	15 - 60	Polyacrylates and polyvinyl acetate are applied

Table 5.1: Add-on of sizing agents depending on the different substrates; related to the warp yarns which have a percentage of the woven fabric of 60% average

With the add-ons of sizing agents mentioned above emissions van be estimated reliably. The same is for the calculation/estimation of organic loads as BOD_5 and COD provide specific BOD_5 and COD values are available. These values are given in Table 5.2.

Kind of sizing agent	Specific COD-value [mg O_2/g]	Specific BSB_5-value [mg O_2/g]
Starch	900 – 1000 *[1]	500 – 600
CMC	800 – 1000 *[1]	50 – 90
PVA	ca. 1700 *[1]	30 – 80 *[2]
Polyacrylates	900 – 1650	< 50
Galactomannans	1000 – 1150 *[1]	400
PES-dispersions	1450 – 1700	< 50
Protein sizing agents	1200	700 – 800

*[1] Considering the usual moisture content of commodity

*[2] For non-adapted inocculi

Table 5.2: Specific COD and BOD_5 values of sizing agents

6 Natural impurities

The most important natural raw materials for textiles are cotton and wool. In addition linen and further cellulosic fibres such as flax, hamp, ramie and sisal. As natural products these fibres are not chemically pure. Cotton for example consists mainly of cellulose but also contains relevant amounts of impurities. These impurities have influence on the mechanical and chemical properties fibres.

The gross composition of cotton fibres depends on the kind of used plants, their origin, their growth conditions and their degree of ripeness. The composition of the outer part of the fibres, the primary wall, is different from the composition of the whole fibre. Table 6.1 shows this difference and serves an overview about the composition of raw cotton.

Compounds	Percentage of the total fibre in [weight-%]	Percentage in the primary wall of the fibre in [weigth-%]
Cellulose	80 – 90	52
Water	6 – 8	?
Hemicelluloses/pectins	4 – 6	12
Waxes and fats	0,5 – 1	7
Proteins	1,5	12
Minerals such as Ca, Mg, K, Na, P	1 – 2	3
Other organic compounds	0.5 - 1	14

Table 6.1: Composition of raw cotton in weight -% - [Ullmanns – TA, 1995; Ebner, 1989]

From Table 6.1 it is obvious that cotton contains 6 – 8% organic impurities (hemicelluloses, pectins, waxes, proteins). When considering sizing agents and preparation agents as well it results a load up to 20 weigth-% undesired impurities which have to be removed during textile pre-treatment and thus appear quantitively in wastewater. On the assumptions that the organic cotton impurities are 7 weight-%, that they are removed during pre-treatment to an extend of 80%, the specific COD-value of the impurities is 1200 mg O_2/g, it results a specific COD-emission of 70 g/kg cotton. This load has to be added to the load caused by preparation agents and overall by sizing agents.

The percentage of impurities of wool are even higher than for cotton. The most important one is wool wax. Table 6.2 gives the approximate composition of raw wool.

Compounds	Add-on in [weight-%]	Explanations
Wool fibre (proteins)	20 – 80	
Wool wax	5 – 50	Wool wax is water-insoluble and consists of mixture of fatty acid esters, free fatty acids and free long-chain alcohols
Wool sweat	2 – 13	Wool sweat is water-soluble and consists of short-chain carbonic acids and aldehydes and inorganic compounds
Other impurities	5 - 40	Vegetable and mineral compounds

Table 6.2: Composition of raw wool – [Ullmanns – TA, 1995]

During pre-treatment of wool the mentioned impurities do not reach the wastewater quantitatively. Especially wool wax is recovered and used for various purposes. Therefore an estimation of the wastewater load without analytical data is not possible.

7 References

[Ebner, 1989]
Ebner, G.; Schelz, D.
Textilfärberei und Farbstoffe
Springer-Verlag, Berlin (1989) 16

[TEGEWA nomenclature, 1987]
Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V. (TEGEWA)
Zur Nomenklatur der Textilhilfsmittel, Leder- und Pelzhilfsmittel, Papierhilfsmittel und Tenside, 3rd revised edition, (1987)

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduktion der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

[Ullmanns-TA, 1995]
Ullmann's Encyclopedia of Industrial Chemistry
Textile Auxiliaries
VCH Verlagsgesellschaft, Weinheim, Vol. A 26 (1995) 227ff

ANNEX II Standard recipes for the pre-treatment of textiles

1 Preliminary remarks

The following standard recipes provide information on kind and quantity of chemicals applied during textile pre-treatment. In practice special conditions may make modifications necessary. The given values have to be considered in light of the performed processes, available apparatus/machines and liquor ratio. For example the specific recipes to be applied for pre-treatment of cotton depends on the origin of the cotton, of the percentage of cotton in case of blends, which finishing targets have to be met (pre-treatment for subsequent dyeing with dark or bright shades or for printing or full bleach qualities without subsequent dyeing etc.), available apparatus/machines etc.. This makes necessary a differentiate and process specific consideration which is typical for the textile finishing industry.
It has to be stressed that continuous processes have significantly lower substrate specific consumption factors (input factors) for chemicals and water than discontinuous processes.
The upper values for discontinuous processes reflect extreme operation conditions.
At first sight the chemicals applied during textile pre-treatment enter wastewater quantitatively. Optical brighteners used for full-bleached, non-dyed textiles are an exception; they mainly remain on the textile substrates. The following information base on [UBA, 1994] which has been partly updated.

2 Cotton and cotton blends

2.1 Woven fabric

The typical pre-treatment steps for cotton woven fabric consist of desizing, scouring and bleaching. In new machines these processes can be combined; this leads to lower consumption of energy and water but not of chemicals. The following standard recipes concern the classic more-step process. Thereby the input values are presented as “Telquel” which means that the quantity is related to the applied ready-formulated chemical product. The concentrations of active chemical substances of these products are different. For detergents and complexing agents the average content of active chemical substances is about 60%. This percentage is valid for liquid formulations; for powder products the range is big being 15 – 100%.

2.1.1 Desizing

2.1.1.1 Enzymatic desizing

Chemical	[g Telquel/kg textile substrate]	Explanations
Enzyme	5	
Complexing agent	1	
Surfactant	1 - 8	In case of discontinuous processes, e.g. desizing in a winch with liquor ratio of 1:20 up to 30 g Telquel/kg textile substrate are applied
Water consumption [l/kg textile substrate]	4 - 6	

Table 2.1: Standard recipe for enzymatic desizing of woven fabric consisting of CO and CO blends

2.1.1.2 Removal of water-insoluble sizing agents by cold oxidative desizing

It is a semi-continuous process. The liquor for oxidative desizing is added at room temperature in a padder with a pick-up of 70-80%. Reaction takes place with a retention time of 16-24 h (max. 72 h). Then the fabric is thoroughly rinsed.

Chemical	[g Telquel/kg textile substrate] continuous and optimised process		Explanations
NaOH (100%)	10 - 20		Usually applied as solution with 33%, mainly with 50%
H_2O_2 (100%)	15 - 25		Usually applied as solution with 30%, mainly with 50%
Surfactants	1.5 - 3		As surfactants a mixture of non-ionic (about 70% average, e.g. ethoxilated fatty alcohol) and anionic surfactants (about 30%, especially alkylsulfonates but also alkyl sulfates and linear alkylbenzene-sulfonates are applied
Complexing agents	2 - 4		As complexing agents polyacrylates and phosphonates are applied but not EDTA or DTPA
$MgSO_4$ (100%)	0.15 - 0.3		Usually applied as solution with 40% $MgSO_4$
Water glass (100%)	5 - 8		Usually applied as solution with 40% water glass
Na-peroxodisulfate (100%)	3 - 6		Usually applied as solution with 20% sodium peroxodisulfate
Water consumption [l/kg textile substrate]	4 – 6 or 8 - 12		4-6 l/kg in case of multi-usage of water or high efficient washing compartments; otherwise 8-12 l/kg

Table 2.2: Standard recipe for the desizing of woven fabric consisting of CO and CO blends sized with water-insoluble sizing agents

2.1.1.3 Removal of water-soluble sizing agents

Chemical	[g Telquel/kg textile substrate] continuous and optimised process	Discontin. Process	Explanations
Complexing agent	1	3 – 15	As complexing agents polyacrylates and phosphonates are applied but not EDTA or DTPA
Surfactant	1 – 3	4 – 20	As surfactants a mixture of non-ionic (about 70% average, e.g. ethoxilated fatty alcohol) and anionic surfactants (about 30%, especially alkylsulfonates but also alkyl sulfates and linear alkylbenzene-sulfonates are applied; to a minor extend alkylether sulfates and alkylethoxi-phosphoric esters). In case of recovery of sizing agents desizing is carried out without surfactants; but then more washing compartments are needed in order to remain under a residual content of sizing agents of 1,2%. Very often surfactant formulations already contain defoaming agents (0.1 – 1 g/kg); if not dosage of defoaming agents is needed. Usually polysiloxanes are used (very low dosage) and to a minor extend hydrocarbons (higher dosage) and trialkyl phosphoric esters
Soda or NaOH (100%)	0 - 3 0 - 2	0 – 3 0 – 2	
Water consumption [l/kg textile substrate]	4 – 6 or 8 - 12	ca. 50 (winch)	4-6 l/kg in case of multi-usage of water otherwise 8-12 l/kg; in continuous processes washing water from bleaching and/or scouring is used for desizing

Table 2.3: Standard recipe for the desizing of woven fabric consisting of CO and CO blends sized with water-soluble sizing agents

2.1.2 Scouring

Chemical	[g Telquel/kg textile substrate]		Explanations
	continuous and optimised process	discontin. process	
NaOH (100%)	20 – 80	20 - 80	The quantity depends both on the percentage of cotton in blends and on the applied processes.
Complexing agents	1 – 6	3 - 30	Some suppliers for complexing agents do not recommend more than 2 g/kg for continuous processes. The application of complexing agents is necessary to extract calcium. For this purpose NTA is not efficient enough. Normally a mixture of different complexing agents such as phosphonates, gluconates, polyphosphates, NTA, polyacrylates and in some cases still EDTA and DTPA are in use. The use of complexing agents can be reduced significantly if an acidic treatment is carried out prior to scouring. In Germany this possibility is very seldom practiced. In some cases combinations of complexing agents and reducing agents are used.
Surfactant	5 - 6	5 - 30	Some suppliers recommend 2 – 4 g/kg for continuous processes. The composition concerns the one which is given for desizing of water-soluble sizing agents (Table 2.3)
Water consumption [l/kg textile substrate]	8 - 10	ca. 50	Rinsing is included: in case of continuous processes the consumption can be lower if water-recycling is practiced.

Table 2.4: Standard recipe for scouring of woven fabric consisting of CO and CO blends

2.1.3 Bleaching

Chemical	[g Telquel/kg textile substrate] continuous and optimised process	discontin. process	Explanations
H_2O_2 (100%)	5 - 15	5 – 15	Stabilised by phosphoric acid and organic stabilisers
NaOH (100%)	4 – 10	4 – 30	At the beginning of the bleaching process the phosphoric acid is neutralised and looses its stabilising effect
Complexing agents*)	0 - 2	0 – 2	For complexing calcium and heavy metal ions the same compounds are used like for scouring; magnesium may not be complexed because it is needed for the stabilisation of H_2O_2
Organic stabiliser*)	0 - 10	0 –20	For the stabilisation of H_2O_2, many products are available which contain complexing agents for calcium and heavy metal ions, such as gluconate, NTA/EDTA/DTPA, polyacrylates and phosphonates; in Germany DTPA is no more applied and EDTA to a minor extend
Surfactant	2 - 5	2 – 10	The same compounds are applied like for desizing and scouring (Table 2.3 and Table 2.4)
Sodium silicate*)	8 - 20		Sodium silicate acts as pH buffer, alkali supplier, anti-catalyte and stabiliser
Water consumption [l/kg textile substrate]	6 - 12	ca. 50	Rinsing is included

*) The consumption of complexing agents, organic and inorganic (silicate) stabilisers vary in total from
0 – 20g/kg. Like for scouring the consumption can be significantly reduced by acidic pre-treatment.

Table 2.5: Standard recipe for bleaching of woven fabric consisting of CO and CO blends

2.1.4 Mercerisation

Chemical	[g Telquel/kg textile substrate]	Explanations
NaOH (100%)	200 - 300	.
Wetting agent	0 - 10	A wetting agent is only applied in case of dry-in-wet-mercerisation (raw mercerisation). They consist of short chain anionic compounds such as alkylsulfates
Complexing agent	2	Only in case of raw mercerisation. The same chemicals are used like for scouring (Table 2.4)

Table 2.6: Standard recipe for mercerisation of woven fabric consisting of CO and CO blends

2.1.5 Alkali treatment

Chemical	[g Telquel/kg textile substrate]	Explanations
KOH (100%) or NaOH (100%)	200 – 300 60 – 230	
Sandoflex A	60 – 80 ml	The product is a liquid formulation with a concentration of active compounds of 50%. It consists of sulphuric acid esters, a fatty acid derivate and an alkylsulfonate.
Wetting agent	5	

Table 2.7: Standard recipe for alkali treatment of woven fabric consisting of CO and CO blends

2.2 Knit fabric

Pre-treatment of knit fabric does not need desizing because sizing agents are not present.

“Light scouring” is applied if bleaching is not needed; this is the case for fabric to be dyed in dark shades (black, brown, dark marine or turquoise etc.). “Light scouring” is also called “alkali pre-washing”; a precise definition is not available.

Usually bleaching is only applied for full bleach qualities which are not dyed subsequently or which are dyed in light and medium shades. However, because of logistic reasons some TFI do bleach all kind of qualities. In case of continuous processes bleaching is usually performed one-stage. There are exceptional cases in which the combined bleaching process with peracetic acid/hydrogen peroxide/optical brightener is applied.

In many cases the so-called combination bleaching, consisting of a two-stage bleaching with sodium hypochlorite and hydrogen peroxide has been replaced by two-stage hydrogen peroxide bleaching and one-stage bleaching with reducing agents. Like for woven fabric consisting of cotton or cotton blends, an acidic pre-treatment which requires a lower dosage of complexing agents in the subsequent bleaching stage which is usually carried out one-stage.

The consumption of chemicals for pre-treatment of knit fabric is similar to the one for woven fabric. However the range is wider because knit fabric is treated much more often discontinuously.

2.2.1 Neutral/acetic demineralisation

Chemical	[g Telquel/kg textile substrate]	Explanations
Inorganic or organic acid	0 - 2	
Complexing agents	1 - 3	The same chemicals are applied like for scouring of woven fabric (Table 2.4)
Surfactant	1 - 3	The same chemicals are applied like for desizing of water-soluble sizing agents (Table 2.3)
Water consumption [l/kg textile substrate]	?	

Table 2.8: Standard recipe for neutral/acidic demineralisation of knit fabric consisting of CO and CO blends

2.2.2 „Light scouring” process (alkali pre-wash)

Chemical	[g Telquel/kg textile substrate]	Explanations
Soda or NaOH (as 100%)	ca. 50 ca. 50	There is a wide range of applied alkali quantity
Surfactant	1 - 3	
Water consumption [l/kg textile substrate]	?	

Table 2.9: Standard recipe for “light scouring” of knit fabric consisting of CO and CO blends

2.2.3 Bleaching

2.2.3.1 Bleaching with hypochlorite

Chemical	[g Telquel/kg textile substrate] continuous and optimised process	discontin. process	Explanations
NaOCl (as active chlorine)	5 – 6	ca. 30	
NaOH (100%)	1 – 3	5 - 15	
Surfactant	2 – 5	2 - 10	
Water consumption [l/kg textile substrate]	?	?	

Table 2.10: Standard recipe for bleaching with hypochlorite of knit fabric consisting of CO and CO blends

2.2.3.2 Bleaching with hydrogen peroxide

Chemical	[g Telquel/kg textile substrate]		Explanations
	continuous and optimised process	discontin. process	
H_2O_2 (100%)	5 - 15	5 – 15	
NaOH (100%)	4 – 10	4 - 30	Usually the lower dosage is applied because in case of knit fabric seed shells are already removed to a high extend
Complexing agents	0 - 2	0 - 2	See Table 2.5
Organic stabiliser	0 – 10	0 - 20	See Table 2.5
Surfactant	2 – 5	2 - 10	See Table 2.5
Sodium silicate	8 – 20	0 - 20	See Table 2.5
Water consumption [l/kg textile substrate]	?	?	

Table 2.11: Standard recipe for bleaching with hydrogen peroxide of knit fabric consisting of CO and CO Blends

3 VISCOSE

3.1 Woven fabric

Usually viscose is treated with alkali. Subsequent bleaching with hydrogen peroxide is carried out exceptionally only. Thereby the applied quantities of chemicals are lower then for cotton because viscose does not contain natural by-products to be removed.

3.1.1 Alkali treatment

Chemical	[g Telquel/kg textile substrate]	Explanations
NaOH (100%)	40 – 60	Normally strength of applied caustic soda lye is 6°Bé
Surfactant	3 – 20	
Water consumption [l/kg textile substrate]	?	

Table 3.1: Standard recipe for alkali treatment of woven fabric consisting of viscose

3.1.2 Scouring

Chemical	[g Telquel/kg textile substrate]	Explanations
NaOH (100%)	ca. 30	In case the scouring process is applied as single stage
Surfactant	3 - 20	
Water consumption [l/kg textile substrate]	ca. 10	

Table 3.2: Standard recipe for scouring of woven fabric consisting of viscose

3.2 Knit fabric

Knit fabric consisting of viscose is not a common product. The standard recipe for bleaching concerns the one for cotton. However the dosage of caustic soda and hydrogen peroxide is reduced to 40 – 70%.

4 Man-made fibres (woven and knit fabric)

Woven fabric and knit fabric consisting of man-made fibres are usually washed in order to remove sizing agents and preparation agents which are normally water-soluble. Scouring is not carried out. The application of bleaching of PES and PAN with chlorite is no more common.

4.1 Standard recipes for washing (continuous and discontinuous processes)

4.1.1 Woven fabric

Chemical	[g Telquel/kg textile substrate]	Explanations
Alkali	0 – 2	For pH-adjustment depending on the kind of sizing agents; normally NaOH, soda or ammonia hydroxide are used, seldom sodium phosphate
Complexing agents	0,5 – 15	
Surfactant	0,5 – 30	
Water consumption [l/kg textile substrate]	4 – 8	In case of micro fibres up to 60 l/kg

Table 4.1: Standard recipe for washing of woven fabric consisting of man-made fibres

4.1.2 Knit fabric

Chemical	[g Telquel/kg textile substrate]	Explanations
Complexing agents	0 – 10	Polyacrylates are predominantly applied, more seldom polyphosphates
Surfactant	2 – 20	
Water consumption [l/kg textile substrate]	?	

Table 4.2: Standard recipe for washing of knit fabric consisting of man-made fibres

4.2 Standard recipes for bleaching and optical brightening

4.2.1 Reductive bleaching of polyamide

Chemical	[g Telquel/kg textile substrate]	Explanations
Sodium dithionite containing formulation	10 – 30	
Optical brightener	5 – 15	
Surfactant	1 – 2	
Water consumption [l/kg textile substrate]	?	

Table 4.3: Standard recipe for reductive bleaching and optical brightening of polyamid

4.2.2 Bleaching of PES or PAC with sodium chlorite

Chemical	[g Telquel/kg textile substrate]	Explanations
$NaClO_2$ (100%)	5 – 15	
Formic acid pH 2,5-3,5 or oxalic acid pH 2,5	?	Contains in addition buffer salts and stabilisers
Corrosion inhibitor (Chemistry = ?)	10 – 20	
Water consumption [l/kg textile substrate]	?	

Table 4.4: Standard recipe for the bleaching of PES and PAC with sodium chlorite

5 WOOL

5.1 Raw wool scouring

In Germany there are only two plants carrying out raw wool scouring.

Chemical	[g Telquel/kg textile substrate]	Explanations
Soda	?	
Surfactant	?	Non-ionic types
Water consumption [l/kg textile substrate]	ca. 4	In case of optimised continuous process

Table 5.1: Standard recipe for the raw wool scouring

5.2 Carbonising (removal of vegetable impurities)

Chemical	[g Telquel/kg textile substrate]	Explanations
H_2SO_4 (100%)	35 – 70	
Surfactant	1 - 3	
Water consumption [l/kg textile substrate]	ca. 3	In case of optimised continuous process

Table 5.2: Standard recipe for wool carbonsising

5.3 Washing and felting

Chemical	[g Telquel/kg textile substrate]	Explanations
Soda or ammonia (100%)	0 – 5 ca. 2,5	
Surfactant	3 – 20	
Water consumption [l/kg textile substrate]	?	

Table 5.3: Standard recipe for wool washing and felting

5.4 Bleaching

In case of full bleach qualities, the standard process for wool bleaching is the application of a combination of oxidation (hydrogen peroxide) with subsequent reductive bleaching (3 g/l reducing agent, e.g. stabilised sodium dithionite and 0,5 g/l surfactant). In case of wool pre-bleaching either hydrogen peroxide or reducing agents can be used. Regarding the standard recipe for wool bleaching it has to be stressed that the dosage of chemicals can vary considerably depending on time and temperature of the process.

Chemical	[g Telquel/kg textile substrate]	Explanations
H_2O_2 (100%)	50 - 75	Because of high dosage the process is often carried out on standing bath
Complexing agents (stabiliser)	5 - 30	
Ammonia (100%)	0 - 20	pH 8 – 9 with buffer system (usually on base of sodium tripolyphosphate)
Water consumption [l/kg textile substrate]	?	

Table 5.4: Standard recipe for bleaching of wool

In some cases acidic hydrogen peroxide bleaching is applied. Then an activator instead of a stabiliser is used. After bleaching rinsing takes place and reductive bleaching (40 – 80 g reducing agents/kg wool) at 60 °C for 30 minutes is carried out. Finally optical brighteners can be added.

In general, especially for bleaching of yarn and knit fabric with hydrogen peroxide stabilisers on bases of protein derivates and of modified phosphoric esters (lecithine types) are used. These stabilisers also act as dispersing agents. Also fatty acid amides are in use; they do no stabilise the bleaching bath only but also serve as softening agent.

5.5 Hercosett-anti-felt-finishing

Chemical	[g Telquel/kg textile substrate]	Explanations
NaOCl (as active chlorine)	?	
H_2SO_4 (100%)	?	
Surfactant	?	
Soda	?	
Na_2SO_3	?	
Polyamide resin	?	
Softening agent	?	
$NaHCO_3$	?	
Water consumption [l/kg textile substrate]	?	

Table 5.5: Standard recipe for Hercosett-anti-felt-finishinf of wool

5.6 Pre-treatment for printing

5.6.1 Pre-treatment with chlorine-containing substances

Chemical	[g Telquel/kg textile substrate]	Explanations
Dichloroisocyanurate (1,2 – 3,8% active chlorine)	20 - 60	
Formic/acetic/sulfuric acid	10 - 30	
Sodium disulfites or dithionite	20 – 40	
Surfactant	2 – 5	
Polymers (100%)	10 – 30	Mainly cationic products
Water consumption [l/kg textile substrate]	?	

Table 5.6: Standard recipe for the pre-treatment for printing of wool with chlorine-containing substances

5.6.2 Pre-treatment without chlorine-containing substances

Chemical	[g Telquel/kg textile substrate]	Explanations
Peroxomonosulfates	20 - 60	
Sodium sulfite or dithionite	20 - 60	
Surfactant	2 - 5	
Polymers (100%)	10 - 30	Mainly cationic but padding with anionic polymers is also common. Cationic and anionic polymers are also applied without pre-oxidation
Water consumption [l/kg textile substrate]	?	

Table 5.7: Standard recipe for the pre-treatment for printing of wool without chlorine-containing Substances

6 REFERENCES

[UBA, 1994]
Schönberger, H.; Kaps, U.
Reduktion der Abwasserbelastung in der Textilindustrie
UBA-Texte 3/94 (1994)

GLOSSARY

General

AOX	Adsorbable organic halogen compounds
AS	Activated sludge
BAT	Best Available Technique
BOD_5	Biochemical oxygen demand in five days
COD	Chemical oxygen demand
ETP	Effluent treatment plant
HM	Heavy metal
L	Conductivity
LR	Liquor ratio
MLSS	Mixed liquor suspended solids
MWTP	Municipal wastewater treatment plant
NF	Nanofiltration
pre-DN/N	Pre-denitrification/nitrification
RO	Reverse osmosis
Q_{WW}	Wastewater flow
SS	Suspended solids
SAC	Spectral absorption coefficient
T	Temperature
TFI	Textile finishing industry
TOC/DOC	Total and dissolved organic carbon
UF	Ultrafiltration
VOC	Volatile organic carbon

Units

°C	degree Celcius
EURO	European currency
g	gram
J	Joule
h	hour
kWh	kiloWatthour
l	liter
m	metre
m^2	square metre
m^3	cubic metre (water)
Nm^3	Standardized m^3 (273K, 1013 mbar)
OU	Odour Unit
ppm	parts per million
s	second
t	ton ($1 \cdot 10^6$ gram)
vol%	Percentage of the volume
W	Watt
y	year
K	Kelvin
a	annum (year)

Prefixes

n	nano	$1 \cdot 10^{-9}$
µ	micro	$1 \cdot 10^{-6}$
m	milli	$1 \cdot 10^{-3}$
c	centi	$1 \cdot 10^{-2}$
k	kilo	$1 \cdot 10^{3}$
M	Mega	$1 \cdot 10^{6}$
G	Giga	$1 \cdot 10^{9}$
P	Pèta	$1 \cdot 10^{12}$
T	Tera	$1 \cdot 10^{15}$

Conversions

2.05 mg NO_2/Nm^3 = 1 ppmv NO_2
2.85 mg SO_2/Nm^3 = 1 ppmv SO_2
1 Watt = 1 J/s

Elements

Al	Aluminium
As	Arsenic
Ca	Calcium
Cd	Cadmium
Cl	Chlorine
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
F	Fluorine
Hg	Mercury
K	Potassium
Mg	Magnesium
Mn	Manganese
Na	Sodium
Ni	Nickel
P	Phosphorus
Pb	Lead
Sb	Antimony
Se	Selenium
Zn	Zinc

Compounds

APEO	Alkylphenolethoxylates
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate
C_xH_y	Hydrocarbons
HCO_3^-	Hydrogen carbonate
HCl	Hydrochloric acid
HF	Hydrofluoric acid
H_2O	Water
N_2	Molecular nitrogen
NH_3/NH_4^+	Ammonia
org. N	organic nitrogen ($N_{kj} – NH_4^+$)
N_{kj}	Kjeldahl-Nitrogen
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_x	Nitrogen oxides
O_2	Molecular oxygen
pH	$-\log [H_3O^+]$
SO_2	Sulphur dioxide
SO_3^{2-}	Sulphite
SO_4^{2-}	Sulphate

Fibres

CA	Celluloseacetate
CO	Cotton
CV	Viscose
PAC	Polyacrylonitrile
PA	Polyamide
PES	Polyester
SI	Silk
WO	Wool

Indications of emissions:

1. Emissions to air

- Mass of emitted substances related to the volume of waste gas under standard conditions (273K, 1013 mbar), after deduction of water vapour content, expressed in the units [g/Nm^3], [mg/Nm^3], [µg/ Nm^3] or [ng/Nm^3];
- Mass of emitted substances related to time, expressed in the units [kg/h], [g/h] or [mg/h];
- Ratio of mass of emitted substances to the mass of products generated or processed (consumption or emission factors), expressed in the units [g/kg], [mg/kg];

2. Emissions to water

- Mass of emitted substances related to the volume of wastewater, expressed in the units [g/m^3], [g/l], [mg/l] or [µg/l].