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Cleaner Technology Transfer to the Polish Textile Industry

Idea catalogue and selected options

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Content

Preface

This report presents the results of a survey of Polish textile industry and the identification of options for pollution prevention and resource savings. The survey has been conducted as a Polish-Danish co-operation programme for transfer of technology to the Polish textile industry.

Partners of the programme were:

- Institute for Product Development, Denmark (Programme leader)
- Textile Research Institute, Lodz, Poland
- DTI Clothing and Textile, Denmark
- VKI, Institute for the Water Environment, Denmark
- Vald. Henriksen Ltd, Denmark

Sponsor of the programme was:

- The Danish Environmental Protection Agency

via the Danish Environmental Support Fund for Eastern Europe

Selected Polish industrial participants in the programme were:

ZTK Teofilów, BZPB Bielbaw, ZPD Cotex, ZPB Zwoltex, WFN Ariadna, ZPD Jarlan, FD Dywilan, ZWO Vera, ZPL Krosnolen, ZPP Sandra, ZPD Hanka, NFN Odra, Texo SA, ZPJ Nowar, ZPB Eskimo, Novita SA, Rena-Kord SA, ZPL Zyrardów, ZP-U Chemeks, and PC Polmerino.

The co-operation with the Polish textile companies has been very positive. The companies have been open and constructive and have provided all necessary information. We thank the companies for their participation and hope that the outcome of the programme, as reported here, will prove beneficial to both the companies and the environment.

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Summary

Areas of pollution prevention and resource savings in Polish textile industry are identified from direct contact to 20 textile dye-houses including a detailed survey of 9 selected dye-houses.

Selection of companies

Companies have been selected to get the various processes in the industry well represented. This selection has been done by the Textile Research Institute in Lodz on the basis of its very thorough and detailed insight in the textile industry. The strategy has then been to go into direct contact with the companies with detailed inspection of processes and recipes, and to identify possible areas of improvement in collaboration with the companies.

Identification of priority areas

The priority areas have been confirmed by the textile industry itself at a total of three seminars with participation of all together 30 Polish and Danish textile companies, and Polish and Danish research institutions.

Focus

The main focus of the programme has been possibilities for cleaner technologies being environmentally and economically sound at the same time. With the present financial situation in the Polish textile industry, this is the most realistic approach to pollution prevention. In general, treatment alone has no realistic economical background for the time being. Only improvements, that imply simultaneous savings in costs, are judged to be realistic. However, possibilities of cost-effective improvements are quite large, and a goal of an overall 50% reduction in water-, energy- and chemical consumption seems achievable with the right cleaner technology strategy.

The identified priority areas are grouped into 4 categories:

Systematic approach

1) *Optimization:* meaning improvements of routines and procedures within the existing equipment
2) *Modernization:* meaning rebuilding old equipment or exchanging it with new
3) *Chemical substitution and savings:* meaning altering recipes towards less consumption of chemicals and more environmentally friendly chemicals
4) *Re-use:* meaning possibilities for treating and re-using selected waste-water streams and the energy and chemical content in these.

Idea catalogue

A total of 41 cleaner technology options are reported in the Idea catalogue Part 2, and some are described in more detail in Part 3.

Implementation projects

Quite good possibilities are seen for every one of the above categories, and possible case examples are found within the 30 companies. Three implementation projects have been initiated comprising some of the most beneficial options. One of these have been successfully finalized. The implementation projects are described in Part 4.

Part 1.
Cleaner technology transfer to the Polish textile industry

1.1 Programme description

Programme period

The programme was initiated in 1992 and finalized in 1996. Priority areas have been identified and their relevance and potential benefits have subsequently been confirmed by the textile industry itself at technology transfer seminars. The strategy from this point has been to go into specific technology transfer, including implementation projects, for selected areas at selected case companies.

Programme phases

The phases of the programme have thus been as follows:

1. Survey of Polish experiences and dyeing procedures. Identification of problem areas
2. Survey of Danish experiences and dyeing procedures. Identification of areas of possible technology transfer
3. Halfway seminars in Poland and Denmark. Selection of priority problem areas and pilot case companies for technology transfer and implementation projects.
4. Elaboration of an idea catalogue
5. Final technology transfer seminar in Poland
6. Identification of full-scale demonstration projects. Identification of further implementation areas and companies for full-scale demonstration.

The programme has been continued by an implementation programme, including as a start, three implementation projects:

Implementation programme

- *Extended Counter Current Operation in Continuous Processes*
- *Implementation of Cleaner Technology in Batch Dyeing of Cotton*
- *Savings and Substitutions of Hazardous Chemicals*

1.2 Survey of the Polish textile industry

The survey of experiences and dyeing procedures in the Polish textile industry comprised *20* companies, including detailed audits at *9* companies for identification of cleaner technology options.

This survey has given a good background for the identification and selection of problem areas. Our criteria for selection of relevant problem areas have been that these should be:

Criteria for
for selecting options

- Environmentally important
- Of broad interest to the textile dyeing industry in Poland
- Economically possible to a textile company, and as far as possible even profitable

Systematic procedure

In analysing the possibilities of pollution prevention and resource savings we have followed a well recognized and well tested procedure for identification of cleaner technology options. This procedure is divided into 5 steps:

I. *Optimization.*
Analyse possible savings by alterations of procedures within the existing equipment.

II. *Modernization.*
Analyse the feasibility of changing old equipment either renewing or rebuilding.

III. *Chemical substitutions and savings.*
Analyse possibilities of altering recipes and saving or substituting chemicals with more environmentally friendly ones.

IV. *Re-use.*
Analyse the possibility for water treatment for re-use of water, energy, and chemicals to save resources and reduce discharges.

V. *Waste-water treatment for discharge.*
As the final option analyse the possibility to treat the remaining waste-water problem before final discharge of the waste-water.

Priorities

These steps are followed almost as a priority list. This is important in order not to use great efforts to treat problems that could be avoided much easier in an earlier step.

Expensive lesson

This experience has been quite expensive to gain for Danish companies and Danish environmental administration. History has unfortunately shown, that environmental problems have been tackled in the opposite direction. First, municipal treatment plants have been built or existing treatment plants have been extended in order for treated waste-water to meet new restricted demands. Expenses for this have been large, and in order to get municipal treatment plants paid for, municipalities have increased costs for water discharge, and taxes have been put on water and energy as well. This has given companies much incentive to implement cleaner technologies, and thereby – one step too late – reduce the need for end of pipe treatment.

Cleaner technology before treatment

This is an overall experience, that we have been transferring from Danish environmental administration to Polish environmental administration: Do not build many treatment plants to treat the amount of water and chemicals discharged from Polish textile industries today. Save water and chemicals instead; this will usually be even profitable. In this way reduce the need for treatment, and then eventually build treatment plants for the remaining waste-water problem.

Control and fines

Apart from the identified areas for cleaner technology implementation, the programme has also identified another very important area for pollution prevention in Polish textile industry, namely the control and fines system for waste-water discharge. Many companies pay large amounts of money for exceeding standards, and many companies claim that water reduction will have a negative impact on the fines, because fines are calculated on the basis of concentrations, and concentrations in the waste-water will increase as the water flow decreases. Standards are not equally set for the various companies, and in some cases standards are set for environmentally less problematic

Mistaken focus on concentrations

parameters such as total dissolved matter, including salts as carbonates and sulfates, that have only little negative impact on the actual receiving water bodies. In most cases the control is based on very few samples making the calculation of fines quite arbitrary.

A small project that analyses the control & fines system and the environmental consequences of this and suggests alternatives would be a good priority. Some experiences might be drawn from Danish control systems that have been developed over a long period of time.

1.3 Conclusions

Focus on cost-effective options

The main focus of the programme has been possibilities for cleaner technologies being environmentally and economically sound at the same time. With the present financial situation in Polish textile industry, this is the only realistic approach to pollution prevention apart from closing down productions. Treatment alone has in general no realistic economical background.

However, possibilities of cost-effective improvements are quite large, and a goal of an overall 50% reduction in water-, energy- and chemical consumption seems achievable with the right cleaner technology strategy.

Enthusiastic companies

The interest in new and better technologies from the Polish textile industry is very large, and the majority of companies are very enthusiastic. There is of course a tendency as also seen in Denmark, that new solutions are to be seen in practice before they are fully believed to work. Because of the financial situation the pay-back time for new technology should be very short, and the risk of production failures etc. when implementing new technology should be close to zero.

Risk covered by project

An important conclusion for the implementation programme is that any risks of economical losses caused by implementation of new technology (e.g. the loss of a production volume caused by potential misdyeing) should be covered by the project funding. It is in most cases no problem to give such a guaranty, as potential losses will be very small compared to the full project budget.

A total of 41 options for implementing cleaner technology have been identified, and a large potential for both environmental and economic improvements exists. Three implementation projects have been started of which one is finalized successfully with very large improvements and savings.

Part 2.
Idea Catalogue

2.1 Introduction

This Idea catalogue presents options for cleaner technology implementations in the textile dyeing and printing industry. The catalogue is elaborated on the basis of surveys in the Danish and the Polish textile industry. A total of 30 dyeing and printing houses have been selected for a detailed investigation of options for cleaner technology implementation, and these companies represent the great variety in the industry very well.

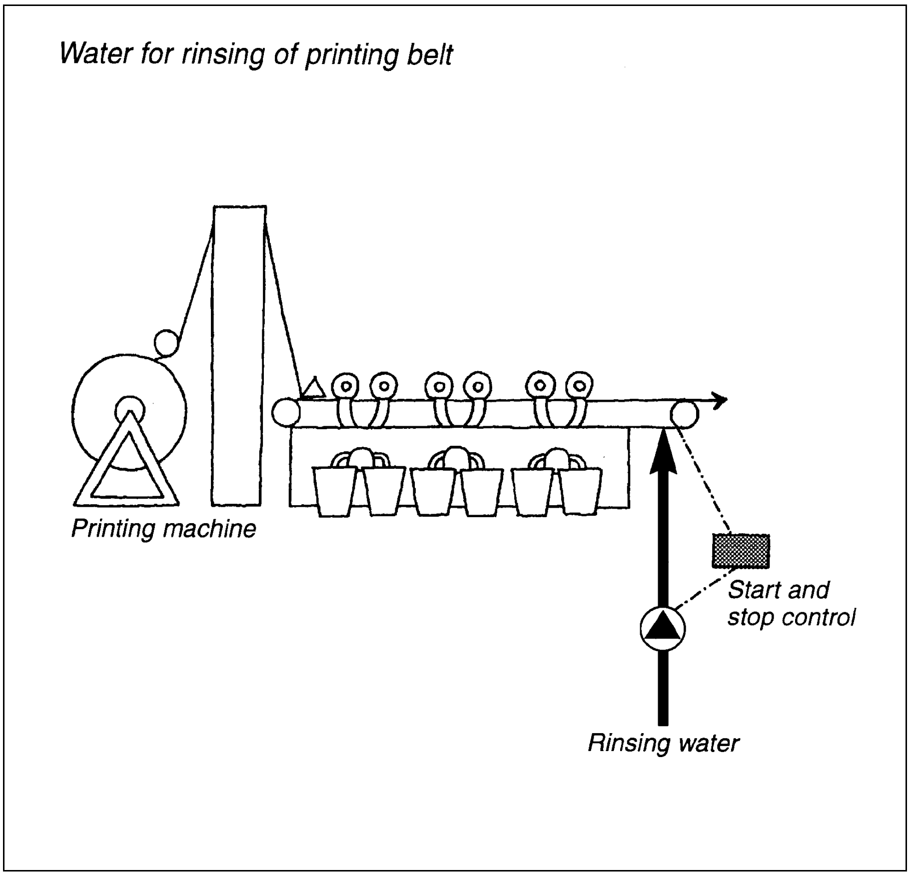
A total of 41 different options have been identified within the four main categories. Optimizations, Modernizations, Chemical savings, and Substitutions and Re-use. For reasons of simplicity, the options are grouped in the three categories

- Savings in water consumption and effluent
- Chemical savings and substitution
- Re-use of water, energy and chemicals

The options are briefly described and the text is supported by a simple drawing illustrating idea. This outline is not meant to go technically in detail, but aims to give basis for thoughts for the textile technician, who can judge the relevance of the idea to his company in each individual case.

Idea catalogue content

Topic 1.
Minimization in consumption of water and/or chemicals in continuous processes in general



Case illustration:
Water for rinsing of printing belt

Concept

In many continuous processes, water and chemicals are dosed independent of the running of fabric. In many cases this means that water or chemicals dosage will continue when the fabric is stopped for whatever reason. This project should assess whether a start/stop of water or chemicals dosage can be automatically connected to the start/stop of the continuous machine and how such an implementation influences the running of the machine and the quality of the fabric. A Danish survey has identified examples of continuous processes in which the mentioned implementation seems possible: water cleaning of the printing belt in printing machines, water cooling of the rubber belt in shrinking machines, water dosage for wetting purposes before drying, water dosage for flushing purposes, etc.

Improvement potentials

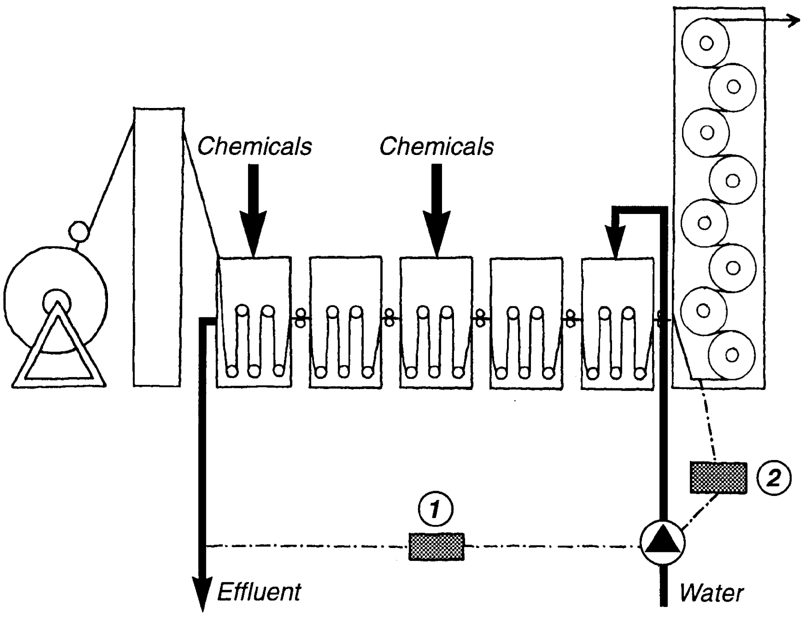
Reduction of consumption of water and chemicals.

Relevance

A large number of continuous processes.

Topic 2.
Parameter controlled flow in continuous processes

Water and chemical consumption on washing and bleaching line



Case illustration:
Water and chemical consumption on washing and bleaching line

Concept

Dosing of water and chemicals to continuous processes is most often kept at fixed level governed by the recipe. These levels are typically determined by empirical findings from worst case operating situations implying overdosage most of the time.

Optimal dosing of water and chemicals to individual sections in a continuous machine could ideally be governed by the instantaneous state of effluent or product quality. The dosing should thus be controlled on the basis of the measurement of the relevant parameter for the specific process e.g. pH, turbidity, absorbance, conductivity, redox potential etc. On-line measurements and continuous control of these parameters exist in related fields of applications, and the possibility of implementation should be judged in each specific case.

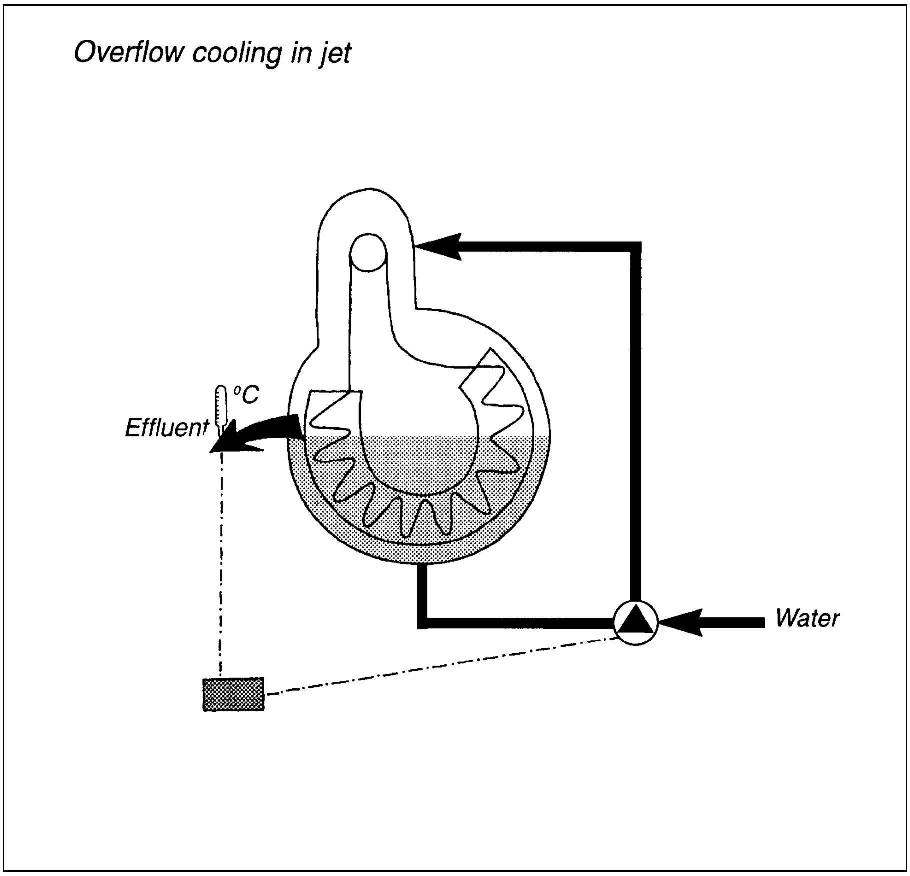
Improvement potentials

Reduction of consumption of water and chemicals.

Relevance

All companies with continuous machines.

Topic 3.
Optimization of cooling by overflow



Case illustration:
Overflow cooling at jet dyeing machine for knitwear

Concept

Cooling of hot baths in batch machines is often conducted by continuous addition and discharge of (overflow) of cold water. The extent of water addition is normally manually or timer controlled, leading to an excessive consumption of water. The project should assess whether it is possible to minimize cooling water consumption by an automated shut-down of water addition when a predefined temperature is reached. The project should have 2nd priority to topic 6 and 16: Stepwise cooling.

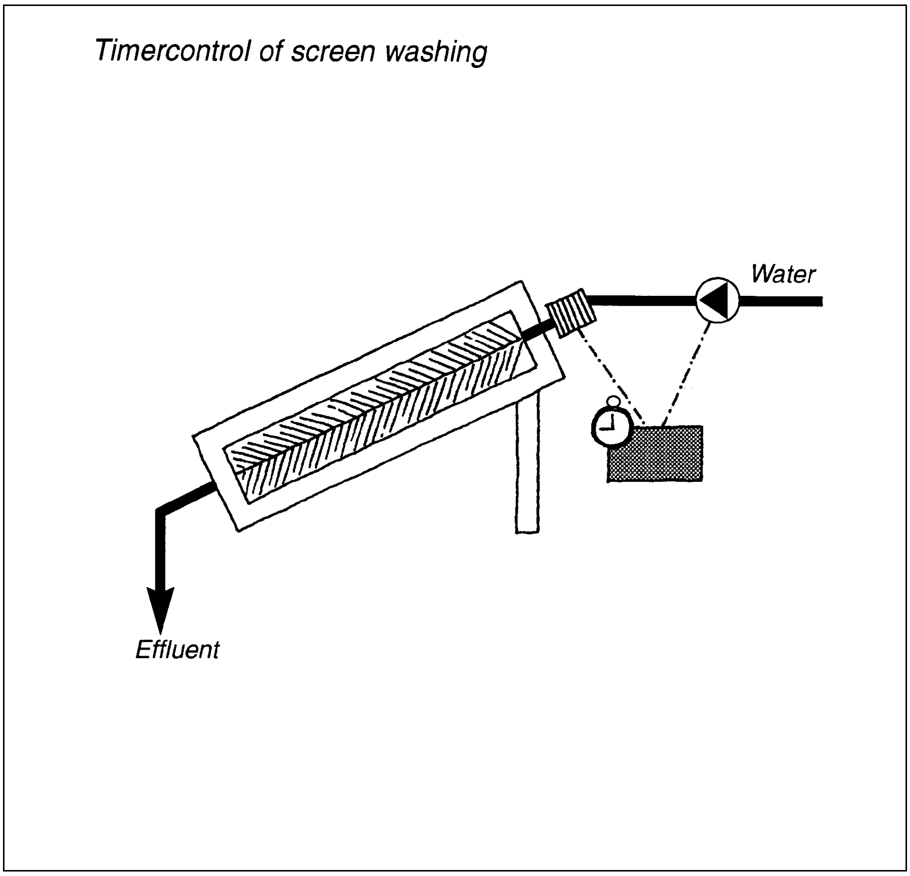
Improvement potentials

Water savings.

Relevance

Companies who carry out overflow cooling on batch machines.

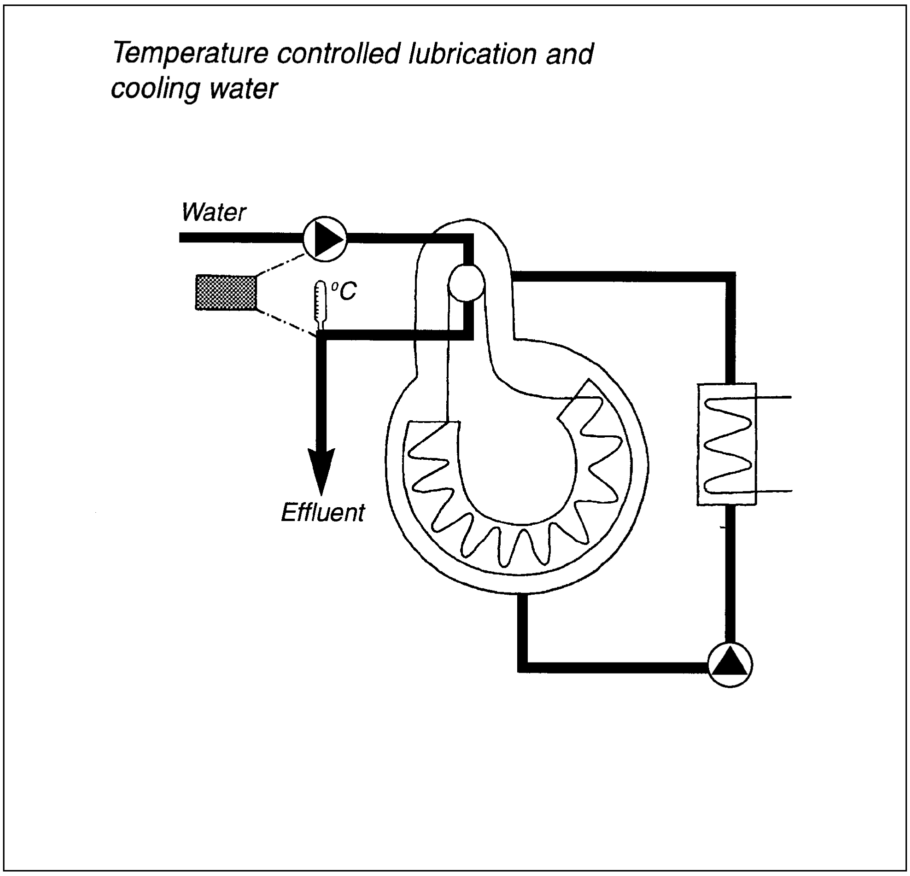
Topic 4.
Timer control of cleaning procedures for machinery and equipment



Case illustration:
Timer control of screen washing

Concept	Duration of automated cleaning procedures for machinery and equipment is often manually controlled by the operator. By implementing automatic timer control, large savings in water consumption and effluent could be achieved.
Improvement potentials	Savings in water consumption and effluent volume.
Relevance	Almost all companies.

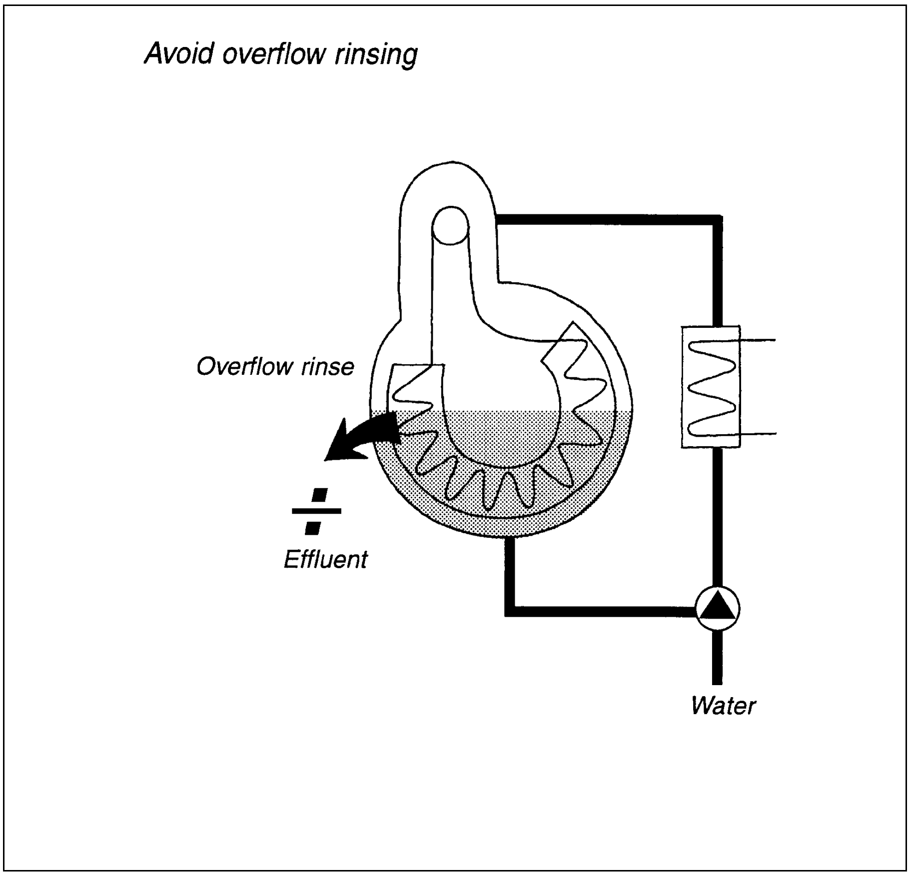
Topic 5.
Temperature control of cooling water supply



Case illustration:
Temperature controlled lubication and cooling water addition for bearings

Concept	Cooling water supply for auxiliary machinery and equipment is often exceeding the sufficient amount. This could be the case for compressors, vacuum pumps, hydraulic stations, bearings etc. By control of cooling water supply as a function of effluent temperature, large water savings could be achieved. This measure should be seen in relation to re-use of the water.
Improvement potentials	Water savings.
Relevance	Most companies.

Topic 6.
Optimization of rinsing water consumption in batch machinery

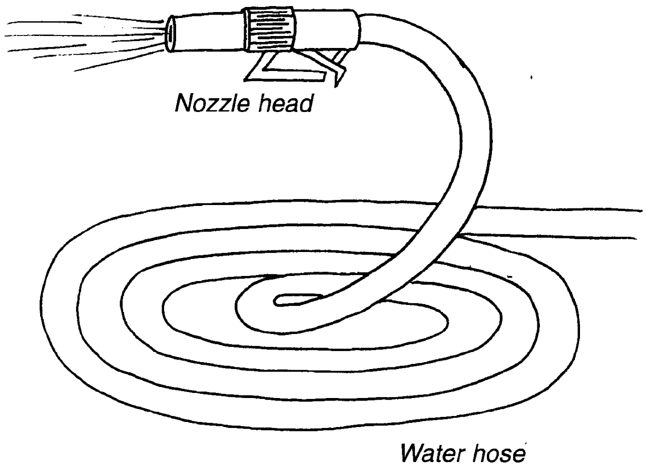


Case illustration:
Avoid overflow rinsing in jets

Concept	The main part of water consumption in textile dyeing processes is water for rinsing purposes. Different types of rinsing procedures for batch dyeing processes exist. These procedures should be investigated as to whether change in rinsing procedures could effect savings in water and effluent volume. Especially rinsing by overflow is known to be water consuming, and this project aims at changing from overflow rinsing to a stepwise rinsing procedure. Parameters included in the experimental plan should be time consumption and fabric quality tests.
Improvement potentials	Savings in water consumption and effluent volume of more than 50% of rinsing water.
Relevance	All dye-houses with batch machines.

Topic 7.
Minimization of water for flushing purposes

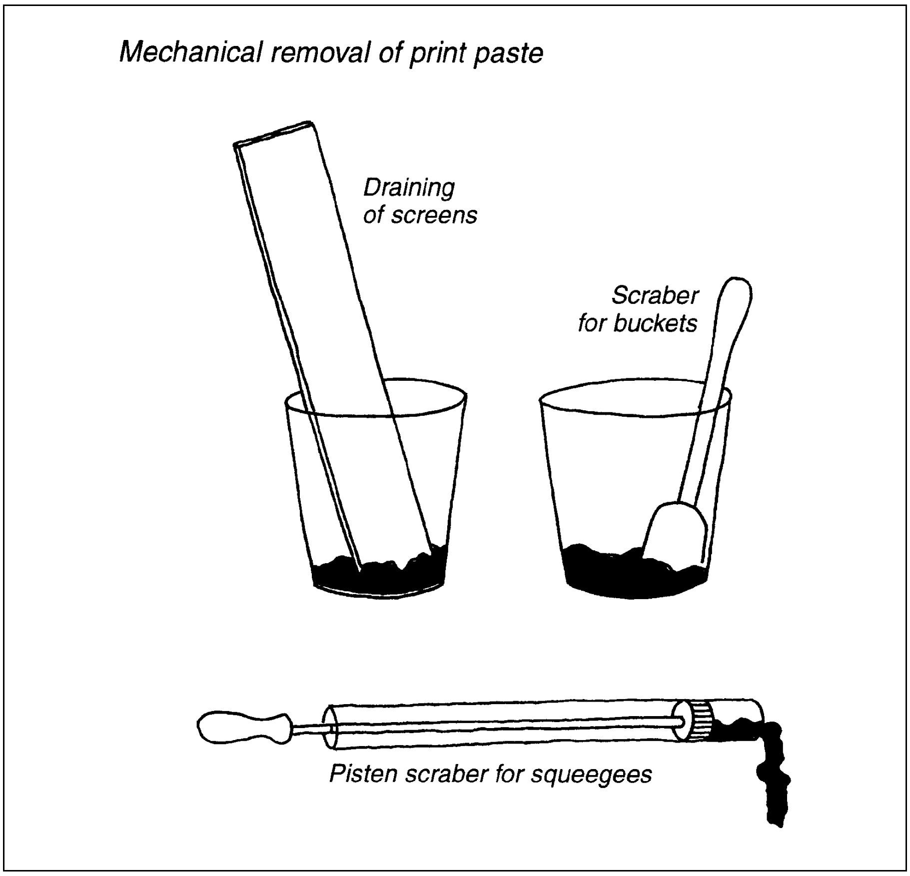
Nozzle head with air intake on water hoses



Case illustration:
Nozzle head with air intake at the end of the water hose to reduce water consumption for flushing

Concept	Quite large amounts of water for flushing and cleaning purposes are lost, because the shut off valve for the hose is situated at a long distance from the area of application. This loss could be avoided by a manually actuated nozzle head at the end of the hose, and further minimizations could be obtained by mounting of a nozzle type with a water saving device. It is also anticipated that large amounts of water could be saved in continuous flushing and cleaning applications. It is often seen that e.g. the arrangement, type and number of spraying nozzles lead to an excessive consumption of water, and it should be investigated whether nozzles function property.
Improvement potentials	Water savings.
Relevance	All companies.

Topic 8.
Mechanical removal of dye paste from printing equipment



Case illustration:
Mechanical removal of print paste from printing equipment

Concept

Large amounts of water for cleaning of e.g. squeegees, screens and buckets are used within the textile printing companies. An improved dye removal before flushing of this equipment would lead to a smaller need for water for flushing. In Denmark, physical devices for removal of dye from buckets have been seen and similar devices could be developed and applied for squeegees and screens, thus leading to minimizations in water use.

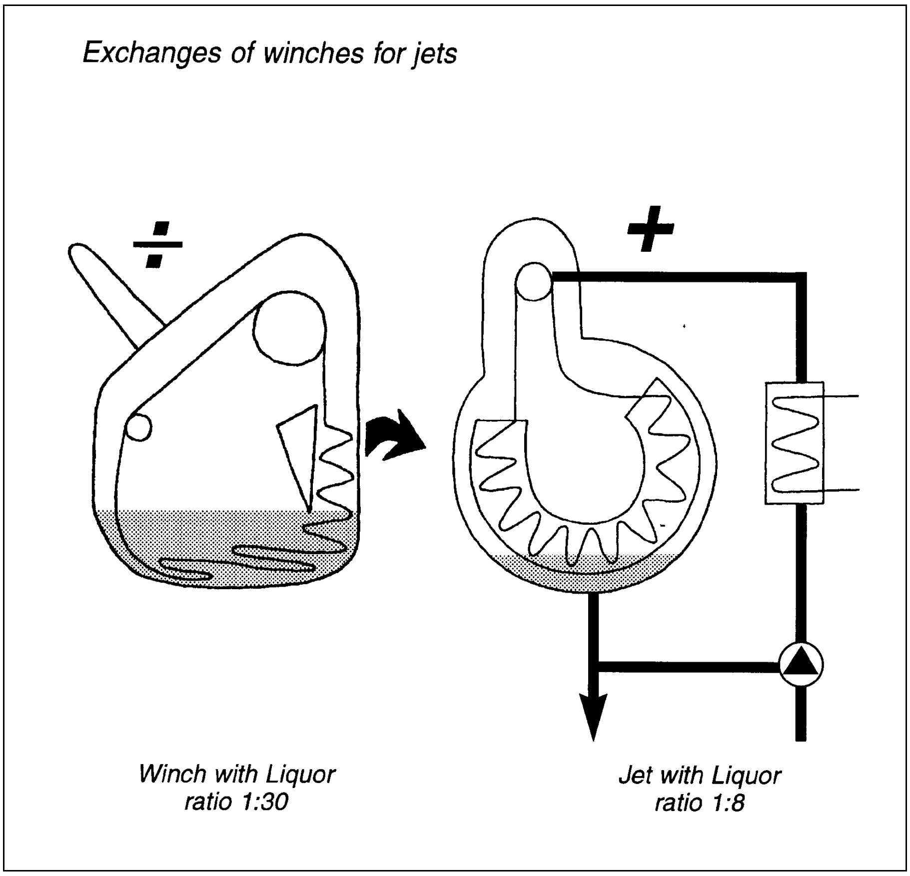
Improvement potentials

Water savings and less water pollution.

Relevance

All companies.

Topic 9.
Exchange of batch dyeing machinery



Case illustration:
Exchange of winches for jets

Concept

Exchange of older equipment (e.g. batch machines with a high liquor ratio) within the industry would reduce all environmental impacts from production. Obtained savings in water, energy and chemicals often imply a short pay-back time.

Improvement potentials

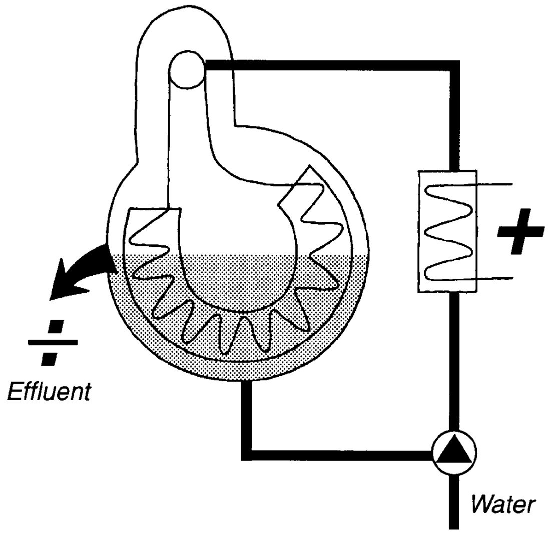
Savings in water, energy and chemicals of about 50%.

Relevance

All companies with old batch machines.

Topic 10.
Reconstruction from cooling/ heating to indirect cooling/ heating

Indirect cooling and heating by heat exchanger



Case illustration:
Indirect cooling and heating by heat exchanger on a jet machine

Concept

Cooling of dye and rinse baths is often practised by an overflow type of cooling, discharging the overflow to the sewer. Heating is in some machines done by direct steam injection. By an indirect type of cooling and/or heating process (e.g. heat exchanger) the water itself and the calorific value contained here in can be re-used. The project should examine whether it is technically possible to reconstruct batch machines to indirect cooling.

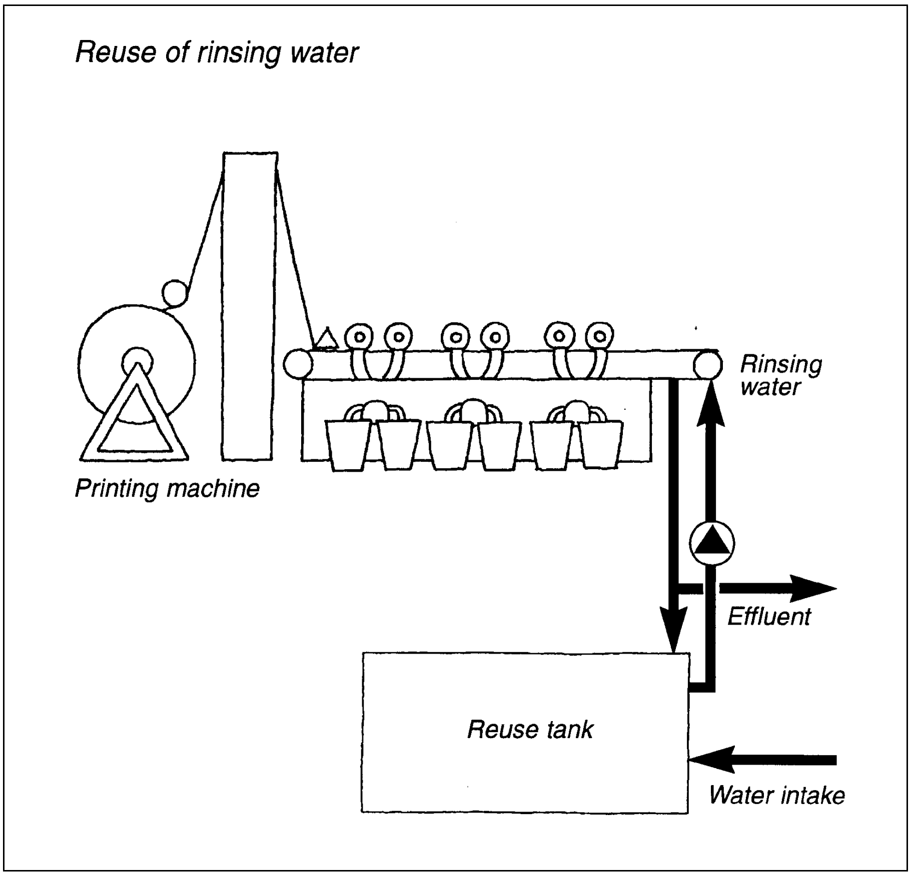
Improvement potentials

Water and energy savings.

Relevance

Companies with direct cooling in batch machines.

Topic 11.
Introduction of in situ re-circulation systems



Case illustration:
Re-use of rinsing water for the pressure belt in printing machines. The rinsing water is filtrated through a 1 mm steel filter cloth

Concept

Most processes and machines within the textile industry are designed without water re-use, and it should be assessed as to whether it is technically possible to modify individual machines for internal re-circulation. One example observed at a Danish printing house is re-circulation of rinsing water for the pressure belt in printing machines. The re-use tank with a coarse filter cloth is placed in the floor beside the printing machine.

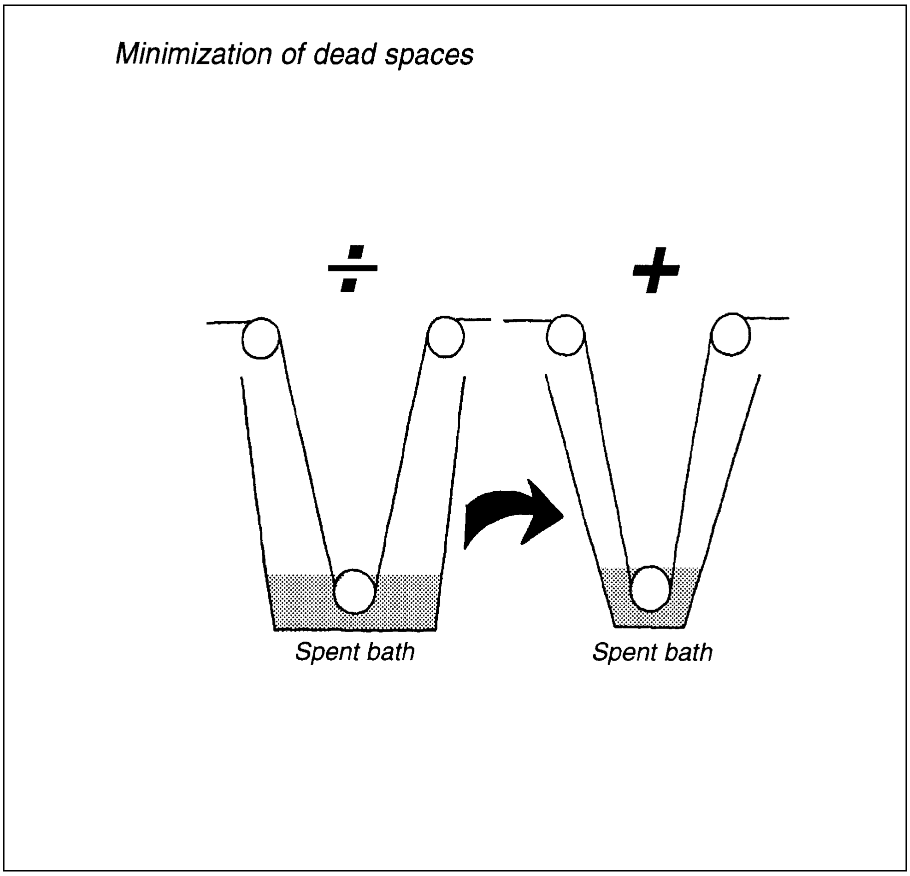
Improvement potentials

Water savings of about 75%.

Relevance

Most companies.

Topic 12.
Minimization of dead spaces



Case illustration:
Minimization volume in foulard vessels

Concept

When recipes are changed and after termination of processes, waste of concentrated dyes and chemicals are often left over, typically in pipes, hoses and machinery. These waste volumes can be minimized by decreasing the volume of equipment occupied by dye or chemicals, e.g. by reducing the internal diameter of pipes and hoses, reducing the active volume of dye in pad mangles etc. In existing equipment a liquor displacer, can be used.

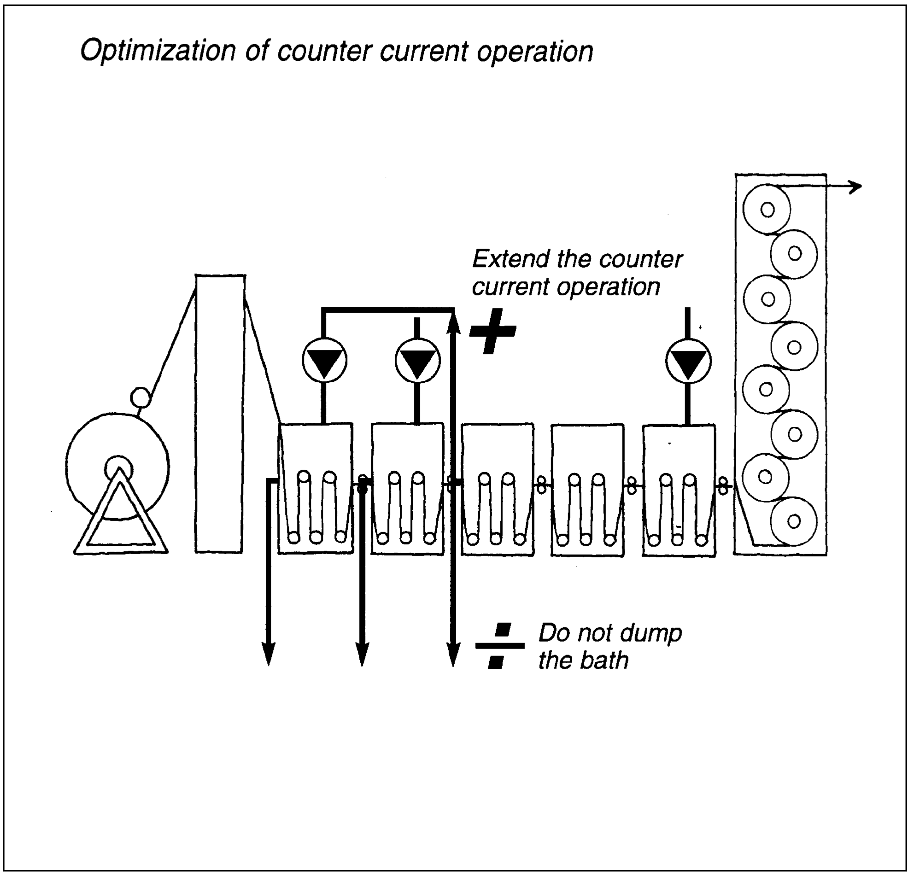
Improvement potentials

Reduction of environmental impact and chemical savings.

Relevance

Most companies.

Topic 13.
Optimization of counter current operation in continuous machinery



Case illustration:
Optimization of counter current operations in continuous machinery

Concept

Continuous machinery is often operated in such a way that fabric is moved in the opposite direction of the water flow. Depending on the specific process, fabric can be treated by a number of processes taking place in separate sections, each section consisting of a number of baths. Numerous continuous machines are operated with inlet to and outlet from the individual bath, thus implying poor utilization of water and chemicals. Observations have indicated that application and optimization of principles of counter current operation could take place in several continuous processes, e.g. dyeing, washing and desizing.

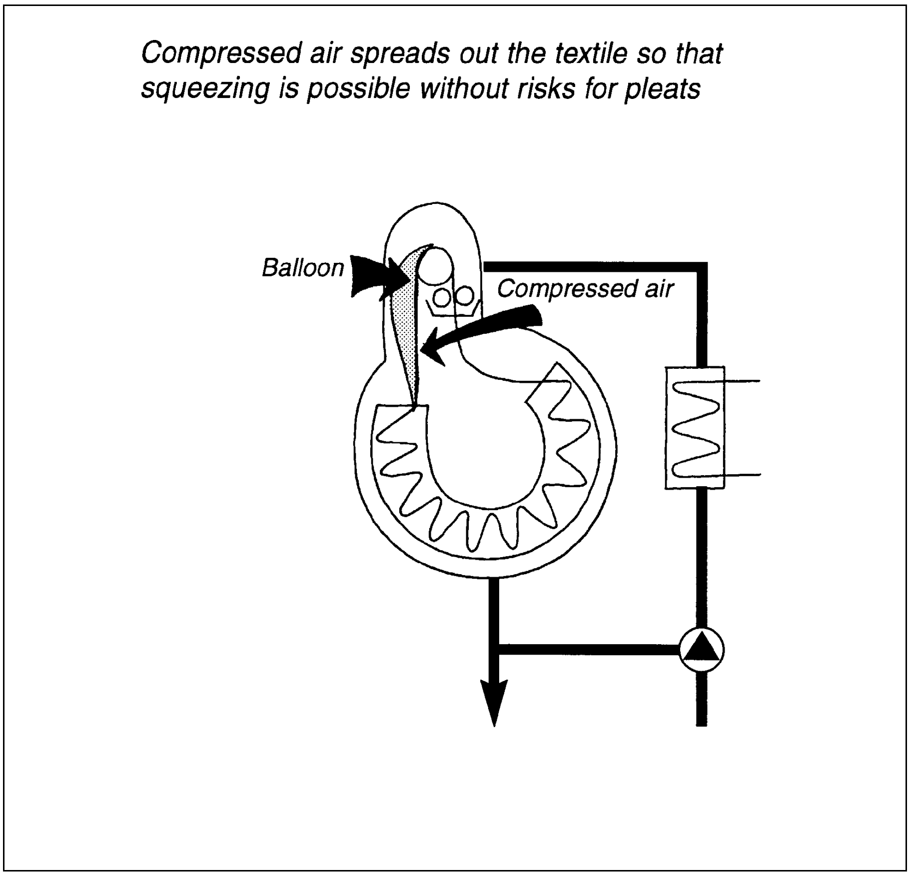
Improvement potentials

Savings of water, energy and chemicals. Up to 75% saving when going from no counter current operation to full counter current operation. Experience with this option is described in more detail in Part 4.

Relevance

All companies with continuous machines.

Topic 14.
Minimization of attachment of water in stepwise rinsing in batch machines



Case illustration:
Compressed air spreads out the textile as a balloon so that squeezing is possible without a risk for pleats. VH/Fong dewatering device®

Concept

Rinsing after washing and dyeing in e.g. batch machine is impeded and delayed due to the water attachment in the fabric. Normally this water cannot be squeezed out due to risk of pleat formation in the textile string. It is thus well known that batch dyeing machines in general, are good dyeing machines, but are poor washing and rinsing machines, due to the lack of a built-in dewatering device in the machine. If the attached amount of water could be minimized, so could the necessary amount of rinsing water. Possibilities for squeezing out or suctioning off of attached water should be assessed for relevant types of machines.

Improvement potentials

Savings in water, energy and production time. Preliminary experience with the VH/Fong dewatering device has proven that more than 90% of the normal water, energy and time consumption for rinsing after re-active dyeing of cotton can be saved.

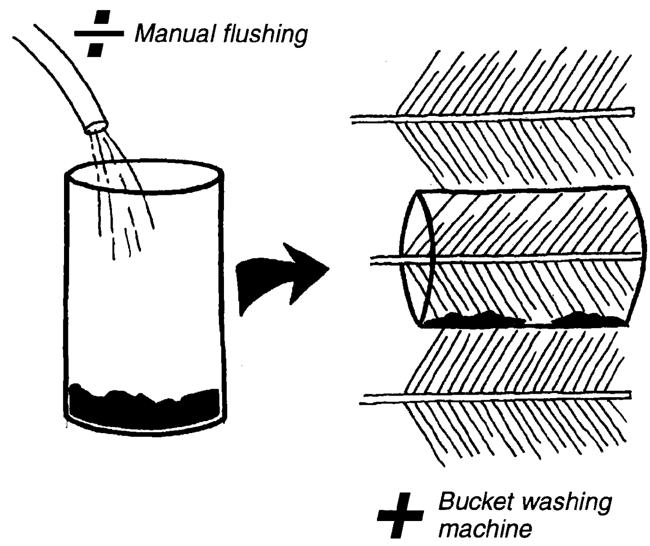
Relevance

All companies who carry out batchwise rinsing.

Topic 15.
Procedure for cleaning of equipment and machinery

Case illustration:
Automated cleaning of buckets

Automated cleaning of buckets



Concept

Large amounts of water are used for manual cleaning of equipment and machinery. Cleaning procedures within the company should be surveyed to determine whether the water consumption could be minimized by revised or perhaps automated cleaning procedures.

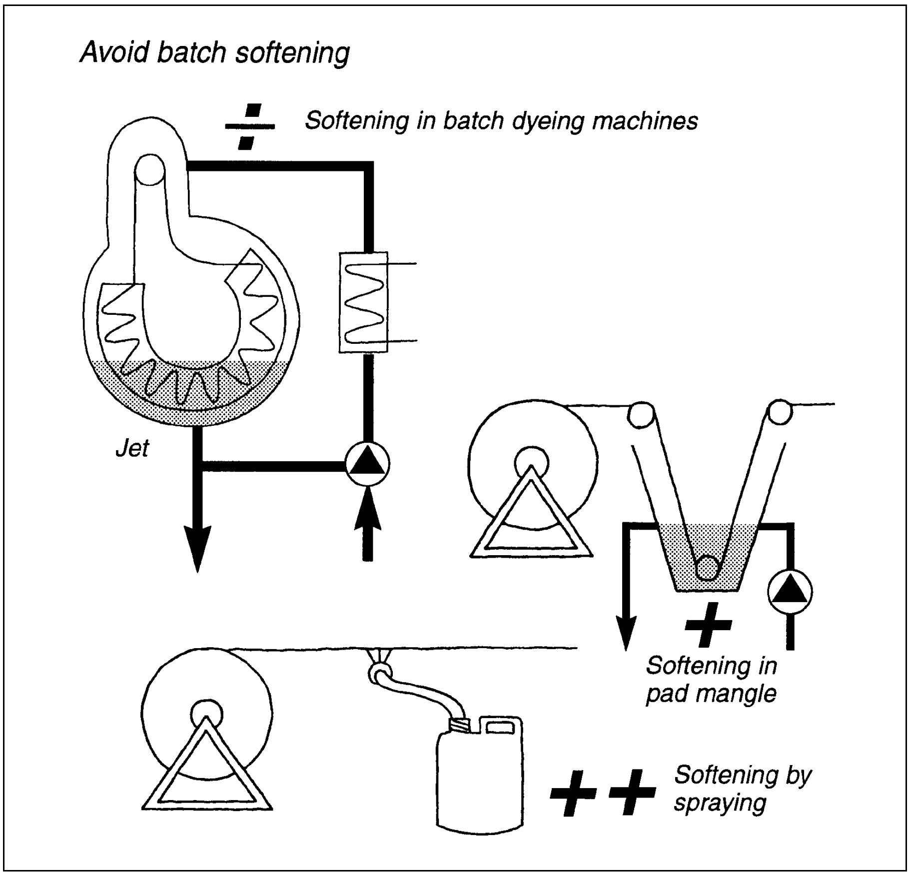
Improvement potentials

Savings in water consumption and effluent volume.

Relevance

All companies.

Topic 16.
Softening in pad mangles or by spraying



Case illustration:
Avoid softening in batch dyeing machines

Concept

The majority softening after batch dyeing is presently done in the batch machinery by exhaustion processes. This is limiting the choice of softening agents to environmental harmful cationic agents and it is giving rise to a 10-20% loss of softening agent together with a loss of the whole volume of warm softening bath. If this process instead is practised in pad mangles or by spraying, other more environmentally friendly softening agents can be used and the chemical loss can be diminished to a few per cent. Furthermore, the warm water volume lost by pad mangle application is much less and the water loss by spraying application is zero. Practical limitations for such a change should be revealed and possible solutions be proposed.

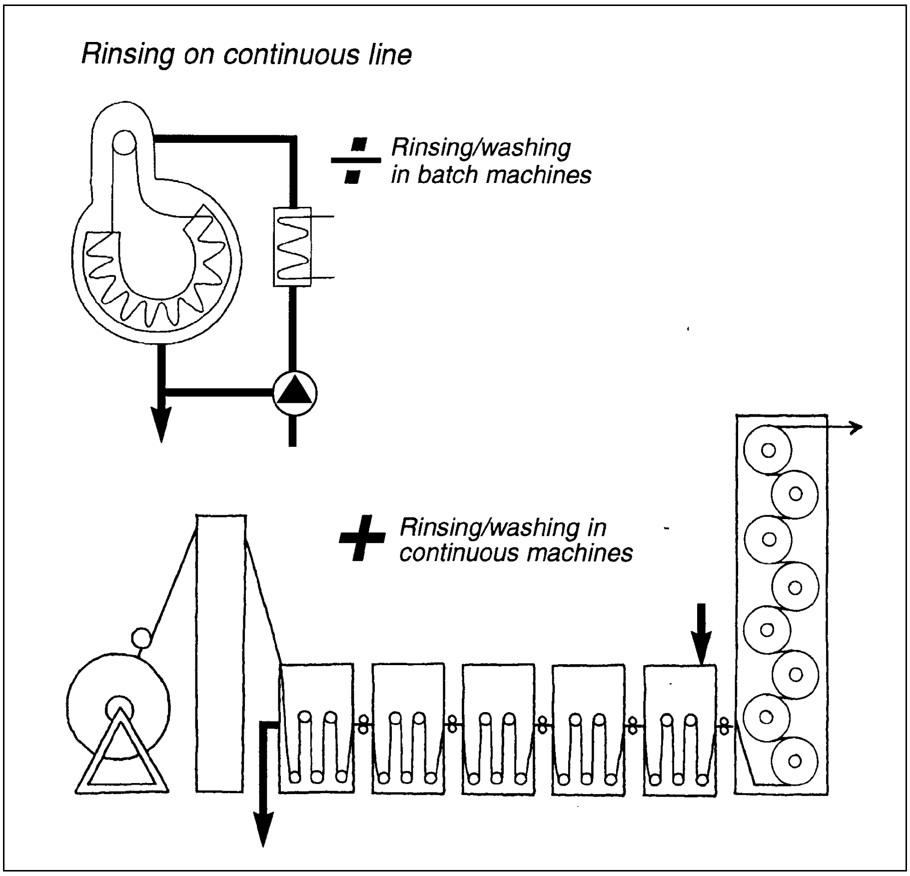
Improvement potentials

Savings in water, energy and chemicals. Introduction of environmentally friendly softening agents.

Relevance

All companies applying softening agents in batch dyeing machines.

Topic 17.
Change from batch to continuous washing



Case illustration:
Change from rinsing in jet machine to rinsing in continuous line

Concept

Rinsing/washing after dyeing in batch machines is normally done in the same machine. In batch dyeing the fabric could be taken out and the rinse subsequently done in continuous machines, implying large savings in resource consumption and effluent. Practical limitations for such a change should be revealed and possible solutions be proposed.

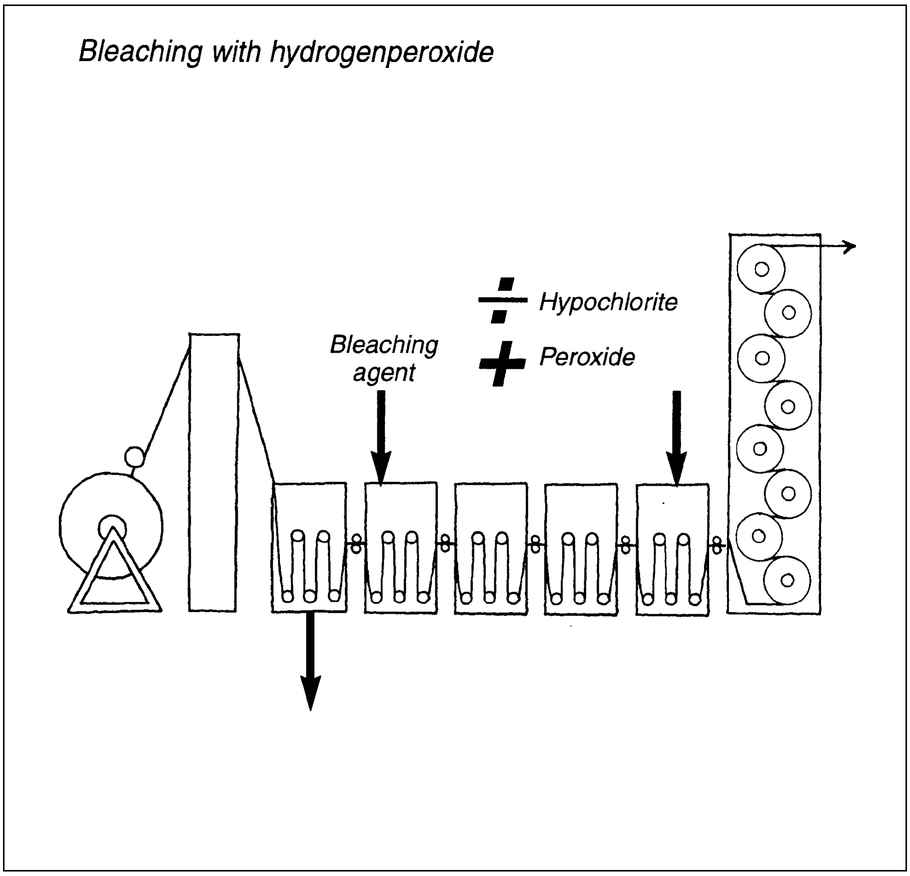
Improvement potentials

Water and energy savings of more than 50% compared to batch rinsing.

Relevance

All companies who carry out batch rinsing.

Topic 18.
Alternatives to bleaching with hypochlorite



Case illustration:
Bleaching with hydrogen peroxide

Concept

In some companies, bleaching with sodium hypochlorite (NaOCl) is still taking place. This agent is environmentally hazardous, partly because of the risk for formation of free chlorine and partly because of formation of chlorinated organic compounds in the waste-water. In many cases, bleaching with hydrogen peroxide could be done but the possibilities and consequences of this substitution should be judged in each case.

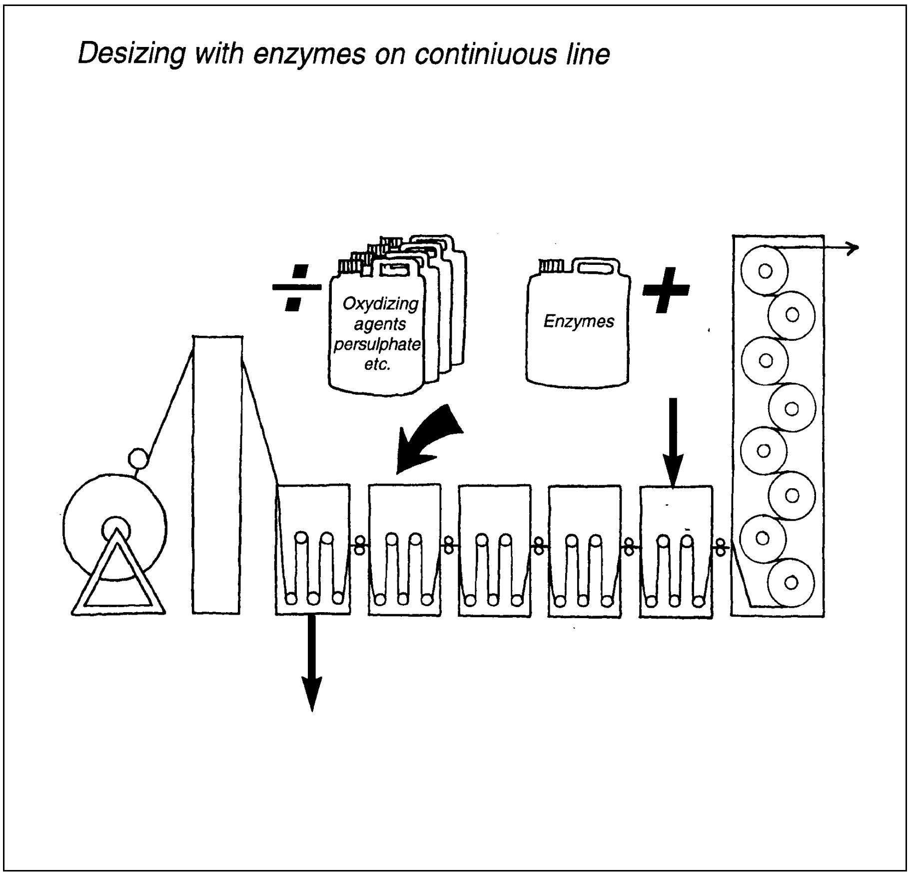
Improvement potentials

Reduction of environmental impacts.

Relevance

All companies doing hypochlorite bleaching.

Topic 19.
Desizing with enzymes



Case illustration:
Desizing with enzymes on continuous line

Concept

In some companies, desizing of woven fabrics with potassium persulfate or other oxidizing agents is taking place; a relatively slow and highly chemical consuming process. In some cases, desizing with enzymes (amylases) could lead to a more environmental friendly process and a very low process time.

Improvement potentials

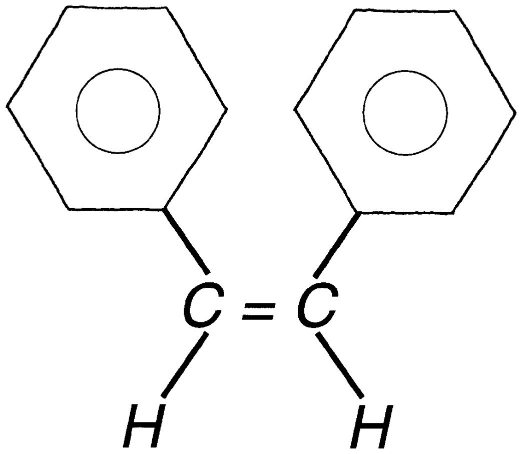
Reduction of environmental impact and process time. Process time can be reduced from 12-24 h using oxidizing agent, to 10-15 min using enzymes.

Relevance

Companies engaged in desizing of woven fabrics.

Topic 20.
Optical whiteners

Stilbene - an optical brightener



Stilbene molecule

÷ *Avoid stilbene derivates*

+ *Choose best alternative*

Case illustration:
Stilbene – an optical brightener

Concept

In many cases, fabrics of cotton or mixtures with cotton are treated with optical whiteners, either for full bleaching purposes or for pre-treatment purposes before printing. Optical whiteners can be characterized as colourless dyes, which often contain environmentally hazardous chemical compounds such as e.g. stilbene derivatives. The reason for use of optical whiteners is often based on a customers demand for a very shining whiteness. Thus, it seems difficult to omit the use of optical whiteners, but still this serious topic should raise a relevant discussion. Alternatively, substitution of the more environmental hazardous chemicals to more environmental friendly ones should be considered.

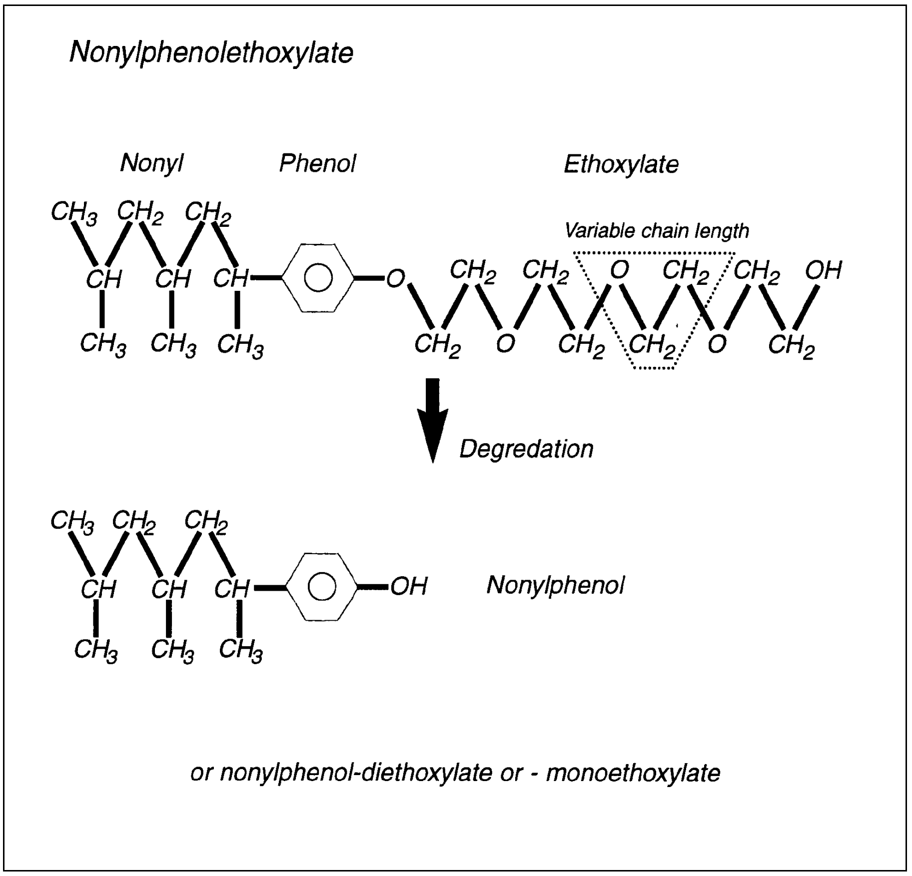
Improvement potentials

Reduction of environmental impacts.

Relevance

Many companies.

Topic 21.
Substitution of APEO detergents in pre-washing for wool scouring and in rinsing



Case illustration:
Nonylphenolethoxylate degredation

Concept

Use of environmentally hazardous APEO detergents in e.g. pre-washing, for scouring of loose wool, in rinsing and after dyeing is widespread within the industry. To some extent, textile industry has volunteered to substitute APEOs with more environmentally friendly detergents, but APEOs are still used to a wide extent. The option is further described in papers in Part 3 and 4.

Improvement potentials

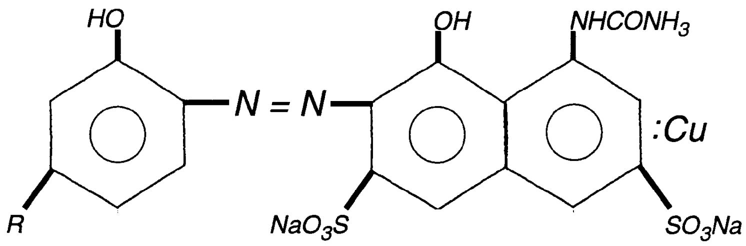
APEOs degrade into alkylphenol and alkylphenol derivates, and these compounds have very bad environmental characteristics: they are almost non degradable, they are somewhat bioaccumulating, they are highly toxic, and they act as oestrogens (female hormones), thus affecting the reproductivity of male organisms. By substitutions these environmental hazards can be avoided.

Relevance

Most companies.

Topic 22.
Substitution of dyes containing heavy metals

Heavy metal based dyestuffs



Reactive violet 5

÷ *Reactive dyestuff based on a cupper complex*

Case illustration:
Reactive dye-stuff based on a cupper complex

Concept

Many textile dyes and pigments contain heavy metals, e.g. Cr, Cu, Co or Ni. These heavy metals are found in metal complex dyes for wool and nylon (PA), in direct dyes for cotton and viscose, reactive dyes for cotton, viscose and wool, and pigments for textile printing. In many cases, it is possible to substitute dyes containing heavy metals with dyes not containing heavy metals. Metal complex dyes may thus be substituted by acid dyes, but problems with sufficient fastness might occur. Some reactive dyes containing heavy metals might be substituted, although it might be difficult to reach the same spectrum of shades.

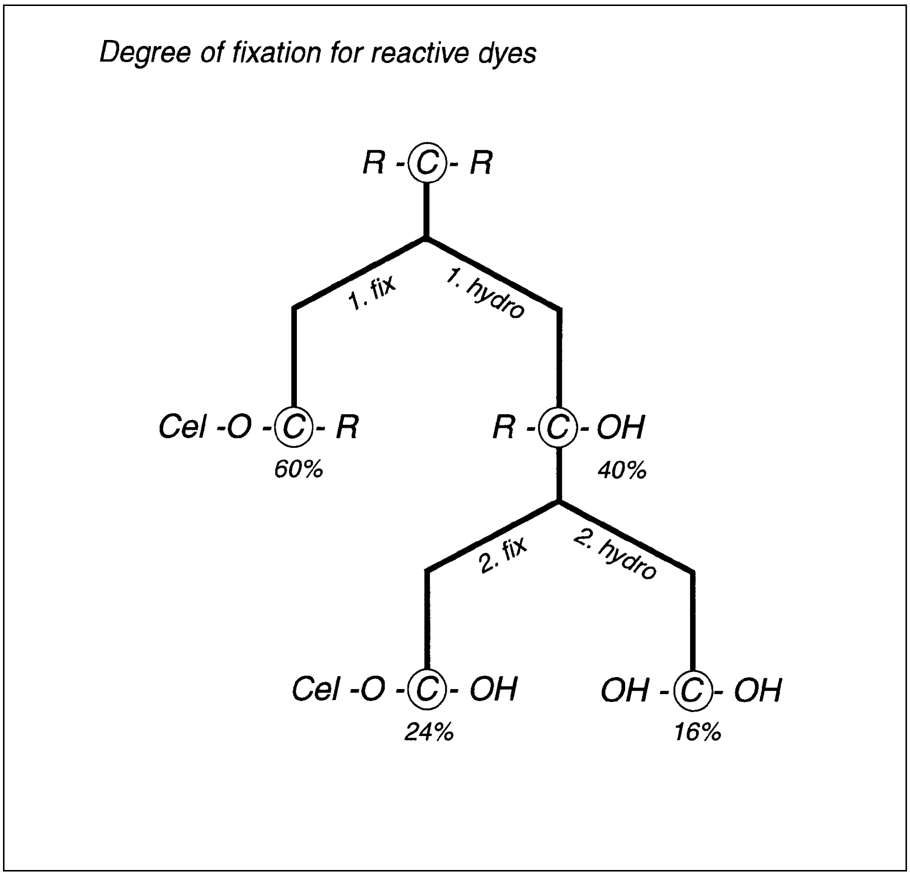
Improvement potentials

Reduction of environmental hazard.

Relevance

All companies.

Topic 23.
Change from monoreactive to bireactive dyes



Case illustration:
Degree of fixation for reactive dyes with a fixation degree at 60% for each reactive group: monoreactive dye-stuff 60%, bireactive dye-stuff 84%

Concept

Until recently, monoreactive dyes have been dominating in the category of exhaustion dyeing in Denmark. These dyes are utilized at approximately 60%, i.e. 40% of the dye ends up in the waste-water. Bireactive dyes on the other hand are utilized 90-95%, so the dyeing companies should have incentive to investigate to what extent a change could take place. Also a possible substitution of vat dyes by bireactive dyes in dyeing of cotton should be considered.

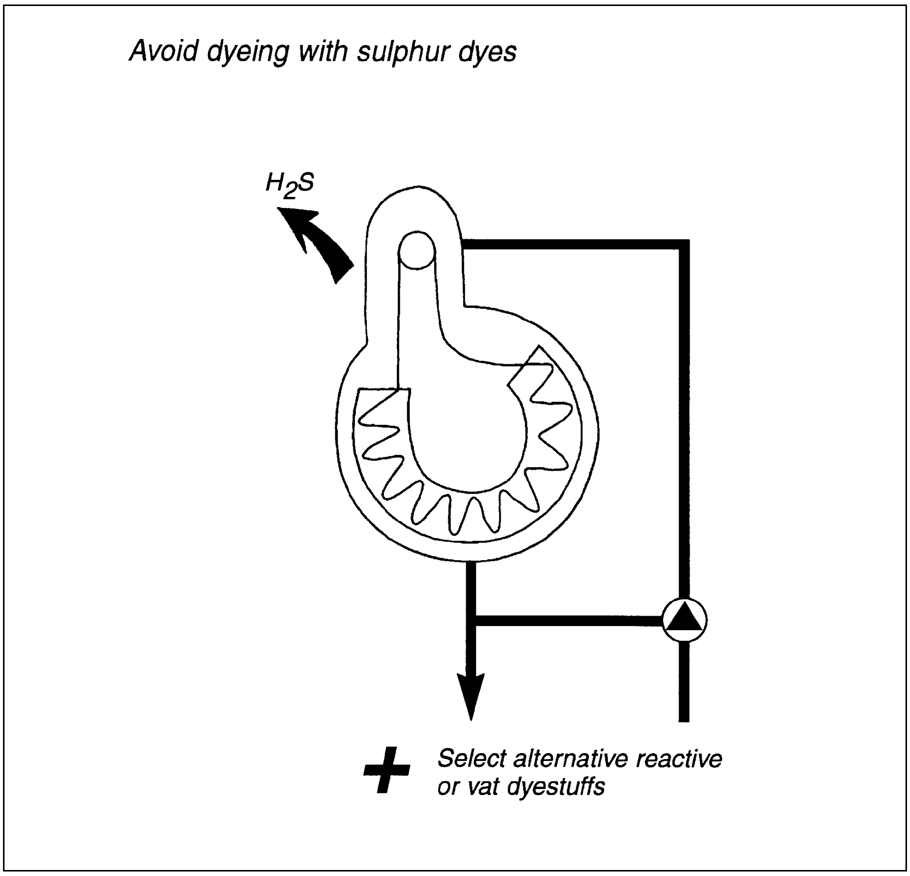
Improvement potentials

Reduction of environmental impacts. Chemical savings.

Relevance

All companies carrying out reactive dyeing.

Topic 24.
Substitution of sulphur dyes



Case illustration:
Dyeing with sulphur dyes in jet

Concept

When dyeing with sulphur dyes sodium sulfide (Na_2S) is normally used as the reducing agent. Na_2S can be a hazardous substance in relation to working environment. Instead it could be recommended to use reactive or vat dyes.

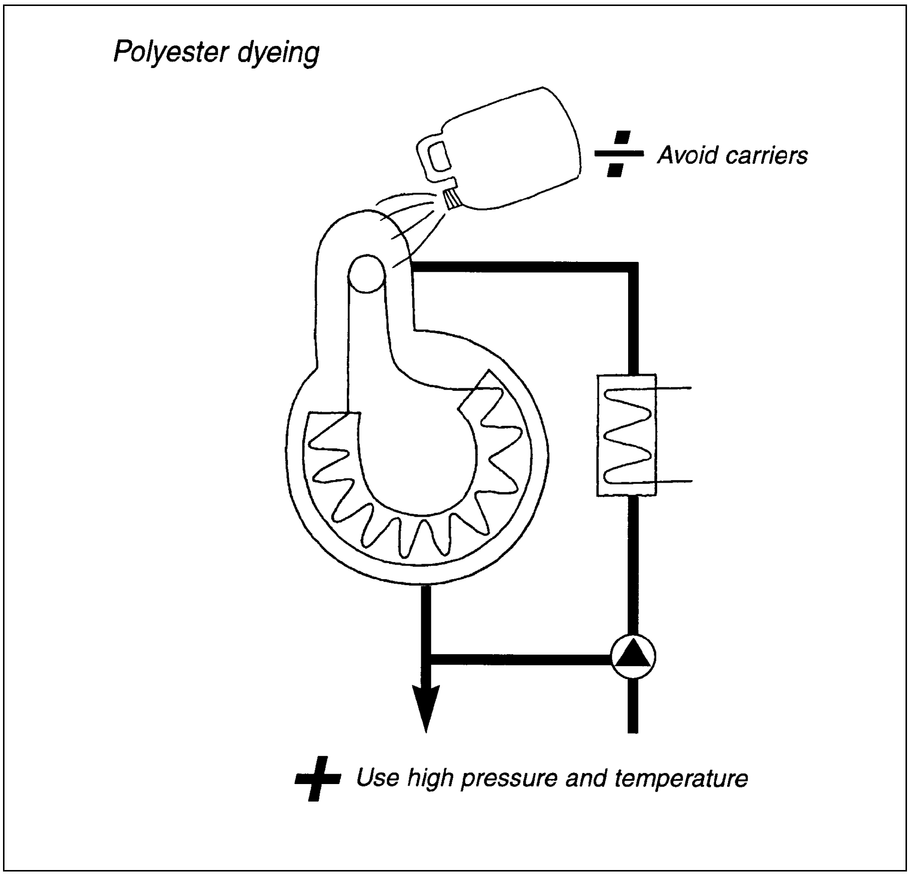
Improvement potentials

Reduction of environmental impacts.

Relevance

Companies engaged in sulphur dyeing.

Topic 25.
Substitution of carriers



Case illustration:
Polyester dyeing

Concept

In dyeing of fabrics containing polyester in winches and other atmospheric equipment, carriers are used. Carriers can chemically be characterized as organic compounds – often chlorinated – of a solvent-like nature. By dyeing in HT-jets or other types of HT-machines, there is no need for carriers. In applications where carriers are still needed, the least hazardous ones should be used. For this purpose the Federation of Danish Textile and Clothing Industries has elaborated guide-lines for evaluating harmfulness of chemicals by assigning different scores to different chemicals.

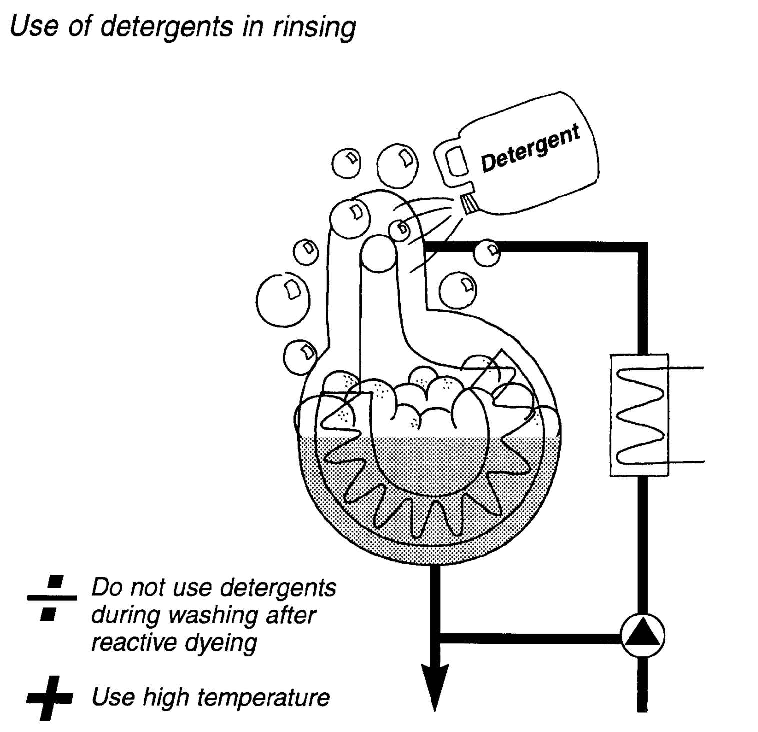
Improvement potentials

Reduction of environmental hazard.

Relevance

Companies carrying out polyester dyeing.

Topic 26.
Detergents and complexing agents for washing after reactive dyeing



Case illustration:
Use of detergents in batchwise rinsing in jet

Concept

Surplus and non fixed reactive dye-stuffs are highly water soluble. Nevertheless, detergents and complexing agents are normally used during washing after dyeing. Both in international literature and in recent Danish projects, it has been shown that detergents and complexing agents do not improve removal of hydrolysed reactive dyes from the fabric. On the other hand, the washing out is improved with increased temperature. In one Danish project, 50 full-scale dyeings have been carried out at various dye-houses without use of detergents or complexing agents. All have succesfully proven that these chemicals can be avoided without negative impact on product quality. Avoiding detergents even tends to increase the effectiveness of the rinse. Rinse without detergents, complexing agents and modified operation of the dyeing process, should be tried in the individual company. This option is documented in detail in a paper in Part 3.

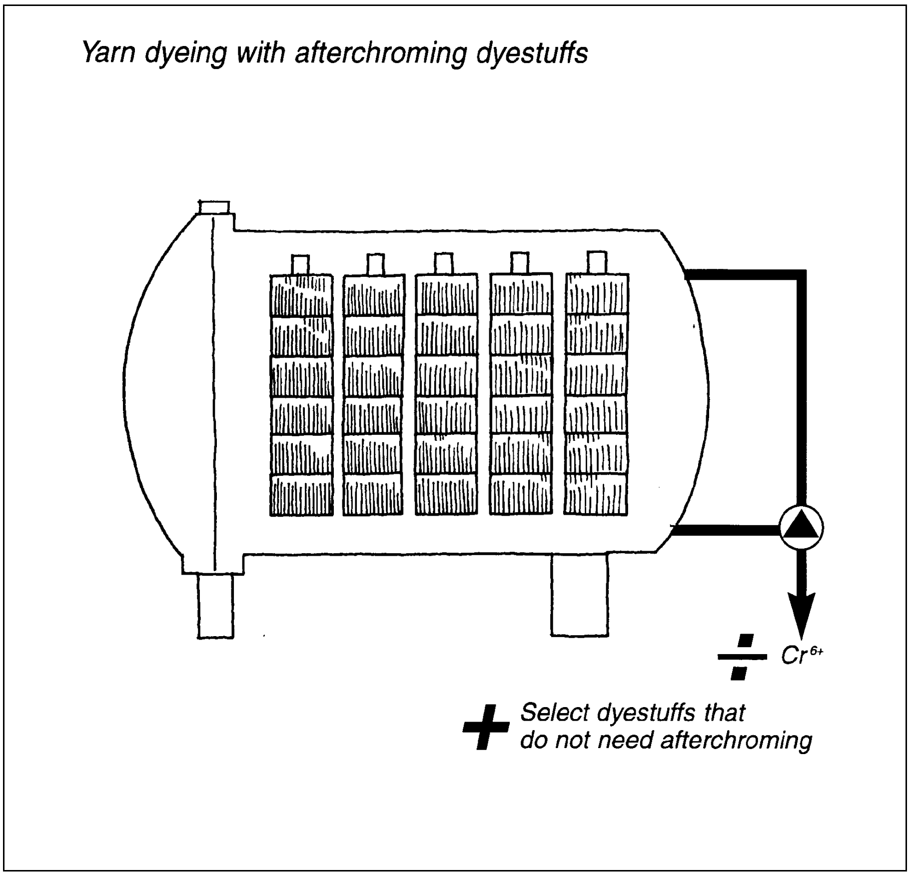
Improvement potentials

Reduction of environmental impacts. Large chemical savings.

Relevance

All companies doing reactive dyeing.

Topic 27.
Substitution of afterchroming



Case illustration:
Yarn dyeing with after chroming dye-stuffs

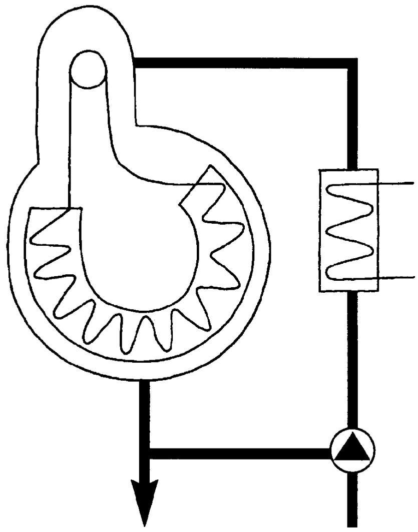
Concept
Certain processes for dyeing of wool top and polyamide supply chromium compounds for fixation of dyes. This leads to an environmentally hazardous discharge of chromium. Substitutions should be considered.

Improvement potentials
Reduction of environmental hazard.

Relevance
Companies engaged in dyeing of wool and nylon.

Topic 28.
Neutralization after dyeing

Case illustration:
Use only neutralization after reactive dyeing of cotton when needed



Concept

After dyeing in the alkaline range, it is normal to neutralize. Typically, acetic acid is used giving a contribution to COD in the waste-water. Acid is added to assure that dyes are not washed out from fibres, e.g. in the first rinse after dyeing with certain reactive dyes. However, often there seems to be no need for this acid addition. Alternatively, formic acid – or an even better mineral acid like diluted hydrochloric acid – could be used giving a smaller or no contribution of COD. This is documented in detail in a paper in Part 3.

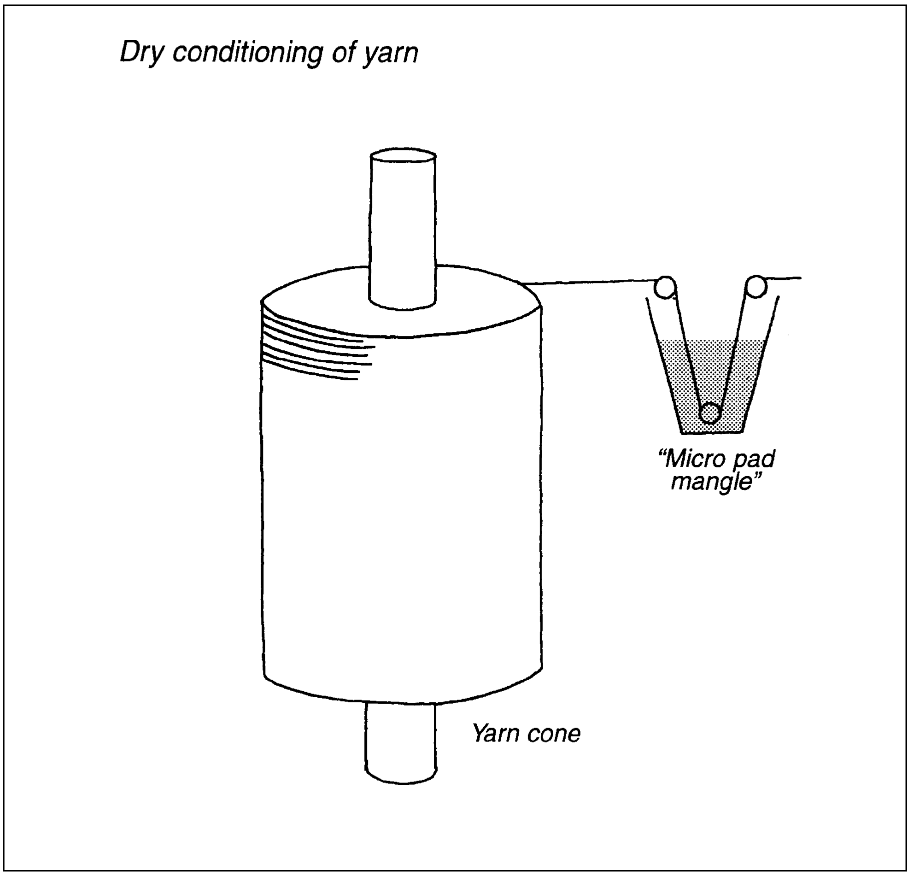
Improvement potentials

Chemical savings. Reduction of COD load.

Relevance

Most companies.

Topic 29.
Dry conditioning



Case illustration:
Dry conditioning of yarn

Concept

In yarn dyeing companies, avivation – supplying of lubricants to the yarn – is often done in one of the rinses after dyeing. It should be assessed if conditioning alternatively could be done in connection with winding, as it is seen when paraffin is applied to certain types of yarn. One should also take into account possible impacts on the working environment when conditioning is done in a dry state.

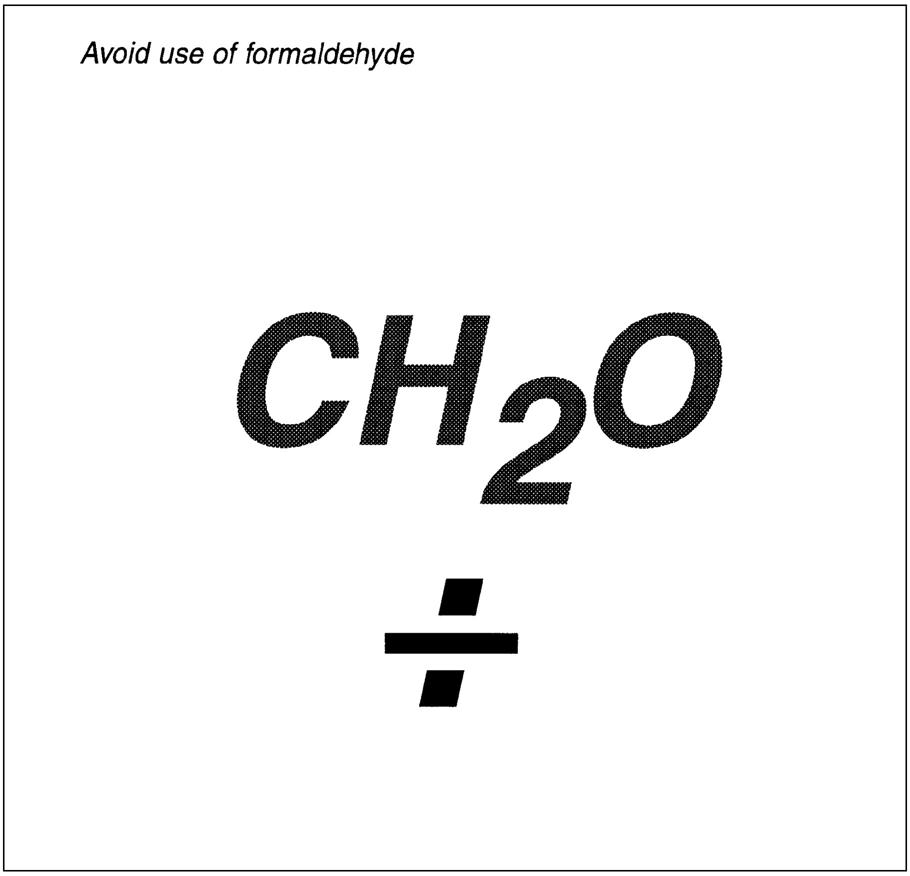
Improvement potentials

Chemical savings. Reduction of environmental impacts.

Relevance

Yarn dyeing companies.

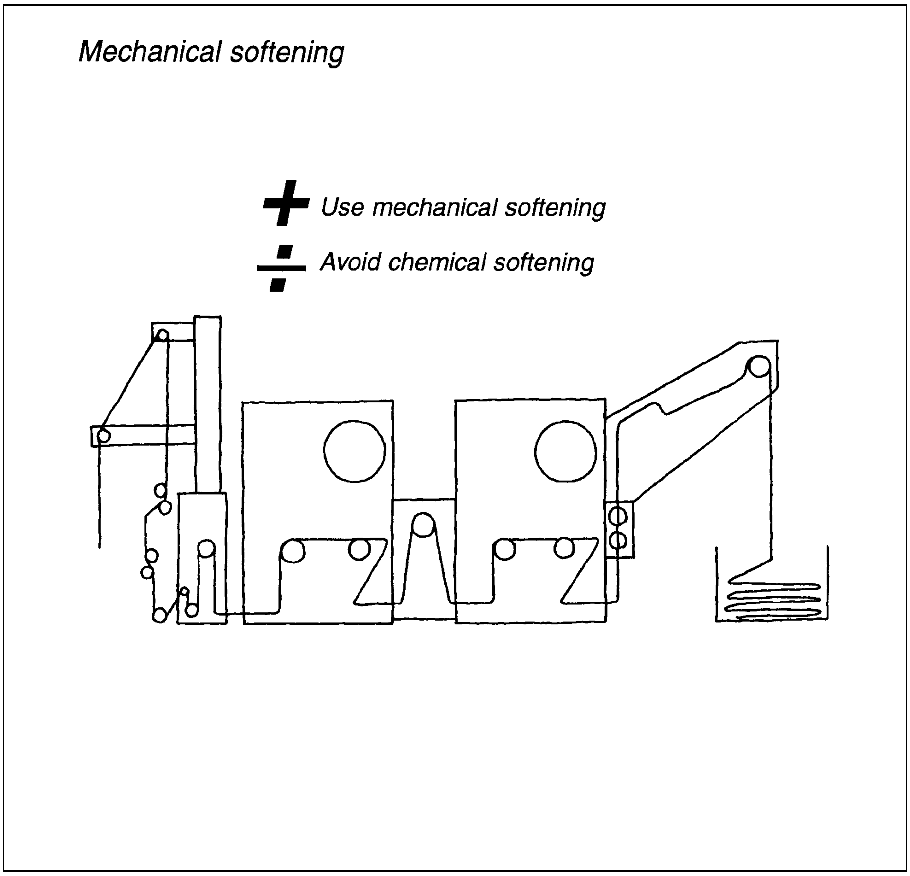
Topic 30.
Products containing formaldehyde



Case illustration:
Avoid use of formaldehyde

Concept	Some finishing chemicals are releasing formaldehyde – either in the application process or later at the consumer – causing risks of allergic reactions. Formaldehyde is even listed as a possible carcinogenic compound. Releasing of formaldehyde is primarily known from compounds assuring crease, shrink-proof fabrics, and as a binding auxilliary in dye-stuffs for printing. New products – low in or even free of formaldehyde – have been commercialized over the past years, but their quality still gives rise to discussion. Many companies apply mechanical means for pre-shrinking and the stabilizing of fabrics without use of chemicals.
Improvement potentials	Reduction of impacts in working environment and on consumers.
Relevance	Most companies.

Topic 31.
Mechanical softening processes



Case illustration:
A mechanical softening machine

Concept

After printing with pigment dyes the fabric usually appears too stiff. This is due to the use of thickening agents and the like. These agents are not washed out, and this raises a need for the use of softening agents. Lately, machines have been commercialized, which in a mechanical way and without use of chemicals are able to soften the fabric. In the individual company, it should be assessed whether mechanical softening will be suitable for their line of products, and whether the overall environmental impacts are improved by changing from chemical to mechanical softening.

Improvement potentials

Chemical savings.

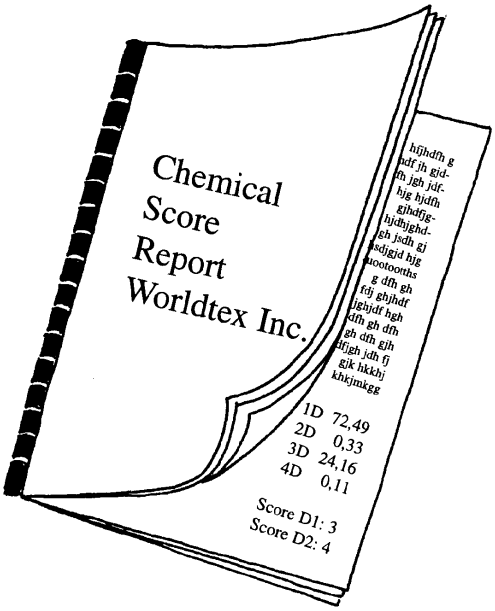
Relevance

Most companies.

Topic 32:
Optimization and substitution of chemicals in general

Case illustration:
Evaluate the chemicals in the production by a score system

Scoring system for chemicals



Concept

Many companies stress the importance of considering the use of certain chemicals, especially detergents, complexing agents and other auxiliaries. Concern should be paid to the amounts and types used. For this purpose the Federation of Danish Textile and Clothing Industries has elaborated guide-lines for evaluating harmfulness of chemicals by assigning different hazard scores to different chemicals. Producers of textile chemicals should be engaged in discussions on possible changes in production of more environmentally friendly chemicals.

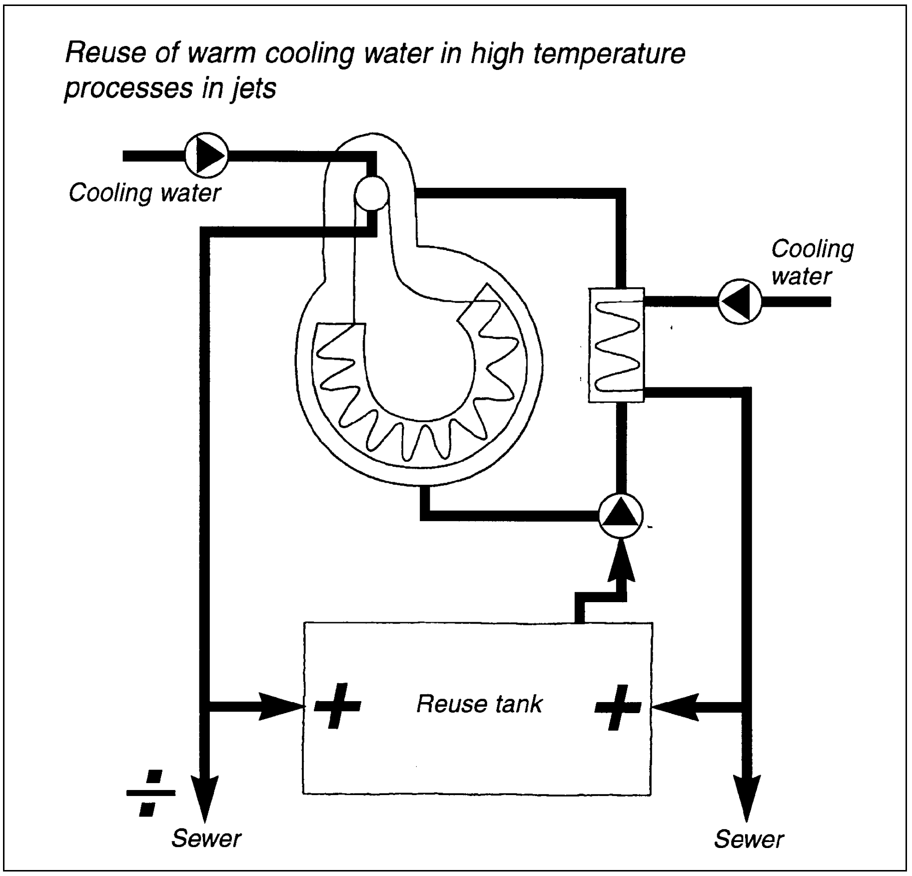
Improvement potentials

Reduction of environmental impacts.

Relevance

All companies.

Topic 33.
Re-use of pure cooling water and condensate



Case illustration:
Re-use of warm cooling water in high temperature processes in jets

Concept

Great amounts of heated up cooling water and condensed steam are produced within the textile dyeing industry, e.g. from vacuum pumps, compressors, bearings, indirect cooling and heating of dyeing machines etc. The only parameter that differentiates this water from normal process water is the temperature. In some cases the pure, warm and often softened cooling water and condensate is re-used with its calorific content, but in many cases this is not the case, and then re-use should be considered.

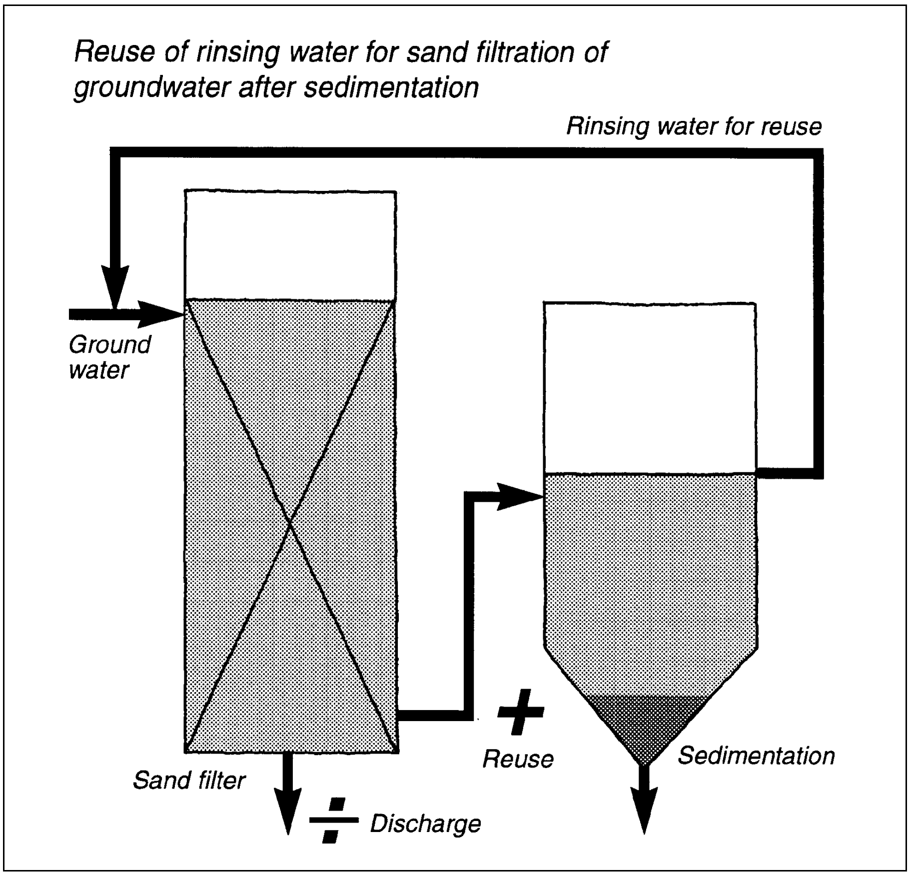
Improvement potentials

Savings in water and effluent by water re-use and energy savings by using the hot water in high temperature processes in the production.

Relevance

All companies.

Topic 34.
Re-use of rinsing water from sand filtration and ion exchange installations



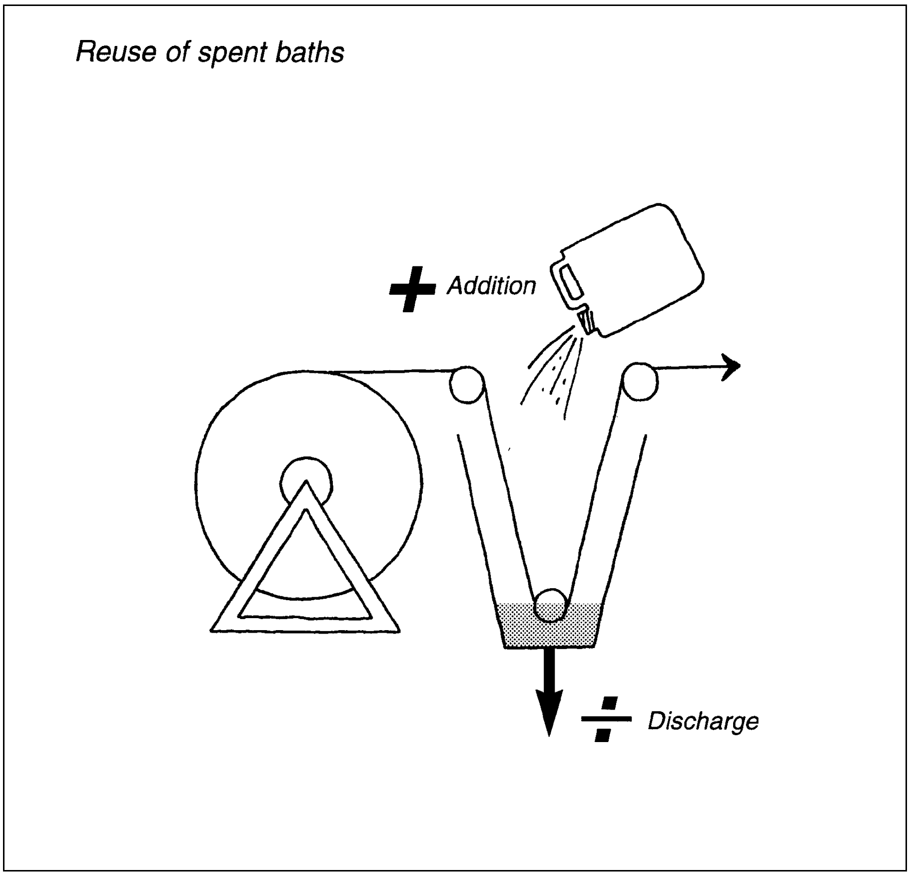
Case illustration:
Re-use of rinsing water for sand filtration of ground water after sedimentation

Concept — Analyses have shown that 50% of the rinsing water from sand filtration of ground water and from ion exchange installations is suitable for re-use.

Improvement potentials — Water and effluent savings.

Relevance — All companies.

Topic 35.
Re-use of chemically loaded spent baths



Case illustration:
Re-use of spent baths by surface treatment in the finishing of textiles

Concept

Chemically loaded spent baths in varying amounts and compositions are produced within the industry. These baths are often discharged along with the waste-water leading to an impact on the environment and waste of resources. Certain baths could be re-used simply by renewed addition of chemicals, others after a simple filtration. The possibility should be examined in each case.

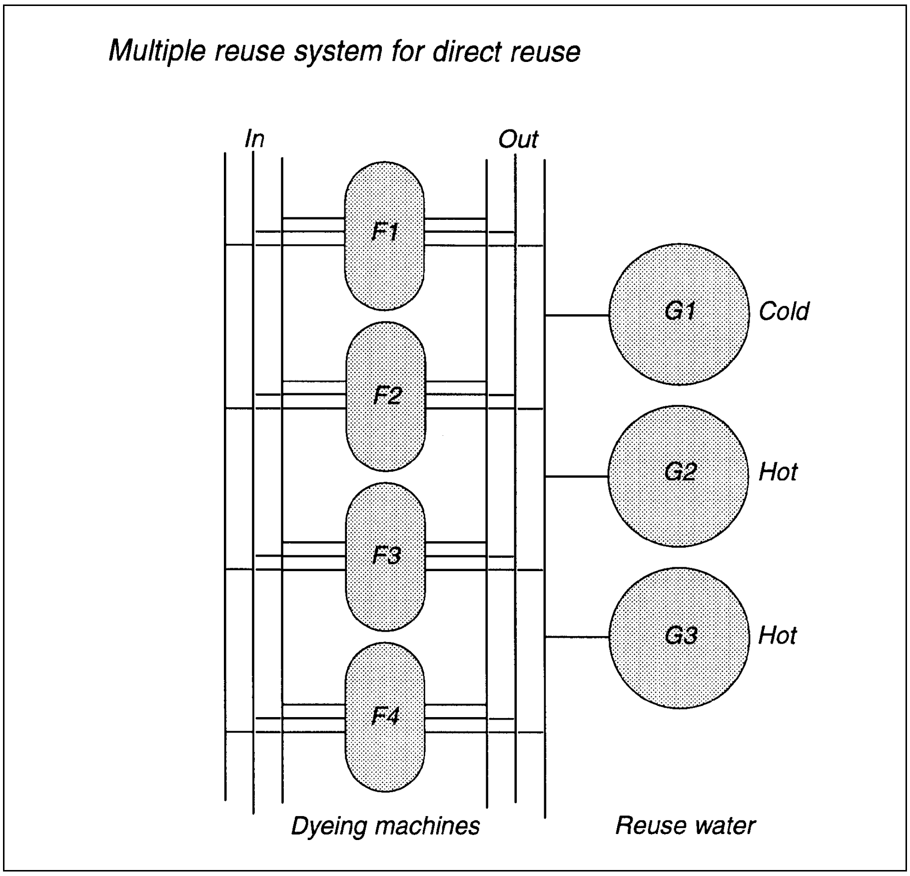
Improvement potentials

Minimization of chemical consumption and reducing environmental impacts.

Relevance

Almost all companies.

Topic 36.
Multi-pipe system for direct re-use



Case illustration:
Multiple re-use system for direct re-use of renewable process water types

Concept

Before the dyeing procedure, almost all fabrics are pre-treated, typically by washing and sometimes bleaching, and this pre-treatment is finalized by a number of hot or cold rinses. After the dyeing procedure, the dyeing bath is followed by a number of baths, the last typically being warm and cold rinses. The rinsing water typically amounts to 70-80% of the total water consumption when fabric is washed and dyed. Danish analyses have shown that especially the last portions of rinsing water – amounting to 20-30% of total water consumption – have a quality indicating a possible re-use as first rinsing water. Re-use of different types of water for different purposes requires installation of a multi-pipe system connected to a multi-tank system. The extent of such a system will depend on local conditions: possible limitations in physical space for new piping and tanks, types of processes and to what extent re-use is possible.

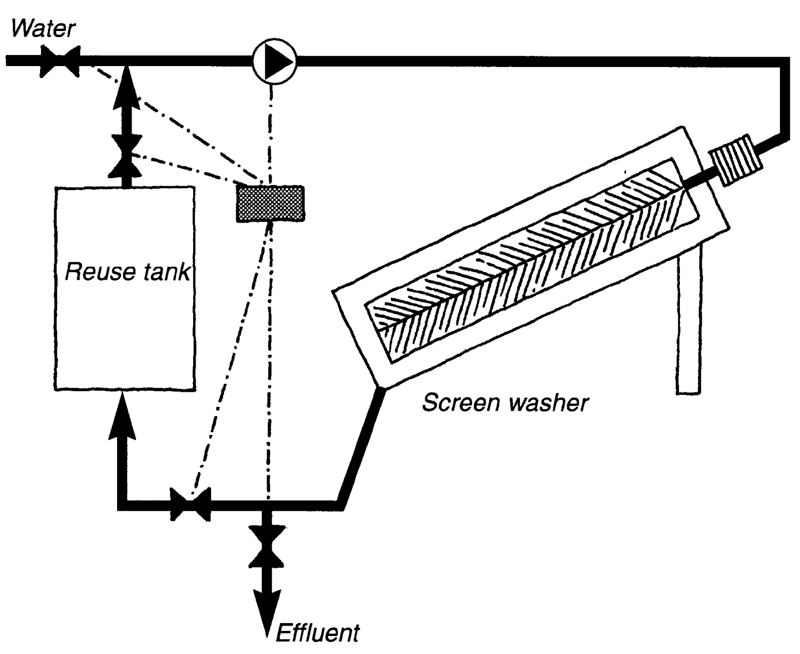
Improvement potentials

Large water, effluent and energy savings. Economical calculation for Danish conditions have shown very short pay-back time for the installation.

Relevance

All companies.

Topic 37.
Re-use of water from rinse of squeegees, screens and buckets



Case illustration:
Re-use of the cleanest part of the rinsing water from screen washer in textile printing

Concept

In cleaning of equipment from textile printing large amounts of rinsing water are produced. The more clean fractions of rinsing water can be collected separately and re-used in applications where the demands to the quality of the water are met. Typically, the first half of the effluent from the rinsing equipment is heavily loaded with chemicals, and the quality demand for reusable rinsing water in this part is low. In the last half of the rinse, clean water is used and effluent is collected for re-use in the first part of the next rinse.

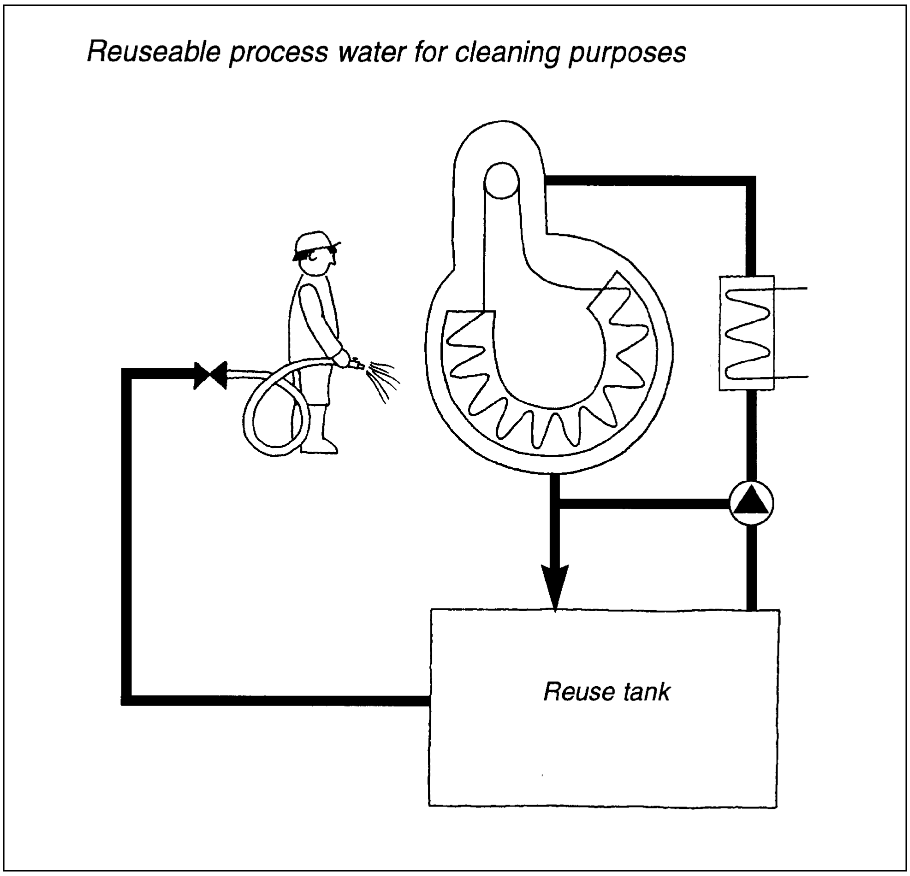
Improvement potentials

50% water and effluent savings for rinsing.

Relevance

All companies.

Topic 38.
Re-use of water for cleaning purposes



Case illustration:
Re-use of re-usable process water qualities for cleaning purposes

Concept

Big amounts of water for cleaning purposes are used within the industry. Being the most obvious field of application for re-use of water, the project should assess the ratio between the consumption of water for cleaning purposes and the obtainable amounts of re-usable water with a satisfying quality.

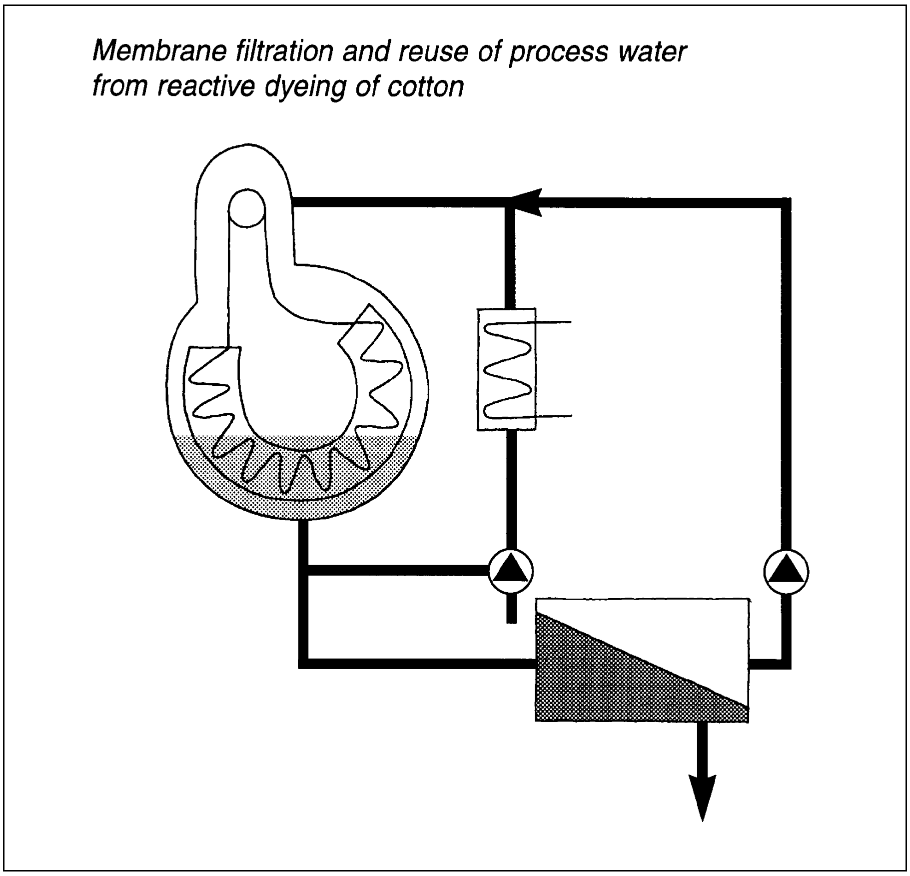
Improvement potentials

Water savings.

Relevance

All companies.

Topic 39.
Separation techniques for reclamation of process water



Case illustration:
Membrane filtration and re-use of process water from reactive dyeing of cotton in jet

Concept

Many types of spent process waters at the point of discharge are so heavily loaded, that a direct re-use is not possible. This applies to e.g. bleaching, dyeing and desizing baths and the most loaded rinsing baths. Danish experience, concerning re-circulation of process water from reactive dyeing of cotton in jets and re-use of desizing baths have shown, that by addressing specific types of process water, economically feasible separation techniques can be found today, and with expectations of increased costs for water and energy in the future, one could expect this tendency to increase. For the overall economical feasibility for a selected reclamation method, one should take into account the water savings possible, the value of desirable chemical agents and/or the calorific value remaining in the process water after reclamation.

Membrane filtration, chemical precipitation, activated carbon and evaporation have been tested. These options are further described in papers in Part 3 and 4.

Improvement potentials

Large savings in water, energy and chemicals.

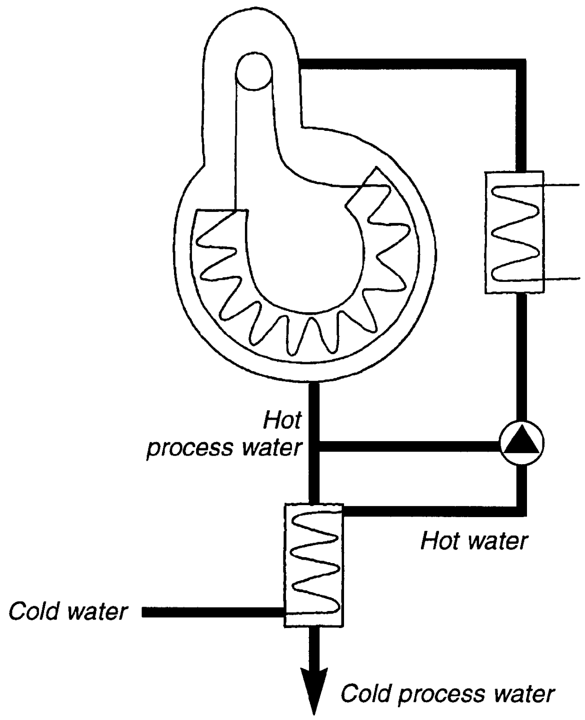
Relevance

All companies.

Topic 40.
Heat exchange of discharged process water

Case illustration:
Heat exchange between outgoing process water and incoming water in jet

Heat exchange between outgoing process water and incoming water



Concept

By far, the largest consumption of energy within the textile companies is used for heating of process water. Supplied energy is widely lost by discharging of hot process water and only a smaller fraction is regained by miscellaneous reclamation processes (heat exchange, indirect cooling etc.). This project should assess the economical and technical possibilities for the reclamation of energy by heat exchange.

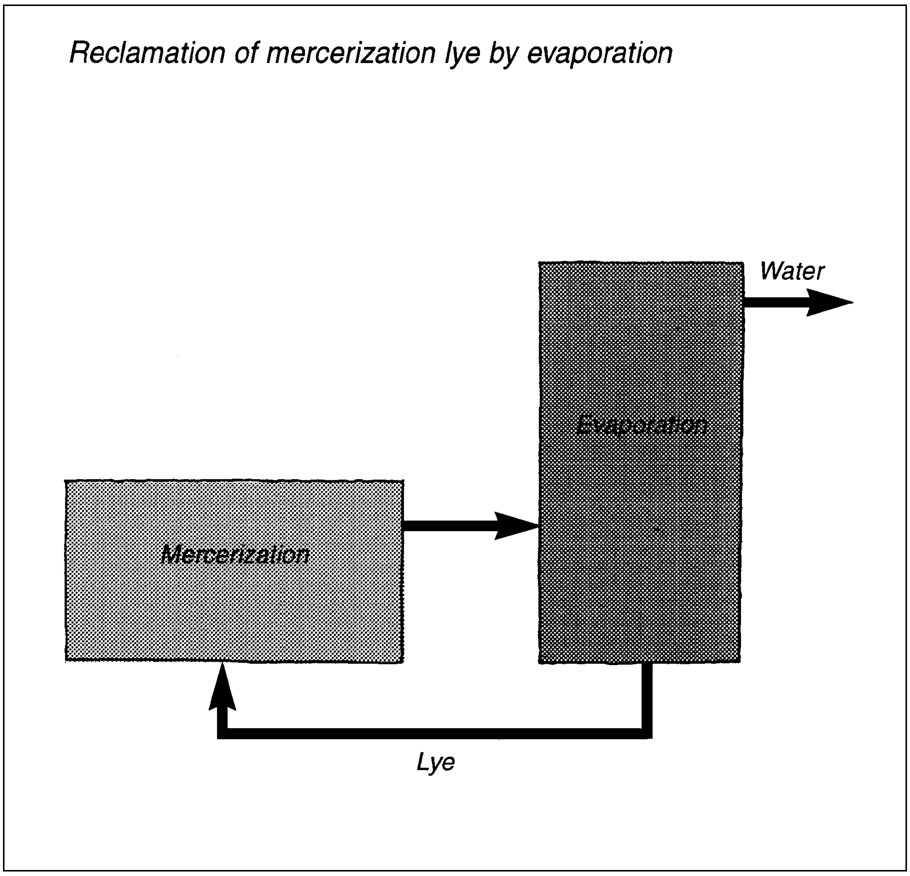
Improvement potentials

Energy savings.

Relevance

All companies.

Topic 41.
Evaporation and reclamation of sodium hydroxide



Case illustration:
Reclamation of mercerization lye by evaporation

Concept

It is technically possible to evaporate process water produced during mercerization for reclamation of the sodium hydroxide content. Thus, this project should assess the economical feasibility by such a measure. In some cases, process water from mercerization is already directly re-used for e.g. desizing purposes. This of course affects the project idea and should be taken into account when evaluating a possible implementation.

Improvement potentials

Chemical savings.

Relevance

Only companies who carry out mercerization.

Part 3.
Papers on selected options

3.1 Introduction

During the Cleaner Technology Transfer Programme two seminars were arranged for Polish factory managers, textile technicians, waste-water technicians and suppliers of chemicals to the textile industry. Both seminars had a duration of two days, and were attended by 76 and 72 participants respectively. About 30 Polish dye-houses and/or printing houses were represented.

The first seminar June 22-23, 1993 in Lodz was entitled »Technology Transfer Programme« and the second seminar November 14-15, 1995 in Dobieszkow was entitled »Options for Cleaner Technology in Polish Textile Industry«. The presentations of these technology transfer seminars went into further detail with some of the options. In this part, some of the papers are presented, the titles are

1. Environmentally friendly recipe in reactive dyeing of cotton
2. Substitution of Alkyl Phenol Ethoxylate Detergents
3. Reclamation and re-use of process water from reactive dyeing of cotton
4. Reclamation of reactive dyeing process water by chemical precipitation
5. Re-use of treated dye-bath after reactive dyeing at Danish dye-house Martensens Fabrik
6. Savings and substitutions in textile dyeing
7. Environmental labeling

3.2 Environmentally friendly recipe in reactive dyeing of cotton

Hans Henrik Knudsen and Henrik Wenzel,
Institute for Product Development, Denmark.

Abstract
The recipe for reactive dyeing of cotton can be divided into three steps: the pre-treatment, the dye-bath and the final rinse. The consumption of chemicals and water in the rinse have been found to be considerable; three quarters of the total COD-discharge of a recipe have relations to auxiliary chemicals used and three quarters of the total water consumption have relation to the rinse. The improvement potentials in the rinsing procedure were found to be considerable, and the newly developed recipe focuses on improvements in the rinse.

Tests with the new recipe have documented, that neutralization, detergents and complexing agents can be left out completely with no adverse effect on product quality. All recognized tests of fastness and shade have been performed and evaluated in co-operation with the dye-houses.

More than 50 full-scale dyeings have been carried out in jets, overflow and drum batch machines. These dyeings include 25 different reactive dye-stuffs, among these – azo, anthrachinon, phtalocyanin and formazan dye-stuffs, including both monoreactive and bireactive dye-stuffs of which 15 had the vinyl sulphone as reactive group. The dye-stuffs have been combined in 20 different recipes covering very light to very dark shades.

Hot membrane filtration of the hot rinsing water has been investigated in parallel projects and it is documented that one new recipe including membrane filtration, saves chemicals, water, and energy, and implies large savings in production time as well.

Introduction

Status for the recipe

In previous investigations, the consumption of water, energy and chemicals for the rinse in the reactive dyeing of cotton was found to be of major importance (D. Fiebig et al., 1985, H. Wenzel et al., 1992). It is common that the rinse has a water consumption above 200 l/kg textile, or more than 60% of the total water consumption in the whole refinement process. About 70% of the COD-load from the reactive dyeing process can derive from auxiliary chemicals used in the rinse.

Status in the dye-houses

The dye-houses state that the large consumption of water and chemicals for the rinse in reactive dyeing of cotton ensures a reliable process. The possible residual content of salts and/or other chemicals in the cotton textile, which are not washed out in the pre-treatment, can influence the quality of the product, and the process is secured by the use of auxiliary chemicals.

Another reason given is, that specific shades require combination of dye-stuffs with so different chemical and physical properties, and that it is only possible to control the rinse and obtain the desired shades with the traditional consumption of water- and chemicals.

The ever increasing demand to shade and wash fastness from the clothing industry together with demand for prompt and faultless supply of relative smaller lots in quick shifting shades implies that the dye-houses use the secure well-known recipe. The dye-stuff producers deliver a recipe draft with the dye-stuff, where the use of auxiliaries is recommended.

The use of auxiliaries is general in all recipes and auxiliaries are used in standard concentrations to ensure a safe procedure, although the dye-houses are aware that parts of the recipes do not need the auxiliaries or only need minor doses.

Project goals

The goal for this research is to develop a recipe for the rinse in the reactive dyeing of cotton without the use of detergents (i.e. surface active agents), complexing agents or dispersing agents. If possible to avoid the traditional neutralization before rinse.

Project strategy

The overall strategy of the research has been to use full-scale dyeings in different batch dyeing machines. The confidence in laboratory research is very limited in the dye-houses, because of the insufficient physical load and the unrealistic way the rinse water is changed in the laboratory containers.

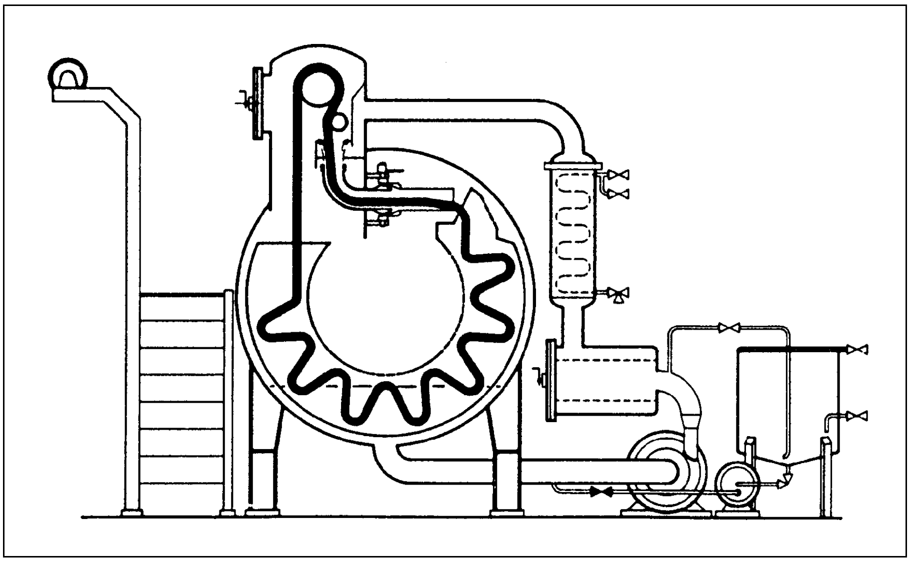
Reactive dyeing of cotton

Reactive dyeing of cotton is the most common wet treatment of textile processes world-wide. Today, batch dyeing is dominating and increasing.

Machines

Batch processes typically take place in a jet, overflow or drum dyeing machines. Figure 1 shows a sketch of a jet machine, where both the liquor and the textile are circulated to reach a quick process performance.

Figure 1.
Cotton dyeing in Jet



Cotton

In the world-wide cotton production only 4 species are utilized, one of these *Gossypium hirsutum* amounts to about 80% of the total production. Despite this apparent homogeneity the difference in areas and methods of cultivation and treatment leads to a very heterogeneous product. The raw cotton consists for 75-95% of cellulose fibres. The remaining 5-25% consist of cotton wax, knitting oil and a large number of inorganic impurities. In this project, the calcium and the magnesium is interesting, because of their ability to precipitate the dye-stuffs. According to table 1 the content of calcium and magnesium in

Table 1.
Purity of different cotton lots (Behnke, 1994).

Content, mg/kg	**Greenhouse**	**Brazil Assai Paraná**	**Brazil Sao Paulo**	**Peru**	**USA Texas**	**USA California**
Ca	400-500	3147	845	700	810	600
Mg	300-400	1156	555	440	365	540

free grown cotton is higher and very fluctuating compared to a greenhouse grown cotton.

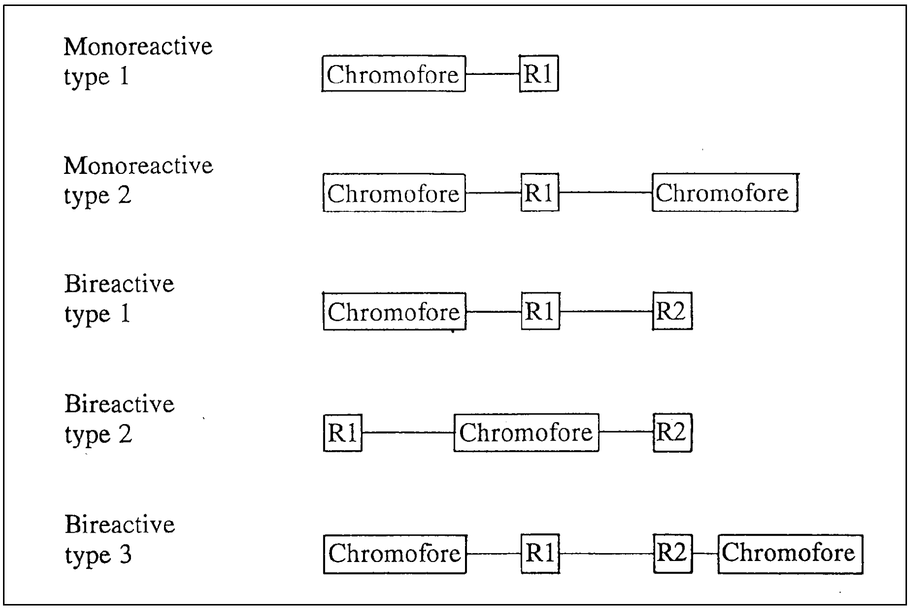
The reason can be found in the different soils where the cotton is grown combined with the use of fertilizers, pesticides and defoliants in the modern cotton production. Large-scale farming and use of harvesters is absolutely necessary to meet a market characterized by insatiability (Behnke, 1994).

Reactive dye-stuffs

Reactive dye-stuffs establish, unlike all other dye-stuffs, a co-valent bond to the textile fibre, and offer great advantages regarding wash fastness of the dyed textile. However, the reactive dye-stuffs react undesired with the hydroxyl ions of the water and form a non-reactive hydrolyzate; a resulting utilization degree of 60-80% is therefore common. To reach the desired wash fastness of the dyed cotton the remaining 20-40% dye-stuff hydrolysate have to be washed out during the rinse.

Reactive dye-stuff molecules consist of chromofore components, giving the colour, and reactive components, establishing the co-valent bond, as schematic outlined in figure 2. The dye-stuffs are called monoreactive respectively bireactive if there are one respectively two reactive groups in the molecule.

Figure 2.
Reactive dye-stuff types.



Reactive groups

Seven reactive groups dominate: Dichlortriazin (DCT), monochlortriazin (MCT), sulfatoethylsulphon (VS), trichlorpyrimidin (TCP), dichlorquinoxalin (DCC), diflourchlorpyrimidin (DFCP) and monofluortrazin (FT).

Chromofors

A great number of chromofors are used, but the most common is the azo group. Others are anthraquinone and phtalocyanine metal complexes.

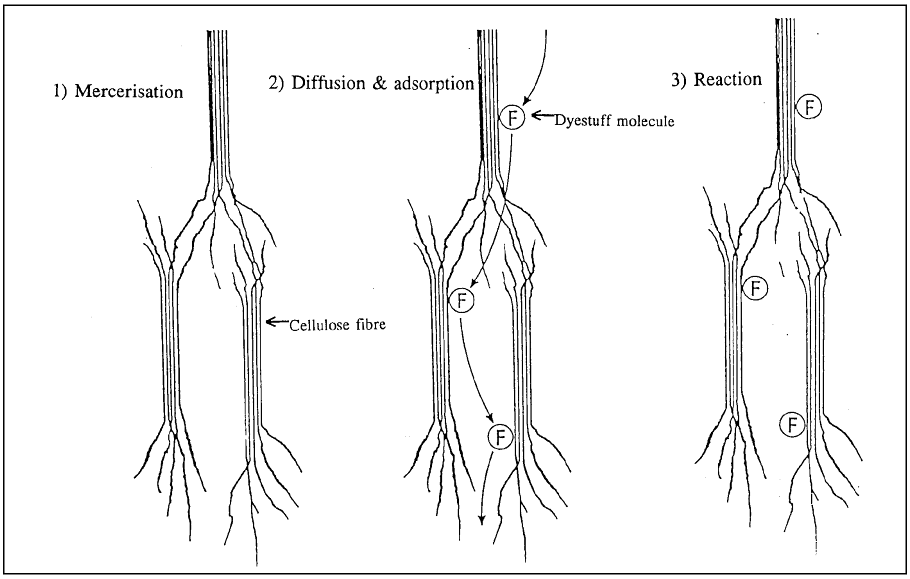
The dyeing process

The reactive dyeing process is outlined in figure 3. During the pre-treatment the cotton fibres are degreased, and to some extent treated with lye to open the fibre structure. By mercerization the fibres are furthermore stretched to give the most open structure, step 1 in figure 3.

The dye-stuff is poured into the dye-bath and a diffusion of the dye-stuff molecules between the cellulose fibres takes place.

After some time salt is added to obtain adsorption of the dye-stuff to the cellulose fibre – step 2 in figure 3. After this, the reaction between the dye-stuff and the cellulose is completed by adjusting temperature (50-80°C) and pH (10,5-11,5) – step 3 in figure 3. Some part of the dye-stuff will be hydrolyzed during this dyeing process, and the absorbed hydrolyzate must be removed in the succeeding rinse.

Figure 3.
Reactive dyeing of cotton. (Ciba-Geigy, 1987)



The rinsing process

The rinse traditionally consists of several rinsing baths, as is seen in table 2, where a typical example of an existing recipe is outlined.

Table 2.
Existing recipe, typical example.

Batch no.	Process	Waste-water (l)	Temp. (°C)
1	Washing & bleaching	700	95
2	Overflow rinse	7300	10
3	Neutralization	700	30
4	Overflow rinse	7300	10
5	Dyeing	700	50
6	Overflow rinse	7300	10
7	Warm rinse	700	50
8	Neutralization	700	60
9	Overflow rinse	7300	10
10	Hot soaping	700	95
11	Warm rinse	700	60
12	Overflow rinse	4300	10
13	Hot soaping	700	95
14	Warm rinse	700	60
15	Overflow rinse	4300	10
16	Neutralization & softening	700	40

The large water consumption in the rinse step is primarily caused by the large number of baths but also by the common use of overflow rinses. Before the temperature is raised in the rinse, the dye-stuff producers recommend a neutralization when dye-stuff types with a VS reactive group are used. This neutralization has, however, in some dye-houses, become usual practice for all recipes.

After neutralization the rinse consists of a number of soaping sequences: hot soaping, warm rinse and overflow rinse. Table 2 shows a typical use of two soaping sequences. In the hot soaping – bath no. 10 and 13 in table 2 – »soaping« additives are used, covering surface active agents (detergents), complexing agents and dispersing agents.

The reason for the use of complexing agents is protection against hardness in the water and/or the cotton together with a need for an additive to hold the dye-stuff hydrolysate dispersed in the water.

The process is finalized with neutralization and treatment with softening agents, necessary for the following sewing process.

Materials & methods

Cotton in the experiments

All analyzed qualities of cotton, also the qualities used in the experiments, have a rather constant total calcium and magnesium content of about 1500 mg/kg.

Dye-stuffs

The investigated dye-stuff in this project are shown in table 3. There are 17 monoreactive and 7 bireactive reactive dye-stuffs, of which 15 dye-stuffs hold the VS reactive group.

Table 3.
Investigated dye-stuff types. Abbreviations explained in text earlier.

Dye-stuff no.	Trade name	Chromofore group	Reactive group	Fixation %
1-4	Remazol	Azo	VS	70-80
5-6	Remazol	Azo	VS/MCT	75-78
7-10	Remazol	Anthrachinone, Phtalocyanine	VS	55-70
11	Remazol	Azo	VS/VS	86
12-14	Cibacron	Azo	FT/VS	73-82
15	Cibacron	Formazan/metal	FT/VS	79
l6-l8	Cibacron	Azo	FT	50-60
l9	Cibacron	Formazan/metal	FT	53
20	Cibacron	Diazo	FT	64
2l	Drimaren	Azo	TCP	64
22	Drimaren	Azo	MCT	56
23	Levafix	Azo	FCP	78
24	Levafix	Anthrachinone	MFP	65

Performed investigations

Table 4 gives an overview of performed investigations. The dye-houses have chosen the recipes, and thus the 24 reactive dye-stuffs in table 3, as »difficult«. Because of the very accurate balance between the used dye-stuffs in light shades, they can be hard to obtain, and for dark shades the fastness can be problematic.

Analyses

Analyses were made according to national standards and include ash content, hardness in water and extract from textile, spectrophotometer scanning for dye-stuff content in process water, conductivity for salt measuring, and pH.

Quality assesments

To assess the quality of the dyed textiles the dye-houses ordinary quality assessments were used: washing, water, wet rub, and dry rub fastness, evaluated on a scale from 1 to 5 with 5 as the best. As always in the dye-houses, colour and shade were assessed by comparing with the customer samples. The main part of the experiments has been performed on production lots.

Table 4.
Overview of performed investigations.

Experiments	50 full-scale tests	
Recipes	20 different recipes	
Dye-stuff colours	Brown, red, black, winered, marine, blue, turquoise, rose, pink, purple, green, mint.	
Shades	Very light to very dark	
Recipe variations	Temperature Neutralization Detergents Complexing agents Soft water No. of rinses	°C ± ± ± °dh No.
Quality assessments	 Washing fastness Water fastness Rub fastness, wet Rub fastness, dry Colour & shade	Scale 1-5 1-5 1-5 1-5 Qualitatively

Results and discussion

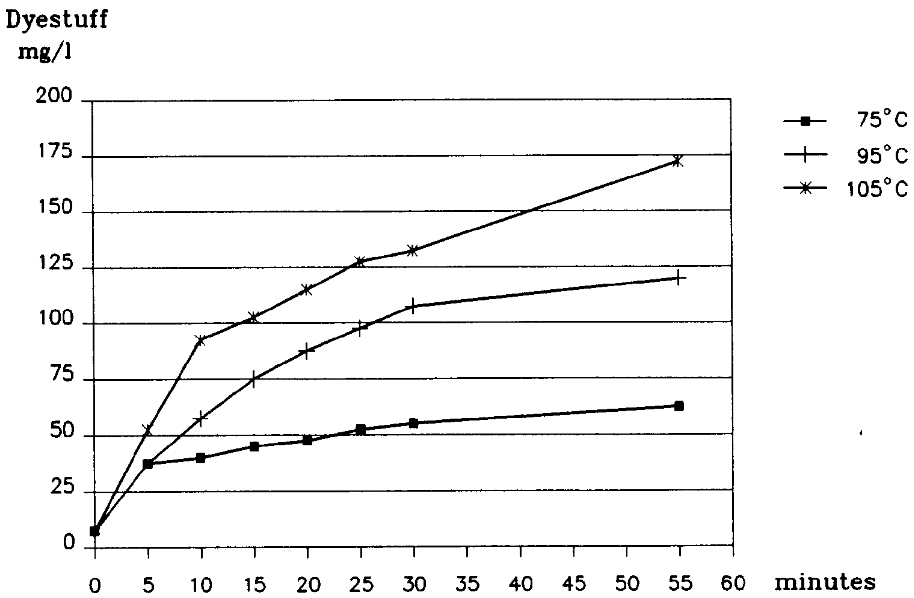
Quality unafffected

None of the performed experiments caused quality reductions in the finished lots, neither when neutralization before hydrolysate rinse were omitted, use of detergents or complexing auxiliaries were omitted, nor when cold overflow rinse were replaced by one cold batch rinse followed by a few 95°C hot batch rinses.

Temperature

The temperature of the process water in the rinse is the decisive factor for washing out the dye-stuff hydrolysate. Figure 4 gives an example.

Figure 4.
Temperature dependency of rinsing.

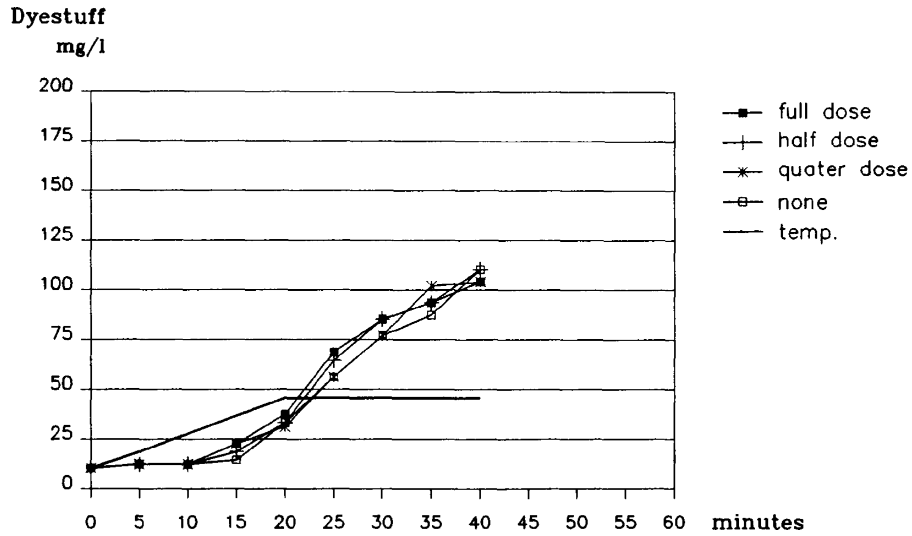


The dye-stuff content in the rinse water versus time, depending on temperature in the rinse, is plotted out in figure 4. By raising the temperature from 75°C to 95°C it is possible to double the dye-stuff content in the rinse water in the same process time. At 75°C and 95°C an equilibrium is reached after approx. 30 minutes process time. The curve at 105°C indicates that the dye-stuff is washed off the textile, and that no equilibrium is reached.

Detergents and complexing agents

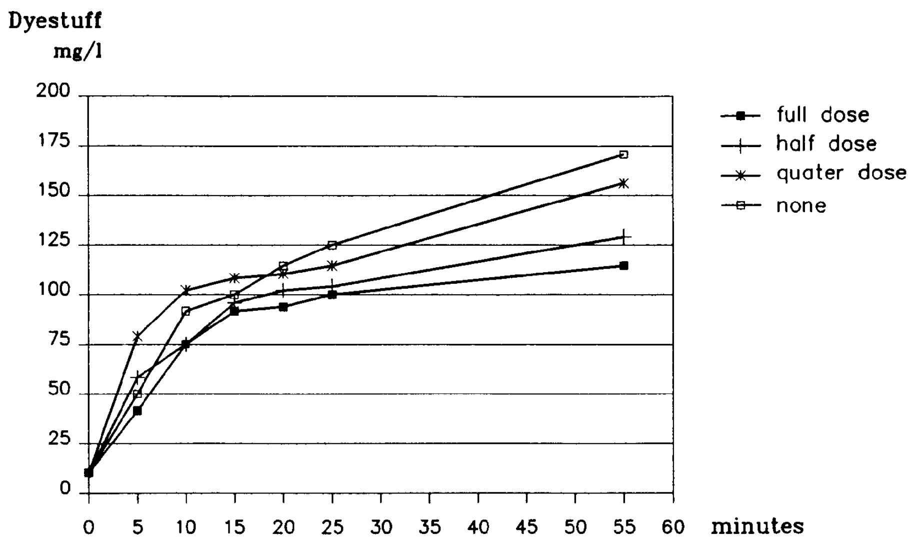
Unlike the temperature, detergents and complexing agents have none or at worst case have an impeding effect on the dye-stuff hydrolysate rinse. In figures 5 and 6, the effect of different auxiliary agents on rinsing is outlined.

Figure 5.
Effect of detergent and complexing agents on rinsing, 95°C.



The dye-stuff content of the rinse water versus time, depending on different doses of auxiliary agents in proportion to normal dose, is plotted out in figures 5 and 6. The heavy line in figure 5 indicates the temperature during heating: 20 minutes heating from 10°C to 95°C, and subsequently constant at 95°C. The curve indicates an exponential coherence between temperature and dye-stuff content in the rinse water up to when the constant temperature and equilibrium is reached. In figure 5 there seems to be no difference between using normal dose, half dose, quarter dose, or no auxiliary agent.

Figure 6.
Effect of detergent/complexing agents on rinsing, 105°C.



In figure 6 there is no heating, temperature constant 105° C. The best result is obtained by no use of auxiliary agent.

Even though the complexing agents did not influence the quality of the finished textile, it was tested whether there was a measurable effect on bound hardness in the textile. Two parts of the same lot were treated identical, apart from use of complexing agent in the hydrolysate rinse. A textile sample of the raw cotton, after wash, after bleaching, and after rinsing was extracted by boiling in 5 g/1 H_2SO_4 in liquor ratio 1:10 and the hardness in the extract determined. The result is mapped in figure 7.

Figure 7.
The effect of complexing agents on bound hardness in the textile.

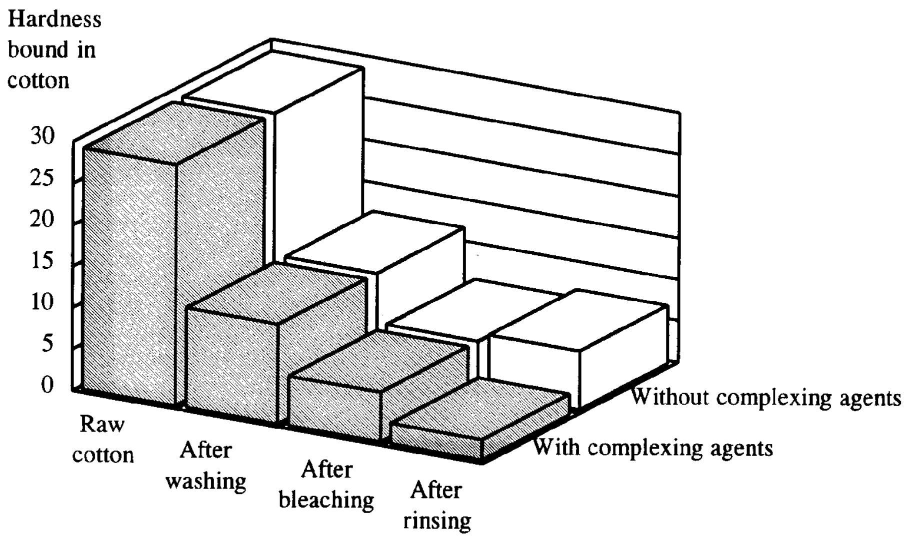


Figure 7 shows that the use of complexing agents can be measured as a reduction of bound hardness in the finished textile, i.e. reducing the content of calcium and magnesium ions in the textile.

Soft water

It has not been possible to detect any influence in textile product quality by using or omitting complexing agents, as long as soft water is used as rinse water. Some experiments done in 5° dH rinse water without complexing agents, indicate a limit of this hardness. It seems that using <3° dH rinsing water will make the rinse process much easier to handle.

pH/Temperature

Consequences of omitting neutralization before the hot rinse are outlined in figure 8. The dye-stuff producers states a maximum pH at 9 – the horizontal heavy line in figure 8 – for VS-dye-stuffs before hot rinse. The course of pH and temperature at a normal performance – i.e. with neutralization – are seen in figure 8 as respectively the squared-curve and the dashed-line. The pH never reaches a value >9 in the hot rinse. If neutralization is omitted the pH will be >9 – the star-line in figure 8 – during the hot rinse. In spite of this, omitting neutralization has caused no detectable quality reduction in the finished textile lots even though 15 of the 24 used dye-stuffs did hold the alleged critical VS reactive group.

New recipe

A new high temperature rinsing recipe, without use of auxiliary agents, was tested by substituting the traditional rinsing step by the one outlined in table 5.

Full-scale tests of new recipe

A total of 9 recipes, covering 13 reactive dye-stuffs combined with very light to very dark shades were tested. Some of the results are shown in table 6.

All shades and fastness were attainable and quality assessments documented normal quality.

Figure 8.
Temperature and pH interrelations.

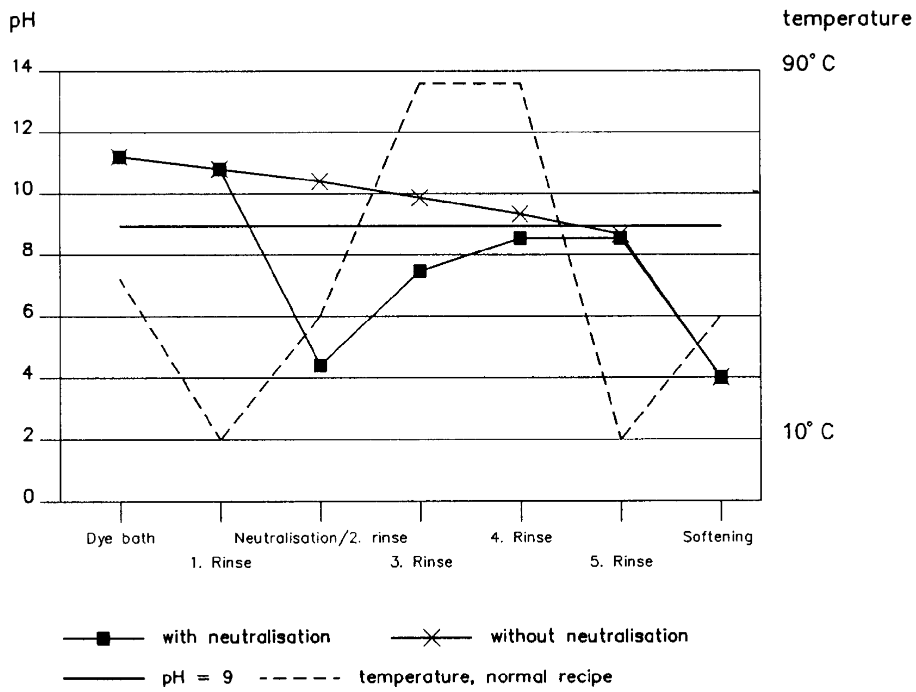


Table 5.
New rinsing recipe.

Batch no.	Process	Waste-water (l)	Temp (°C)
5	Dyeing	700	50
6	Cold rinse	700	10
7	Hot rinse	700	95
8	Hot rinse	700	95
9	Hot rinse	700	95
10	Neutralization & Softening	700	40

From table 6 it appears that it is possible to obtain desired shades and fastness when omitting neutralization before rinse and any auxiliary agent during rinse, solely by using a few 95°C rinse baths and <3° dH rinsing water.

Table 6.
Obtained results by the high temperature recipe free of auxiliaries.

Shades	**Light**					**Medium**	**Dark**			
Recipe	Mint	Rose	Purple	Pink	Turquoise	Blue	Dark red	Red	Marine	Green
Dye-stuff	3 Ciba	3 Ciba	2 Ciba	3 Ciba	3 Remazol	1 Ciba 1 Levafix	2 Reniazol	2 Ciba	3 Ciba	3 Reniazol
No. of 95°C rinses	1	1	4	3	3	1	5	3	7	2
Water reduction	35%	35%	30%	40%	44%	38%	43%	50%	45%	42%
Time reduction	20%	20%	20%	25%	20%	20%	20%	25%	25%	25%

Membrane filtration

Hot membrane filtration of the hot rinsing water has been investigated in a parallel project and is documented successfully (J. Oldrup, 1993).

Environmental benefits

The environmental improvements by introducing the high temperature chemical free recipe and the membrane filtration solution towards the traditional rinsing recipes has been illustrated by the use of a life cycle assessment (A.G.

Reduced process time

Seilund and C.B. Nielsen, 1994). The improvements are great, no chemical used, water consumption reduced about 90%, energy consumption reduced about 70%, and process time reduced about 60% in one new recipe.

Pay-back time for the membrane filtration plant is estimated to be less than one year.

Conclusions

A chemical free, high temperature rinse, using a reduced number of batch rinses, is successfully documented. Neutralization before rinse and use of detergents and complexing agents during rinse can be left out completely.

When introducing the new recipe, it is important that soft water – <3°dH – is used for the rinse. When omitting neutralization before rinsing in recipes using reactive dye-stuffs with VS-reactive groups, it is recommended to observe potential desorption of dye-stuff carefully during the first rinse.

The total water consumption can be reduced about 35-50%, and the total time consumption for the recipe about 25%.

In combination with hot membrane filtration of the hot rinsing water the reduction in water and time consumption is even higher and the energy consumption is reduced about 70%.

Acknowledgement

The project for water reclamation and re-use in cotton dyeing is sponsored by the Danish Council for Recycling and Cleaner Technology within the Danish programme for water reclamation and re-use in the textile industry. We would especially like to acknowledge the programme chairperson, Ulla Ringbaek, for making the project possible and for her constructive comments and kind help. The experiments were carried out at Martensens Fabrik A/S in Brande, Kemotextil A/S in Herning and Sunesens Textilforaedling ApS in Videbaek.

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3.3 Substitution of Alkyl Phenol Ethoxylate Detergents

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Introduction

Over the last 15-20 years, there has been a growing attention to environmental problems, and this tendency has positively influenced the attitudes of individuals and societies to develop improvements.

The textile industry has made great efforts to meet environmental requirements through investments in modern technology to reduce energy, water, and chemical consumption. For example nearly all polyester dyeing is today done on high temperature dyeing machines in extreme short liquor ratio and at the same time without using carriers.

Other environmental improvements have been made by substitution of environmentally unacceptable chemicals and auxiliaries with products having higher biogradability and without toxicity but still meeting the technological and economical requirements. Such substitutions have for example been made for alkylphenol ethoxylates to a wide extent.

Problem formulation

The alkyl phenol ethoxylates – APEO especially the octyl – and nonyl phenol ethoxylates have represented the largest group within the nonionic wetting and washing auxiliaries in textile industry.

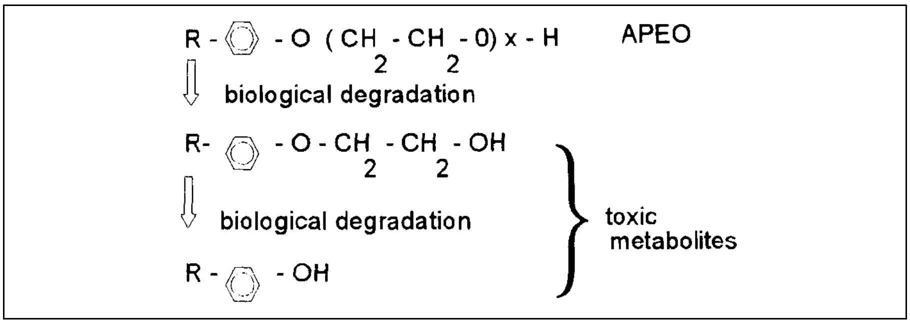
It was the general opinion, that the APEOs beside their excellent technological properties and their relatively low price also were readily biodegradable and had low toxicity. The high biodegradability was seen in biogradability tests (e.g. Modified OECD Screening Test and OECD Confirmatory Test), which measure the biodegradation as removal of organic carbon from the water phase of the test system.

However, several investigations (e.g. Ginger (2)) have shown that the APEOs are only partly biodegradable and that stable degradation products (metabolites) such as alkyl phenol and alkyl phenol with fewer ethoxy groups are produced. Especially the alkyl phenol is very adsorbable to particulate matter (e.g. activated sludge) which explains why the organic carbon was removed in the OECD tests causing the APEOs to be considered as readily biodegradable in the first place. Furthermore, the produced alkyl phenols are highly toxic, and recently they have proven to be oestrogenic as well, i.e. they act as female hormones.

Generally, it is requested that organic chemicals discharged to waste-water treatment plants and the environment should be degradable and may not be toxic. This is not the case with the APEOs.

At the end of 1988 the TEGEWA decided voluntary to stop the use of APEOs in wetting – and washing agents. This decision was a great challenge for the producers to develop more environmentally acceptable nonionic detergents with the same technological advantages known from the APEOs.

Tabel 1.
Degradation af APEO.



Requirements to the detergents

Table 2.
Requirements to detergents.

Technological	Environmental
good wetting capacity	high biodegradability
good washing effect	no toxic characteristics
good emulsifying power	
low foaming tendency	
resistance to alkaline	
resistance to acid	
resistance to hardness	
resistance to oxidant agents	
resistance to reduction agents	

As we look at this list it must be obvious that no single product can fully meet these demands. The producers of detergents therefore very often tries to find mixtures – so called multifunctional detergents where synergism sometimes can be utilized to achieve the optimum.

Anionic detergents

Table 3.
Anionic detergents.

R - CH_2 - COONa	R = C_{10-16} soap
R - C_6 H_4 - SO_3 Na	R = C_{10-13} alkyl benzene sulphonate
R, R_1 > CH - SO_2 Na	R, R_1 = C_{12-16} alkane sulphonate
R, SO_3-Na > CH-C(=O) OCH_3	R = C_{14-16} α-sulpho fatty acid
R - CH_2 - O - SO_3 Na	R = C_{11-17} alkohol sulphate
R -CH_2 - O - (C_2 H_4 O)$_2$ -SO_3Na	R = C_{12-14} alkohol ether sulphate

Soap
Today, soap has no importance as detergent in modern textile production. The resistance against water hardness is very poor.

Akyl benzene sulphonate
The linear alkyl benzene sulphonates are mainly used in household detergents. Compared with alkane sulphonates they have a greater foaming tendency. Mostly, we find them as components in combination with nonionic surfactants.

Alkane sulphonates
These represent an important group within the anionic detergents. The chain-length of C_{14-16} have shown the best washing ability (3). A disadvantage is their foaming tendency. Therefore they often are combined with nonionic products to reduce the foam problem. The washing and emulsifying ability is excellent. From the environmental aspect, they are especially interesting, because they are the most readily biodegradable.

Fatty alkyl sulphonates
These have been the first large scale produced detergents, but because of very heavy foaming, they are not suitable for washing processes on modern machines.

Alkyl ether sulphates
These are relatively resistant to hardening substances and to alkaline. Their washing power is excellent already in low concentrations. But also their application is limited because of high foam tendency. They are environmentally acceptable.

Olefin sulphates
Depending on the chain length, these products also have foaming tendency, but some of them have good washing ability and good biogradability.

Nonionic detergents

Table 4.
Nonionic detergents.

$R - C_6H_4 - 0(CH_2 - CH_2 - 0)\ nH$	$R=C_{8-12}$ alkyl phenol ethoxylate n=5-10	
$R - CH_2 - 0 - (CH_2 - CH_2 - 0)\ nH$	$R=C_{10-18}$ alcohol ethoxylate	n=3-15

This group of products consists of a number of compounds with the hydrophilous chain of ethylene oxide in common, and as the hydrophobic part of the molecule, we find alkanols, alkyl phenols, fatty acids, fatty acid amides, and fatty amides.

Products which have gained importance in the textile industry include ethylene oxides with alkyl phenols and alkanols. The alkanols include native or synthetic fatty alcohols and oxy alcohols.

Depending on the ethylene oxide chain length, the nonionic surfactants are either liquid or wax-like compounds. The solutions of ethylene oxide addition products tend to demulsify and become turbid when they are heated. The optimum of washing effect is near the turbidity point very often between 40-60°C.

In the textile industry the nonionic surfactants play an important role, because of their high washing power and their excellent emulsifying ability.

Alkylphenol ethoxylates (APEO)
This had been the most important group within the nonionic surfactants. They are characterized by proper technological properties and economic advantages. It was obvious, after their environmental disadvantage had been discovered, that it would be difficult to find substitutes with equal good technological properties.

Fatty alcohol ethoxylates
These have been known for a long time, without getting any commercial importance. Their washing and emulsifying abilities have been judged lower than the APEO's.

Investigations have been made to find a connection between the chain length and the technological properties. The investigations included fatty alcohol ethoxylates with chain length from C_4 to C_{14} up to a degree of ethoxilation between 3 and 9. The wetting time, the foaming tendency and the washing efficiency were measured together with the emulsifying ability (3).

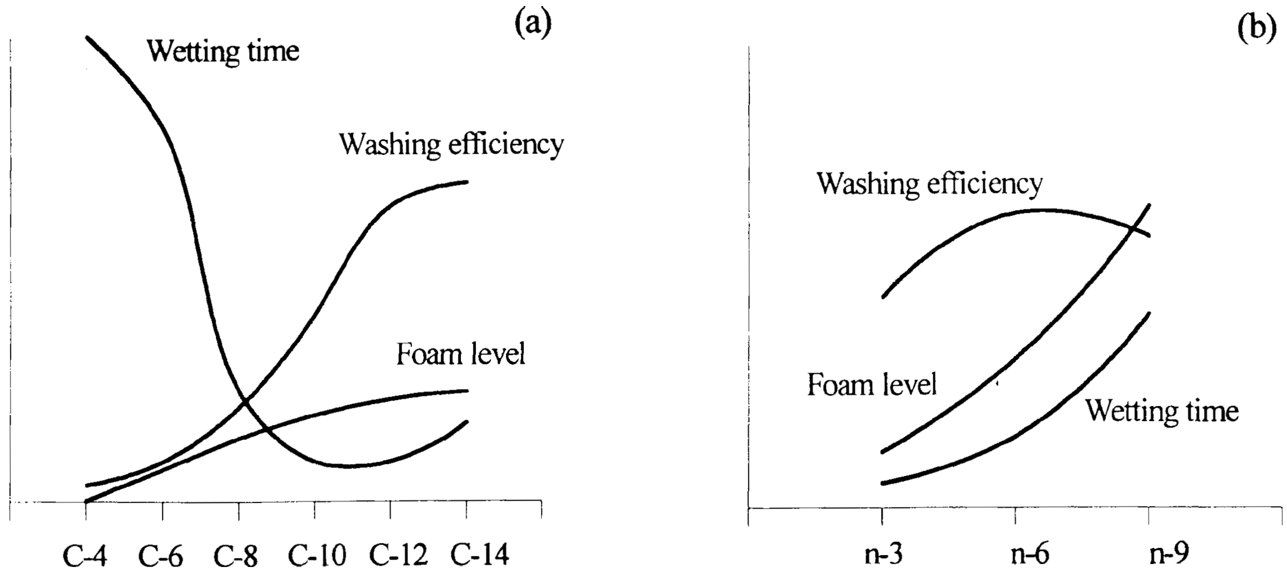


Figure 1.
Influence of chain length in alkyl group (a) and ethoxylate group (b) on detergent properties.

The conclusion was that fatty alcohol with chain length between C_9 and C_{12} have interesting properties. The influence of the degree of ethoxilation has also been examined as shown in the illustration.

Conclusion
As it was attempted to find the best possibilities to substitute the APEOs, it became clear that this will not be possible by a single product. However, the fatty alcohol ethoxylates in selected chain lengths are absolutely acceptable alternatives. They represent today the main group within the nonionic detergents for the textile industry. Very often, these detergents are synergetic mixtures of different alcohol ethoxylates, like for example Hostapal FA and Hostapal JET, which have good technological and ecotoxicological properties. However, it has become obvious that mixtures of fatty alcohol ethoxylates with selected anionic surfactants will result in products of higher quality.

The anionic component of the detergent mixtures used in the textile industry are mainly alkyl benzene sulphonate, alkane sulphonates like Leonil UM and olefin sulphonates.

Today, fatty alcohol ethoxylates in mixtures with anionic surfactants (e.g. LAS; linear alkyl benzene sulphonate) are used in commercial washing powder in Western Europe. However, further development in this field may be necessary and will be performed in the next years.

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3.4 Reclamation and re-use of process water from reactive dyeing of cotton

Henrik Wenzel, Hans Henrik Knudsen, Institute for Product Development, Denmark, Gert Holm Kristensen, VKI Institute for the Water Environment, Denmark and John Hansen, DTI Clothing and Textile.

Abstract

This paper presents Danish experiences with water reclamation and re-use in reactive dyeing of cotton. Experiences include development of new dyeing and rinsing recipes and of water reclamation techniques, leading to large savings in time, water, energy, and chemicals. Investigated water reclamation techniques are chemical precipitation, membrane filtration, activated carbon absorption, and counter current evaporation/condensation.

The advantages and limitations of each technique have been identified in lab-scale and documented in pilot-scale. An overall solution has been chosen, based on membrane technology for the rinsing water and activated carbon adsorption for the dye-bath itself. The solution implies hot water re-use in rinsing, re-use of filtration remanence in anaerobic digesters, and re-use of dye-bath water and salts. This solution is implemented as a small demonstration plant at a Danish cotton dye-house.

Introduction

A large Danish programme for water reclamation and re-use in the textile industry was initiated in 1992. The programme covers several applications of water reclamation techniques in textile dyeing and printing with the largest focus presently on dyeing of cotton. The programme is conducted by a Danish research group consisting of three institutions: the Institute for Product Development/Technical University of Denmark, VKI – Institute for the Water Environment, and DTI Clothing and Textile, and with participation of several textile companies.

The water generating process studied in this research is reactive dyeing of cotton knitwear in batch. This process is widely spread world-wide, and becoming increasingly used. Cotton represents approximately half of all textile world-wide, and nearly all cotton is today dyed by reactive dyes.

The overall strategy of the research has been to identify environmental improvements by a stepwise procedure:

1. Process optimisations and water savings.
2. Potential modernisations of dyeing equipment.
3. Chemical savings or substitutions.
4. Water reclamation and re-use of water, energy and chemicals.

This order of priorities should be respected as far as possible in order not to treat problems that could be avoided succesfully by process alterations.

Not respecting this order of priority could lead to wrong dimensioning of water reclamation equipment, and in the worst case, total misinvestment.

The strategy for the water reclamation research has been to introduce reclamation and re-use closely integrated in the dyeing process. This implies to work upstream, where water characteristics are still process specific, and not downstream, where substreams have been mixed and water characteristics represent an overall average. This strategy is believed to be optimal as long as large scale advantages and flexibility are not lost by the tight process integration. For the water types in reactive dyeing of cotton the strategy has been found very suitable, and our experience shows that it will result in the environmentally and economically optimal solution.

Furthermore, and not least important, the strategy has been to seek for re-use not only of water but also of the energy and chemical content in the water.

Recipes

In dyeing processes the *recipe* is the fundamental specification of the process. Water consumption, chemical consumption, temperature, salinity, pH, etc. are all specified by the recipe. Process water characteristics, therefore, are given by the recipe and the quality of the cotton.

A comprehensive investigation of recipes in reactive dyeing of cotton form the background for the research of optimisations and water re-use. The essential process water characteristics have been found to be: *dye-stuff content, salinity, temperature, COD (deriving from additives such as acetic acid, detergents and complexing agents), pH,* and to some extent *suspended solids incl. cotton fibres.* Essential points to the applicability of water reclamation techniques are:

Dye-stuff content

Reactive dyes are typically azo-based chromophores combined with different types of reactive groups (Ciba-Geigy, 1987). The relative large chromophores place reactive dyes in the molarweight area of 700-1000 g/mol. The reactive groups can be based on e.g dichlortriazin or vinyl sulphonic acid and will be negatively charged. Beside the reactive groups, other negatively charged groups are found, too, typically sulfonic acid groups. The reactive groups react with hydroxyl groups in the cellulose fibre during the dyeing reaction. However, a relatively large part of the reactive groups will react with water, leaving then the dye-stuff at an unreactive stage. Due to the properties of the chromophore, the dye-stuff is quite adsorptive to the cellulose, and the hydrolysed dye-stuff requires large amounts of water, preferably at high temperature, in the preceeding rinses to be washed out properly.

Salinity

Salinity in the dye-bath typically varies in the area of 40.000-80.000 mg/l. In the preceeding rinses, salinity will decrease typically by a factor 3 for the batchwise rinse and much more by the very water consuming »over flow« rinse.

Temperature

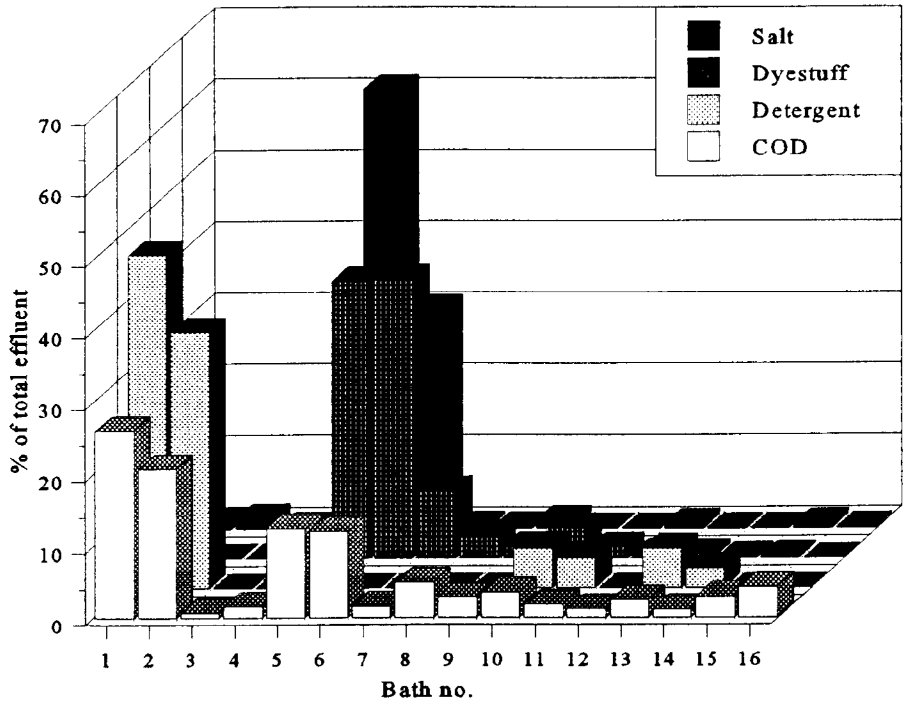
At pH above 10 and temperatures above 50-60°C certain types of reactive dye-stuffs are sensitive to breaking the established covalent bond to the cellulose. Therefore, the dye-bath (having pH >10) and the first batch rinse to follow need a temperature not higher than 50-60°C. After this first rinse a temperature of 90-95°C is preferable to the rinsing. For economical reasons some of the rinses are often kept colder.

Additives
Various kinds of dispersing and complexing agents are used in the rinsing and the last subsequent softening of the textile. Some of these have been found to be cationic and based on quaternary ammonium ions.

pH
Usually, pH is above 11 in the dye-bath, after which a neutralisation follows, typically by addition of acetic acid, or more seldom by dilution. After neutralisation and throughout the rinsing process, pH will not exceed 10.

A typical profile of the process water characteristics throughout the various batches of the recipe can look as illustrated in figure 1 (Knudsen and Wenzel, 1995).

Figure 1.
Typical process waters from batch recipes.



The research has shown that, from a water reclamation point of view, process waters should be divided into 3 types:

1. pre-treatment water (1-4)
2. dye-bath + first rinse (5-6)
3. rinsing water (7-16)

This implies that each water type will have its own specific characteristics giving optimal conditions for reclamation. Our research concerns type 2 and 3 only.

Our research on process optimisations and chemical savings or substitutions concerns improvements of the recipe examplified in figure 1. Comprehensive lab-scale, pilot-scale, and full-scale investigations have been carried out, involving a number of textile companies. It has been documented, that water consumption for rinsing can be reduced by 50%, provided hot water (90°C) is used throughout all rinsing baths. Detergents and complexing agents in rinsing can be left out completely, providing good pre-treatment and use of soft water for rinsing (Knudsen and Wenzel, 1994), as also shown earlier in the lab-scale (Fiebig 1989).

Thus, rinsing water characteristics may well be changed, and reclamation of hot rinsing water without content of detergents or complexing agents may well be the future task.

Water reclamation

Chemical precipitation

Removal of reactive dyes by precipitation with various precipitants has been shown possible by other researchers (Fiala et al., 1980), (Kolb et al. 1987), (Schulz et al., 1988), (Beckmann and Sewekow, 1991). On this basis advantages and limitations of techniques based on precipitation were sought in lab-scale and pilot-scale, and a number of metal salts and organic polymers were tested.

Table 1.
Overview of results from laboratory- and pilot-scale tests with chemical precipitation of reactive dye.

Precipitating agent	**Chemical composition**	**Dye removal**	**Dosage kg/kg dyestuff**	**Comments**
Organic polymers (10 compounds)	Cationic polymers of amines or amides with quaternary ammonium as active group	Very good	1-4	Accurate dosing is necessary. Both underdose and overdose lead to failing dye removal.
Polyaluminium-chloride (PAC) (9 compounds)	A polymer containing Al-, OH-, Cl-, and SO_4-groups.	Good	1-4 (~0.2 kg Al/kg dye)	Not all dye-stuffs are removed completely.
Iron sulphate and lime	$FeSO_4$ and $Ca(OH)_2$	Poor*	5-15 (as $FeSO_4$)	*Decompose dye-stuffs, but after some time they recompose!
Ironchloride mixture	$FeCl_3 + FeCl_2$	Not too good	–	Difficult to dose. Very pH-sensitive.
Alum. sulphate	$Al_2(SO_4)_3$	Poor	–	No effect on reactive red.

A total of 39 different dye-stuffs have been tested in synthetic process waters, as well as actual process waters. Organic polymers and PAC's have been proven most succesfull. They work in the pH range of 2-10, having lowest polymer consumption at low pH levels, but best flocculation/sedimentation properties at higher pH levels. Temperature optimum for precipitation were found in the area of 20-40°C with decreasing efficiency at higher temperatures, but for some polymers full dye removal could be seen till 70°C. Above this temperature, precipitation has its limitation. Increasing temperature and increasing salinity will increase the amount of precipitant needed, and for the high salinities seen in the dye-bath, precipitation becomes impossible. For the dye-bath, and maybe the first rinse, precipitation is thus not realistic.

The mechanism of polymer precipitation is establishment of an ionic bond to the negatively charged groups of the dye-stuff. Absorption on metal hydroxyl flocs gives only a poor removal, and the worst for the red dyes, for which e.g. $Al_2(SO_4)_3$ has no effect at all. Precipitation have been found to leave a certain amount of impurities from precipitants and dye-stuffs, and in some cases surplus precipitants, in the water phase. This would increase the need for fresh water renewal in case of re-circulation, or actuate the need of a secondary

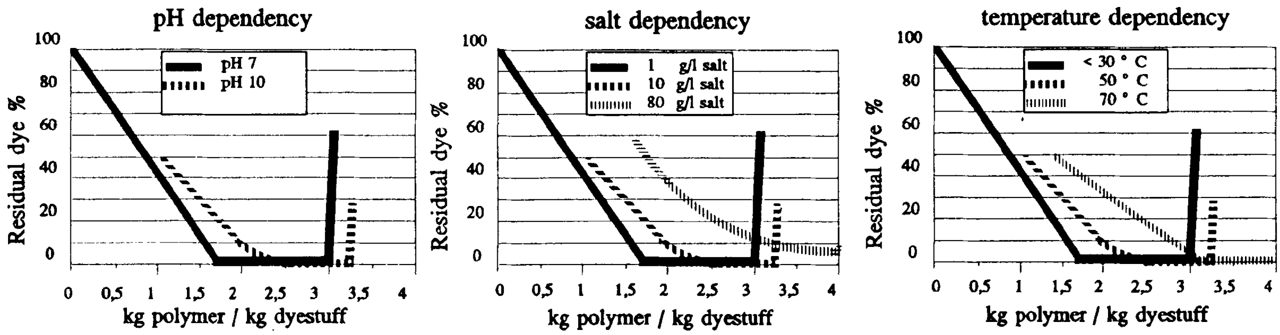


Figure 2.
The dependency of precipitatipitation on pH, salinity, and temperature.

treatment, e.g. by activated carbon. Flotation, filtration, and centrifugation have been tested for separation of precipitates (Thau, 1993), and a water quality of 2-3 mg/l of suspended solids can be achieved in first step separation by all techniques. An extra polish may be necessary for the re-use of the water.

Membrane filtration

Membrane filtration of process water in textile industry has been reported succesfull earlier (Gaeta and Fedele, 1991), (Erswell et al., 1988), the latter reporting research on process water from reactive dyeing. Our research focused on RO-, nanofiltration-, and tight ultrafiltration membranes, and a total of 10 different membranes were selected and tested. The general picture of the experiences can be illustrated as in table 2.

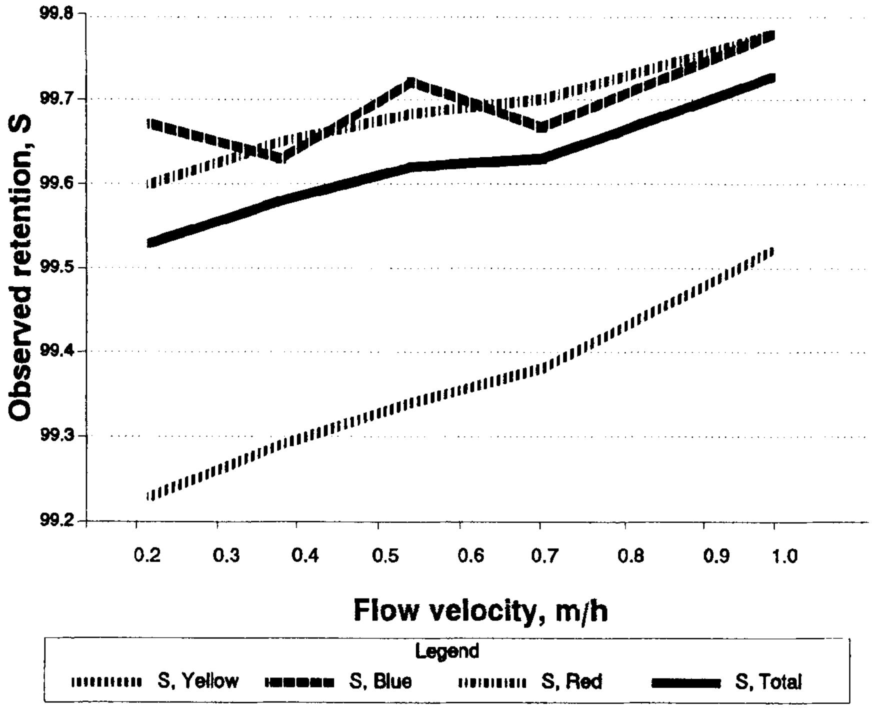
Polysulphone nanofiltration membranes having a negatively charged polyamide coating (presumably carboxylated) were found to have specifically high retentions and very high fluxes, presumably due to repulsion of the negatively charged dye-stuff molecules (Donan effect). Temperature dependency in the range from 20-90°C was tested, and temperature was found to increase flux and lower retention somewhat. Increasing salinity will decrease dye-stuff retention, presumably due to reduction of the Donan potential. Salinity in the magnitute of the dye-bath, thus, renders the tested nanofiltration membranes unsuitable because of dye-stuff penetration, and RO-membranes unsuitable because of too high trans membrane osmotic pressure. pH in the area of 2-11 is acceptable. Cationic detergents should be avoided, and quaternary ammonium ions will foul the membrane to a state of allmost complete destruction.

Table 2.
Overview of experiences from tests in laboratory and pilot-scale with 10 different membranes.

Membrane type	**Water flux**	**Dye removal**	**Salt removal (20°C)**	**Bulk concentration at visible bleed-through**
Ultrafiltration	Medium-High	95-99%	0%	40-200 mg/l
Nanofiltration	Medium-High	99.5-99.9%	10-20%	400-2000 mg/l
Rev. osmosis	Low	100%	100%	no visible bleed-through

Spiral wound membrane elements (4”, 6.4 m^2/element, 1.2 mm parallel spacer) were used for the rinsing water in the pilot-phase. Operation at 90°C was tested and optimal operation conditions investigated. A simple 5 µm cotton bag was used for prefiltration.

Figure 3.
Dye-stuff retention as a function of flow velocity across the membrane surface. (m^3 per hour per m^2 membrane = m/h)



It was found that operation at 90°C was possible without problems with telescoping of the elements at flow velocity 6.2 m^3/h pr. element (1m/h). Fluxes of 30 $1*m^{-2}*h^{-1}$ were optained at trans membrane pressure of 4,5 bars, and stable operation achieved. The dependency of dye-stuff retention on flow velocity was investigated, see figure 3, and an optimum of approx. 9 m^3/h pr. element (l.4 m/h) was calculated. This flow velocity, however, has not been investigated, and potential problems with telescoping at this high temperature and flow exist.

Activated carbon

12 different activated carbon products were tested, showing very different capacities, all but two, though, being able to remove dye-stuff completely. Adsorption capacities from lab-scale batch test in the range of 10 to >100 kg carbon/kg dye-stuff were found. In continuous operation in pilot-scale, giving higher concentration gradient for the adsorption, capacity was found to increase to 3-4 kg carbon/kg dye-stuff. The dye-stuff adsorption was positively affected by salinity presumably due to a reduction of the Donan potential, i.e. the repulsion forces between carboxyl groups on the carbon and the negatively charged groups on the dye-stuff molecules. High temperature increases capacity, and the content of detergents or complexing agents does not seem to reduce adsorption capacity towards dye-stuff. Activated carbon adsorption reclaims water and salt together, and extracts dye-stuff and COD.

Counter current Evaporation/condensation

As the process water contains only highly water soluble compounds with low vapour pressure, evaporation is technically feasible. The very high salinity of the dye-bath has, though, been a limit for the tested equipment, due to the increase of boiling point versus the capacity of the vacuum pump. Yet, evaporators exist that can operate in this area of salinity, too. However, costs are much higher than for membrane filtration with which evaporation must compete as application for the rinsing water. For the dye-bath evaporation does not allow for the salt content to be re-used as does activated carbon adsorption, making evaporation economically unfavourable. Evaporation reclaims water and leaves a residue of salt, dye-stuff, and COD together.

Advantages and limitations of the water reclamation techniques

Besides the above presented technical advantages and limitations of the water reclamation, water reclamation techniques, economical estimates were given on the basis of not binding offers from suppliers. Economical estimates are expressed as US$/$m^3$ of process water including both operation costs and investment costs amortized over 5 years. Only the water reclamation equipment is included, *not* buffer reservoirs, pipes etc. being equal for all solutions. Table 3 below gives the comparison in a total overview.

Table 3.
Comparison of 4 water reclamation techniques in reactive dyeing of cotton.

Waste-water characteristic	**Membrane filtration**	**Chemical precipitation**	**Activated carbon**	**Counte current evaporation**
Initial high dye concentration	0	0	+	0
High salt concentration	–	–	+	–
Detergents and other COD	–*	–	0	0
High temperature	+	–	0	+
pH	(2)-7-9-(10)	(2)-8-10	2-10	(2)-7-10
Costs	≈ 1 US$/$m^3$	≈ 1-2 US$/$m^3$	≈ 10-15 US$/$m^3$	≈ 10-15 US$/$m^3$

Signatures: 0 = not influenced significantly, + = positive influence, – = negative influence, * = specific compounds, e.g. cations, can influence negatively.

Surplus costs can be expected for chemical precipitation, as heat exchange and polishing of suspended solids and excess chemicals may be necessary. The costs estimates concern the rinsing water except for activated carbon, for which they concern the dye-bath.

Re-use of water, energy and chemicals

Two water types were reclaimed in pilot-scale: The dye-bath itself by activated carbon adsorption, and rinsing water by membrane filtration in the nano, and RO range.

Reclaimed dye-bath

Laboratory- and pilot-scale tests with dye-baths reclaimed after decolourization by activated carbon adsorption showed promising results. A number of recipes was tested showing that re-use of the warm saline and decoloured dye-baths was possible with no adverse effects on fabric colour or fastnesses. Not all types of recipes have, though, been tested, and problematic recipes may exist. Both the water, the energy content and the very high content of salts are utilized again by this option.

Reclaimed rinsing water

The rinsing water reclaimed by membrane filtration was tested on a number of recipes and used succesfully for rinsing in all. The hot water re-use speeds the rinsing process up by a factor of 2 compared to the traditional recipes, thus saving 50% of the time consumption for rinsing, and thereby increasing production capacity of the equipment. Both the water and its energy content are utilized again by this option.

Remanence from reclamation of rinsing water

Anaerobic digestion of remanences from reclamation of rinsing water was tested in laboratory scale reactors. A possible re-use of the remanences is to convert the remanence dye-stuff to biogas through co-digestion in municipal WWTP digesters together with municipal sewage sludge. The experimental programme covered four digesters operated in parallel.

One digester was operated as a reference digester fed with municipal sewage sludge. The three parallel digesters were operated with a mixture of municipal sewage sludge and up to 20% by volume of metal salt dye-stuff precipate, polymer dye-stuff precipate, and membrane filtered dye-stuff concentrate, respectively.

The results from the experimental work showed that the digesters fed with dye-stuff remanences performed with similar COD reduction and gas production as the reference digester fed with sewage sludge alone. Thus no disturbance of the anaerobic digestion could be detected.

The experimental work was also tested for breakdown and possible redissolution of dye-stuff during the anaerobic treatment. In figure 4 are shown results from spectrophotometric scanning measurements of filtered feed samples and filtered effluent samples from the digesters. From the figure (left) it can be seen that in the *feed* samples no dye-stuff was present in the dissolved phase, except for the feed containing membrane remanence, which as expected showed significant amounts of dissolved dye-stuff.

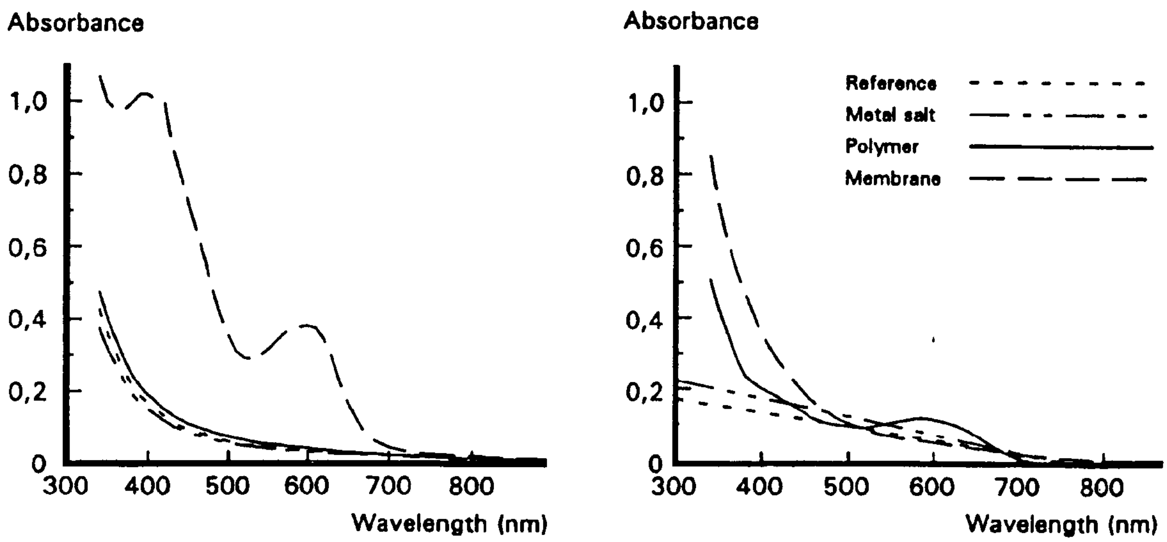


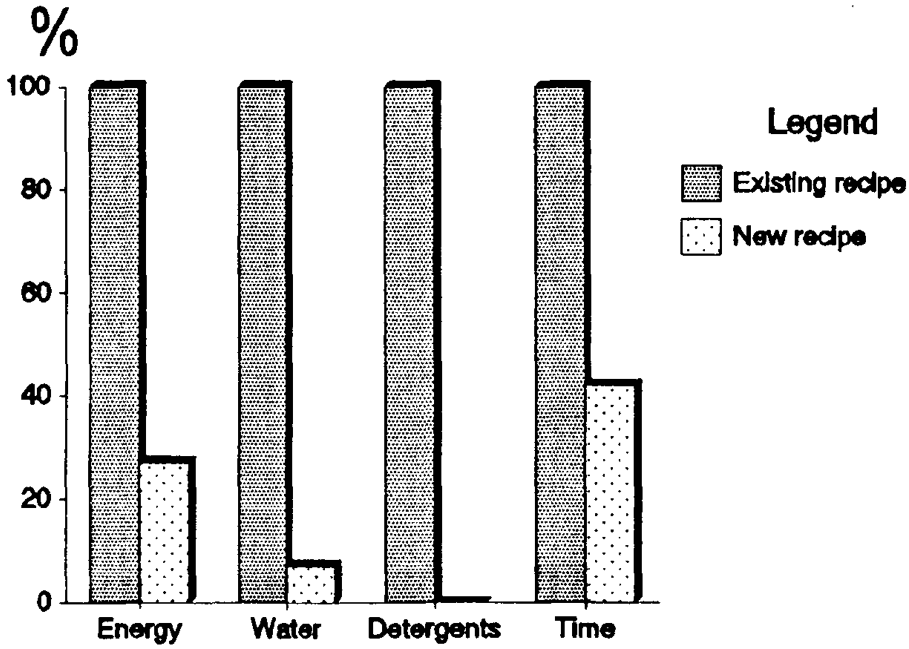
Figure 4.
Results from spectrophotometric scanning measurements of filtered digester feeds (left) and filtered digester effluents (right).

From figure 4 it can be seen that no dissolved dye-stuff was found in the filtered *effluent* samples, except for the sample from the digester fed with polymer precipitate, in which a small concentration of dissolved dye-stuff could be observed. The dissolved dye-stuff in the membrane remanence thus was degraded through the anaerobic digestion. The small amount of dye-stuff observed in the effluent from the digester fed with polymer precipitate indicated release of some precipitated dye-stuff caused by degradation of the applied polymer. The released dye-stuff concentration is small and will be invisible when possibly returned into the sewage with the reject after sludge dewatering.

Environmental benefits

For reclamation and re-use of the rinsing water a comparative study of the environmental impacts *before* and *after* rinsing water re-use has been carried out. The study concerns a re-use solution based on membrane filtration. All changes in use of water, energy, and chemicals are included in the study, including also the membrane plant, reservoirs etc. from raw material extraction, to production, use, and disposal of the equipment (Seilund and Nielsen, 1994). This study is a so-called life-cycle assessment of the solution, performed according to intentional practice (Consoli et al., 1993), (Wenzel et al., 1996). The study concerns *only* environmental impacts from the rinsing process.

Figure 5.
Environmental benefits of introducing new rinsing recipe.



Conclusions

The optimal solution has been found to be to separate the process water in two water types: 1) dye-bath + the first rinse, and 2) rinsing water.

Dye-bath can be reclaimed by adsorption of dye-stuff and COD on activated carbon, and re-use of the reclaimed dye-bath, including salt content, has proven possible both in pilot-scale and full-scale studies. The economic value of the salt content of the dye-bath is equal to the cost for reclamation, rendering the solution economically feasible.

Recipes for rinsing can be altered to leave out dispersing and complexing agents completely, provided that pre-treatment is well performed, and provided that soft water is used for the rinsing.

The rinsing water can be reclaimed by membrane filtration in the nano and RO range and re-used for rinsing purposes. Operation at 90°C has been shown feasible giving very high fluxes and allowing for direct hot water reclamation and re-use without supplementary heat exchange. Hot water re-use speeds up the rinsing process by a factor of 2 compared to the conventional recipe, thus increasing production capacity of the equipment substantially. A life-cycle assessment has shown, that environmental improvements by such a new recipe based on hot water reclamation and re-use by membrane filtration are large.

The savings due to water and energy re-use are much larger than the costs for investment and operation of the membrane plant giving a simple pay-back time of 1-2 years for Danish conditions (1996).

The increased productivity due to the time savings is even more profitable, and if this is incalculated, the pay-back time will be less than one year.

Dye-stuffs in remanences from membrane filtration are degraded in anaerobic digestion with no negative influence on performance of the digester.

A demonstration plant based on these solutions has been established at a Danish cotton dye-house, and its succesfull operation has been demonstrated.

Acknowledgement
The project for water reclamation and re-use in cotton dyeing is sponsored by the Danish Council for Recycling and Cleaner Technology. We would especially like to acknowledge the programme chairman Ulla Ringbaek for making the project possible and for her constructive comments and kind help.

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3.5 Reclamation of reactive dyeing process water by chemical precipitation

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Reactive dyeing of cotton
Reactive dyeing of cotton is the most common wet treatment of textile processes world-wide. Today batch dyeing is dominating and increasing.

Batch processes typically take place in a jet machine, where both the liquor and textile are circulated to reach a quick process performance.

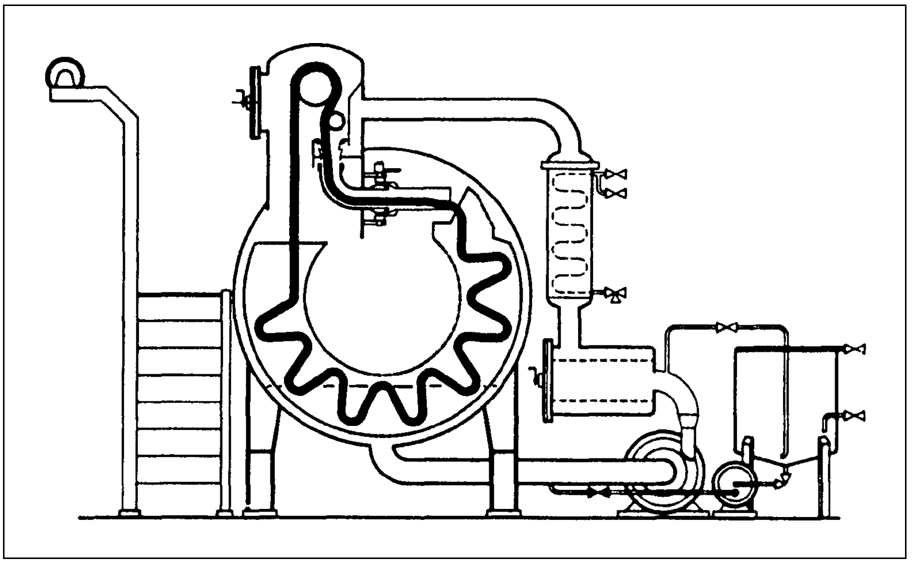


Figure 1.
Vald. Henriksen Jet.

Reactive dye-stuffs have utilization degrees of 60-90%. The remaining dye-stuff hydrolysate has to be washed out during a rinse and, thus, ends up in the waste-water.

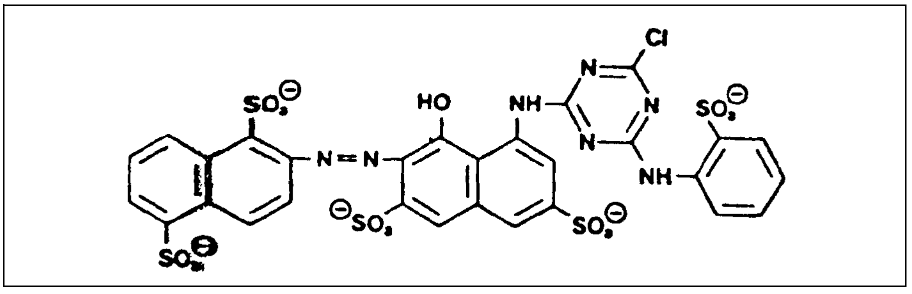


Figure 2.
A reactive dye-stuff.

Reactive dye-stuffs consist of chromofore and reactive components. Chromofores are the coloured part of the molecule, typical an azo group between aromatic groups, each carrying anionic sulfonic acid functional groups. The reactive are typical triazine, pyrimidine or sulfatoethylsulphone.

Process water

Essential for the application of water reclamation technique is:

- Dye-stuff content

typically varies between 0,5-1 g/l in dye-baths.

- Salinity

typically varies between 40.000-80.000 mg/l. In the preceeding rinse salinity will decrease by a factor 3 in each batch rinse.

- Temperature

the dye-bath and first batch rinse need a temperature >50-60°C, the following rinse a temperature of 90-95°C.

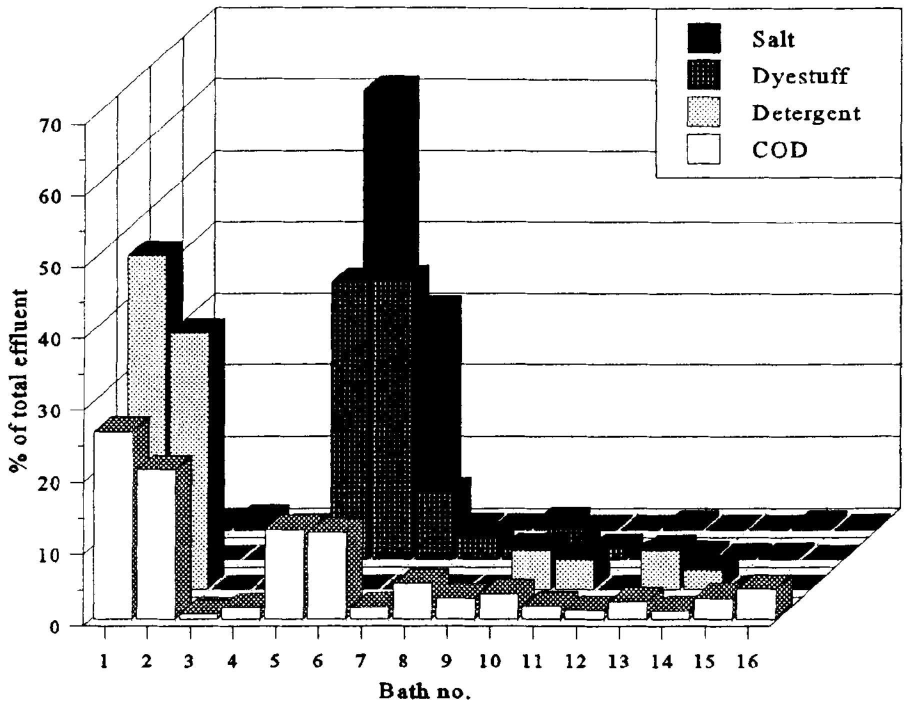
- Additives

process water contains dispersing and complexing agents

- pH

typically >11 in the dye-bath, followed by neutralisation with addition of acetic acid. After neutralisation pH will not be above 10.

Figure 3.
Typical process water from batch recipes.



Chemical precipitation

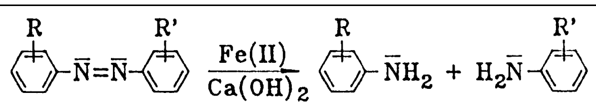
Adsorption on metal salt hydrolysates

The mechanism in the precipitation with aluminium compounds, as $Al_2(SO_4)_3$ and ironsalts, as $FeCl_3$, is formation of large metal hydrolysates and entrainment of adsorbable compounds.

Decomposition by Fe(II)

$Fe(II)/Ca(OH)_2$ decomposes azodyes by a reduction reaction. Lime is dosed to reach pH at 9, and the hydroxides sedimentates under entrainment of the decomposed dye-stuffs.

Figure 4.
Dye-stuff decomposition by $Fe(II)/Ca(OH)_2$.



Organic polymers

Organic polymers with quaternary ammonium as active group form heavly soluble salts with reactive dye-stuffs. The chains form bridges between the salts. The resulting effect is both precipitation and coagulation.

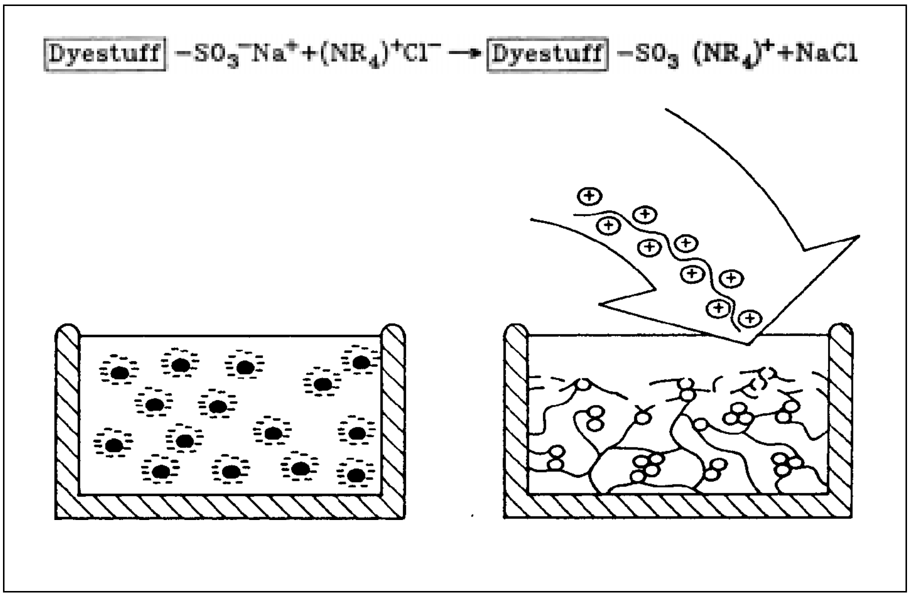


Figure 5.
Dye-stuff precipitation/coagulation by organic polymers.

PACs

Polyaluminiumchlorides (PAC) with aluminium ions as active groups are able to precipitate and coagulate the reactive dye-stuffs by the same mechanism.

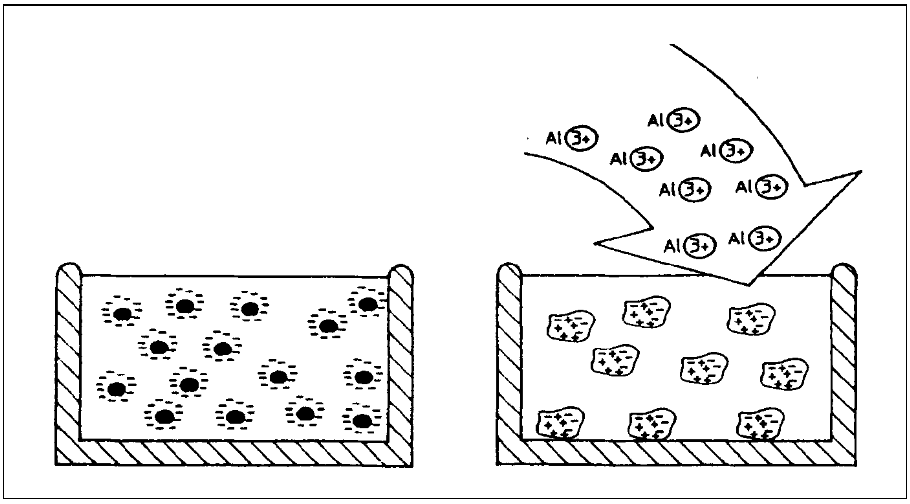


Figure 6.
Dye-stuff precipitation/coagulation by polyaluminiumchlorides (PACs).

Table 1.

Selected chemical for delcolouring of process water.

Trade name	Precipitant	Producer	Effect
Iron chloride	metal salt	Kemira, Sweden	Entrainment
Aluminium sulphate	metal salt	Kemira, Sweden	Entrainment
Ferrosulfat-heptahy-drate/lime	metal salt	E. Merck, Germany	Reductive decomposition/ entrainm.
Magnafloc 1597®	cationic organic polymer	Allied Colloids, England	Coagulation of anion components
Superfloc C 577®	cationic organic polymer	Cyanamid, USA	Coagulation of anion components
Magnafloc 1797*	cationic organic polymer	Allied Colloids, England	Coagulation of anion components
Levafloc R®	cationic organic polymer	Bayer, Germany	Coagulation of anion components
Colfloc RD®*	cationic organic polymer	Ciba-Geigy AG, Switzerland	Coagulation of anion components
Magnafloc 1597®	cationic organic polymer	Allied Colloids, England	Coagulation of anion components
Plex 3026 L®	cationic organic polymer	Röhm, Germany	Coagulation of anion components
Rohafloc KF 945®	cationic organic polymer	Röhm, Germany	Coagulation of anion components
Rohafloc KL- 915®	cationic organic polymer	Röhm, Germany	Coagulation of anion components
Praestol 185 K®	cationic organic polymer	Stockhausen, Germany	Coagulation of anion components
Polysinth PAC 200®	PAC, 5% w/w AI	HWT, Germany	Coagulation of anion components
Polysinth PAC 2000®	PAC, 10% w/w AI	HWT, Germany	Coagulation of anion components
Sachtoklar®	PAC, 5.2% w/w AI	Sachtleben Kemie, Germany	Coagulation of anion components
M 36®	PAC, 9,4% w/w AI	Kemira, Sweden	Coagulation of anion components
M 142®	PAC, 5,3% w/w AI	Kemira, Sweden	Coagulation of anion components
PAX XL 1®	PAC, 5,3% w/w AI	Kemira, Sweden	Coagulation of anion components
UPAX 6	PAC, 8,7% w/w AI	Kemira, Sweden	Coagulation of anion components
UPAX 10	PAC, 11,5% w/w AI	Kemira, Sweden	Coagulation of anion components
UPAX 12	PAC, 5,2% w/w AI	Kemira, Sweden	Coagulation of anion components

* Specialized polymers developed especially for precipitation of reactive dye-stuff hydrolysates.

Lab-scale tests
Precipitation test were carried out in synthetic composed process water.

Reactive dye-stuffs were hydrolysed according to the following conditions:

Table 2.
Conditions for hydrolysation of reactive dye-stuffs before precipitation tests.

Dye-stuff concentration	2 g/l
Temperatur	80°C
pH	11
Time of hydrolysis	2 hours

Process water from representative recipies was classified in 6 types and the coloured water types were tested with selected precipitants.

A total of 39 different reactive dye-stuffs were tested in synthetic and actual process water.

Jar-test equipment with 6 mechanically connected stirrers and variable speed was used for precipitation experiments.

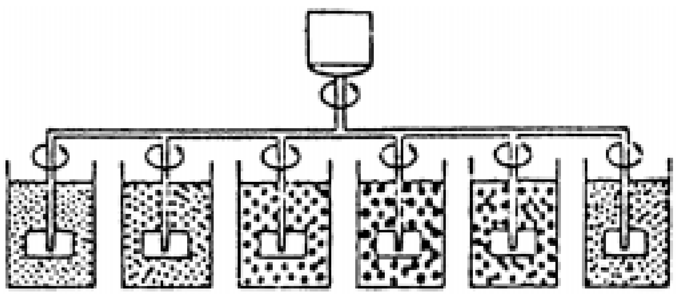


Figure 7.
Jar-tester.

For each dye-stuff a concentration standard series was produced. Conditions of the Lambert-Beer equation were fulfilled in the absorbance analysis.

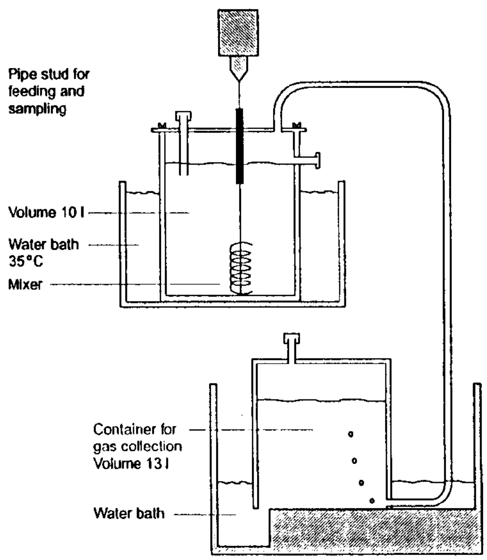


Figure 8.
Lab-scale anaerob digester.

Anaerobic digestions of precipitates were tested in lab-scale digesters. Digestion was performed as co-digestions with municipal sewage sludge. Three digesters were operated in parallel. One as reference with municipal sewage sludge, two with a mixture of municipal sewage sludge and chemically precipitated dye-stuff. Up to 20% by volume of metal salt dye-stuff precipitate and polymer dye-stuff precipitate respectively were added to the municipal sewage sludge.

Precipitation results

The tests show that $FeSO_4/Ca(OH)_2$, PAC and some coagulation polymers are suitable.

$FeSO_4/Ca(OH)_2$ precipitation could decolourize all the hydrolysate solutions, but dye-stuff molecules could to some extent recombine in the filtrate after some time. Dye-stuff was thus found in the filtrate and were accordingly not totally precipitated with the hydroxides.

The PACs could decolourize the hydrolysate solutions for almost all tested dye-stuffs. The decolorization was negatively influenced by increased concentrations of salts. By 1 g/l NaCl a reduced decolourization could be observed. The presence of anionic additives in the process water increased the consumption of PAC dramatically. An advantage was the relatively low price of the PACs.

The three specific products, developed particularly for precipitation of reative dye-stuff hydrolysates (Magnafloc 1797®, Levafloc R® and Colfloc RD®), differed from the other coagulating polymers by having a wide dosing interval giving full dye-stuff removal.

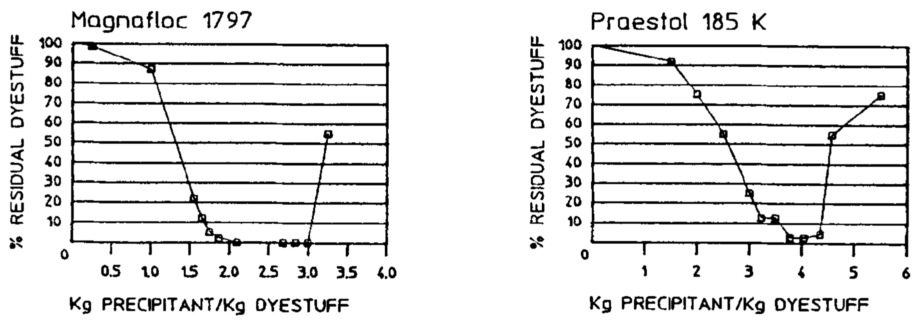


Figure 9.
Profiles for dye-stuff precipitation for the polymers specialized for reactive dye-stuff precipitation (here respesented by Magnafloc 1797®) and other polymers (here respesented by Praestol 185K®)

Organic polymers work in the pH range of 2-10, having the lowest polymer consumption at low pH levels but best flocculations/sedimentation properties at higher pH levels. Temperature optimum for precipitation was found between 20-40°C with decreasing efficiency at higher temperatures, but for some polymers full dye removal could be seen at 70°C. Above this temperature, precipitation has its limitations. Increasing temperature and increasing salinity will increase the amount of precipitant needed, and for the high salinities seen in dye-bath, precipitation becomes impossible. For the dye-bath, and maybe the first rinse, precipitation is thus not realistic.

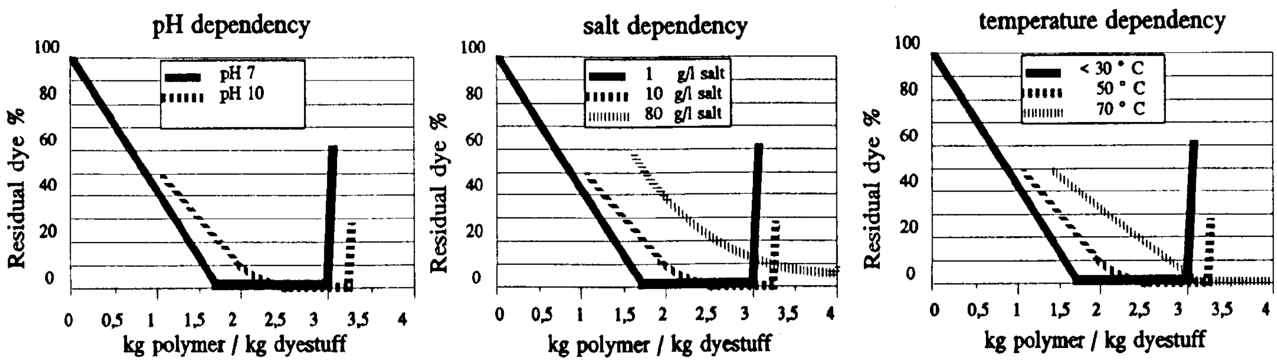


Figure 10.
Polymer precipitation dependency on pH, salinity and temperature.

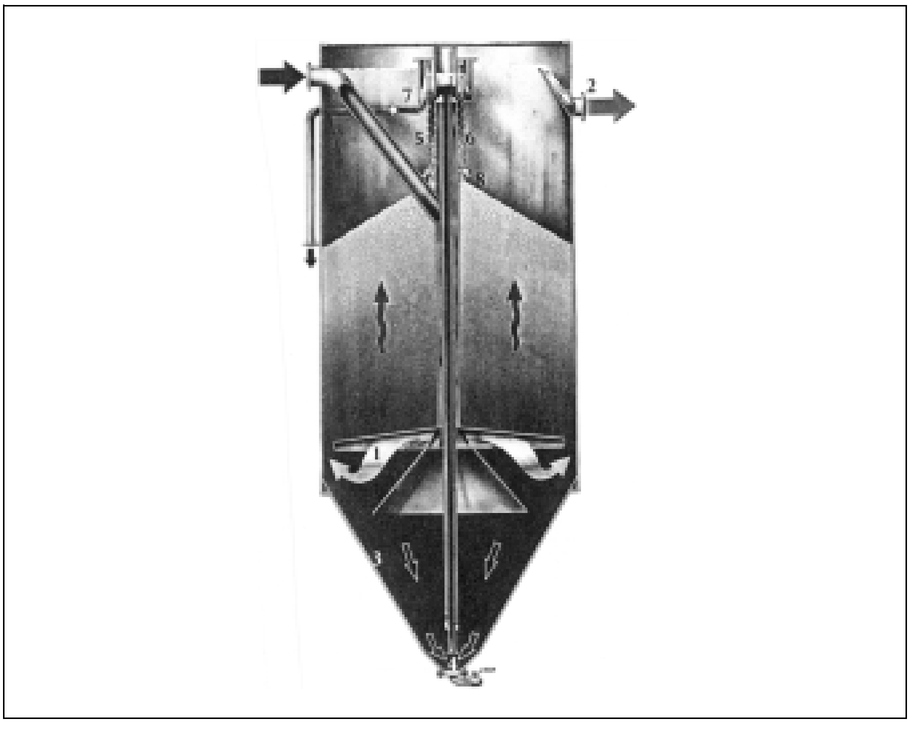
Demonstration plants
Flocculation, precipitation, filtration, flotation and centrifugation have been tested in pilot-scale for concentrating and dewatering the suspended precipitates. A reduction in suspended solids of 99-99.5% is possible.

Flocculation with very high-molecular anionic polymers at a level of 2-5 ppm quickly gathered the suspended precipitates and flocculated within few minutes with a very low level of suspended solids in the water. Further more, high-molecular anionic polymers precipitate the cationic coagulation polymers, whereby a surplus, if present, will flocculate out of the water.

Based on pilot-tests, a DynaSand contact filtration system was installed to decolourize the biologically treated waste-water at Martensens Fabrik A/S. Designed waste-water flow is 4.000 m^3/day, but the flow can be as low as 1.000 m^3/day.

The system comprises five DynaSand units and a flow-proportional in-line addition of one of the specialized organic polymers.

Figure 11.
A DynaSand filter.



Conclusions

The optimal use of chemicals can be reached when dozing PAC successively followed by one of the specialized organic polymers and finally dozing a very high-molecular anionic polymer.

The organic polymers can be used alone, but are more expensive.

A spiral tube with inline mixers for dozing and mixing the chemicals and a sandfilter can decolourize the waste-water for about 1-2 US $\$/m^3$.

Through laboratory-scale experiments it was demonstrated, that a possible way of reusing the chemically precipitated dye-stuff would be to transport it to the municipal WVTP, and dose it into the digester for co-digestion together with the municipal sewage sludge.

Attention must be taken not to overdose organic polymers. The decolouring effect decreases by overdosing and the organic polymers have a high fish toxicity.

References

Wenzel, H., Knudsen, H.H., Kristensen, G.H., Hansen, J. Reclamation and re-use of process water from reactive dyeing of cotton. Desalination, 1995.

3.6 Re-use of treated dye-bath after reactive dyeing at a Danish dye-house, Martensens Fabrik

John Hansen, DTI Clothing and Textile, Denmark

Abstract
Spent dye-bath is treated with activated carbon in order to remove residual dye-stuffs and other organic chemicals. The treated water is re-used for the new dye-bath including its content of salt, alkali and energy.

Lab-scale tests with activated carbon
The objective of these tests were to find the best types of activated carbon for this purpose. 12 different brands were tested in jar-tests. 4 Cibacron C or F dyes were used: Navy, Orange, Yellow and Red.

The results can briefly be summarized as follows:

- All the investigated reactive dyes can be removed using a proper amount of activated carbon
- No environmentally harmful substances are introduced
- Salt enhances the dye-adsorption on the activated carbon
- Detergents and other organic chemicals are removed
- The adsorption can be run at any temperature

The method is, however, in general relatively expensive and should thus only be preferred when membrane filtration or other techniques are not feasible. This is the case with the dye-bath because of its very high salinity, The activated carbon adsorption is not negatively influenced by the salinity and furthermore allows for re-use of the salt. These advantages cannot be met by any of the other reclamation techniques and they outweigh the excess cost for activated carbon.

Lab dyeing tests with water treated with activated carbon
In a lab dyeing machine a large number of dyeing processes were tested, using waste-water from previous dyeing processes treated with activated carbon and in all cases in comparison to a normal dyeing process using normal process water.

For each test-dyeing the results as well as fastness tests (rub, wash) were assessed.

Good results were obtained with the following dye-stuffs:

- Cibacron C, E and F
- Drimaren X and B
- Remazol
- Sumifix Supra

The conclusion based on lab-scale results was that waste-water from reactive dyeing of cellulose can be treated with activated carbon to an extent, that the purified water can be re-used for the dye-bath with its content of salt, some alkali and energy. The results, however needed verification on a larger scale, and subsequently semifull-scale and full-scale tests were therefore conducted.

Semi-full-scale activated carbon treatment plant

Investigations were carried out with a semi-full-scale activated carbon treatment plant, comprising two 400 1 serial tanks and working with a capacity of 400 l/h. Retention time, thus, 1 h per tank.

More than 10 m^3 have been run through the plant without reaching the adsorption capacity of the carbon.

Full-scale test dyeings

A series of test dyeings have been carried out at the dye-house on small but ordinary production machines. Approx. 25 kg of cotton knitwear were dyed with a liquor ratio of between 1:14 and 1:16.

The water for the dye-baths came from former exhausted dye-baths plus some first rinsing baths after a treatment in the activated carbon plant.

The following types of dye-stuffs were used:

- Remazol
- Cibacron C and F
- Drimaren X

In all cases, the results of the dyeings were tested by the dye-house staff. In all cases the dyeings were accepted and normal fastness levels were reached. The lots were delivered to – and accepted by – the custumers.

As the purified waste-water to be used as process water contains salt and alkali, measurements must be carried out of salinity and pH before adjusting the amounts of salt and alkali.

Typical amounts and savings are shown below:

	Normal procedure g/l	**Test procedure g/1**	**Savings g/1**
Salt	80	72	8
Soda	5	0	5
NaOH	2	2	0

In these cases the treated water contained a lot of rinsing water from the first rinse which is the reason for the relatively low savings in salt consumption. Normally this saving would be much larger.

As the treated water is already heated, there will also be a considerable saving in energy and production time.

3.7 Savings and substitutions in textile dyeing

Henrik Ellerbæk, Kemotextil, Ltd. Denmark

The Danish company Kemotextil was established in 1968 and is a medium sized commission dyer situated in Denmark. The company has 28 employees, 18 working in a two-shift production. The land on which the company is based, was bought from the local authorities under the conditions that the municipality had to receive and rinse the company’s waste-water, supply fresh water and electricity, all of course against payment.

In 1982 Kemotextil obtained an environmental approval from the Danish authorities. The approval describes the company’s production in detail, e.g. daily working hours, noise level inside and outside the building, the contents of chemicals in the waste-water, emissions to air from buildings and drying machines, and all other waste arising from the production.

In 1986 Kemotextil decided to reduce the amount of water, energy and chemicals used in production. The consumption at this time was approx. 140,000 m^3 water per year. In the dye-house there were 36 winch dyeing machines, 4 jet and 4 beam dyeing machines. Dyeing production was about 3.5-4 tons per day. In the following two years experiments were made with different production processes to optimize production and at the same time reduce resource consumption. In 1988 approx. 20 winch dyeing machines were taken out of production, and instead production on the jet- and beam dyeing machines was increased. Until 1990 almost all machines were replaced with new jet dyeing machines. From 1986 to 1988 the company saved 18% electricity and 22% water. From 1988 to 1989 another 17% electricity and 15% water relative to the 1986 consumption. On to 1995 the winch dyeing machines were replaced with 9 high technology jet dyeing machines from Thies in Germany. The machines in question are Rotostream and Eco-soft jet dyeing machines and the total savings from 1986 to 1995 are: electricity 39%, water and waste-water 60%, fuel for steam production 46%, dye-stuff and chemicals 20%, other purchases 32%, wages 27% and other costs 16%.

To reach these results, Kemotextil changed the machine controlling system from PLC based controllers to microprocessor-based controllers (PC computer systems). The change was implemented to make the system more user friendly in programming and handling. Each machine has its own Personal Computer, which again is connected to a central computer from which the dyeing machines are programmed and controlled.

Each recipe is put together by several modules, all in all approx. 50 different modules, and each recipe is carried out by putting together 1, 2, 3, or 4 modules including the adding system. The dye-stuff and chemicals are added automatically by the computer, either liniary or logarithmically into the dyeing machine from the adding tank.

The company’s investment in dyeing machines and equipment amounts to approx. 2.5 millions US $. So far, the company has not made any investments which did not recover the expenses fully within months or few years.

During the period from 1992 to 1995, the company has been involved in the RECIPE and MEMTEX projects, headed by the Institute for Product Development, and financed by the Danish Environmental Protection Agency and the participating companies. In the RECIPE project, the aim has been to reduce water, waste-water, chemicals, and substituting chemicals.

In Kemotextil's newest Thies Roto Stream machines, the liquor ratio is 1:5 on 100% cottons, and on the older Roto Stream and Eco Soft machines from 1984 and 1985, the liquor ratio is 1:8. Before being involved in the RECIPE project, the dyeing ratio was 1:10. Today (1995), the company has abandoned overflow rinsing. Rinsing is only done between two different levels, or as considered the best way, by adding fresh water through a flow-meter, which is built into the machine. Consequently, the optimal use reduces the consumption of water. The ratio 1:5 and 1:8 are used in every single bath during the whole process.

During pre-treatment of the fabric, the use of water is 2 baths. When dyeing, the use of water is 2 baths. In rinsing light shades, the use of water is 4 baths and possible 1 bath for softening. In medium and dark shades, 5 baths, of water are used and possible 1 for softening.

Total use is:

Pre treatment	**Dyeing**	**After treatment Light colours**	**Medium and dark colours**
2 baths	2 baths	4 to 5 baths	5 to 6 baths
Pre treatment	New bath	Rinse cold 10 min.	Rinse cold 10 min.
Rinse	Dyeing	Rinse cold 10 min.	Rinse 60 C 10 min.
		Rinse 90 C 10 min.	Rinse 90 C 10 min.
		Rinse cold 10 min.	Rinse 60 C 10 min.
		Possible softening	Rinse cold 10 min.
			Possible softening

Light shades use between 8 and 9 baths, depending on whether they undergo softening or not. Ratio of 1:5 to 1:8 depending on the type of dyeing machine. Total consumption of water is between 40 and 72 litres per kilogram of fabric. Medium to dark shades use 9-10 baths, depending on whether they undergo softening or not. Ratio 1:5 or 1.8, depending on the type of dying machine. Total water consumption is between 45 litres and 80 litres per kilogram fabric.

There are of course variations with lower and higher consumptions of water per kilogram of fabric if the dye-lot is too small to fit into the optimal loading capacity of the machine.

During pre-treatment detergent and soda were previouly used. Today (1995) 1 gram/liter sequesttants are added to avoid transport of calcium to the different later baths and to secure the lowest possible water hardness in the process.

In the dyeing process, because of the low water hardness, 75% of the sequesttants, which are Beiquest from CHT, are saved and they are biologically degradable.

In the after treatment (the rinsing) only water, but no detergents or other chemicals are used. It is noted that washing fastness is 0,5 higher than before, where detergents were used.

No acid is used to neutralize the fabric. After 4-6 different baths, the fabric is found to be neutral and free from salt.

The dye-stuffs used are Cibacron C for medium and dark colours, and Cibabron LS for the light to medium colours. The Cibacron C dyes have a normal consumption of salt, and the Cibacron LS dyes have a consumption of only 20% salt compared with the Cibacron C.

At present (1995), no foamkillers are used, but a lot of hard work with recipes, processes, dye-stuffs, and chemicals was done before reaching this goal.

In 1986 the percentage of errors in dyeing was 7.8%, in 1994 2.3% and the goal for 1995 is 1.5%.

The consumption of water in 1994 was 92 litres per kilogram dyed fabric.

3.8 Environmental labelling

John Hansen, DTI Clothing and Textile, Denmark.

Introduction

The growing interest in society for protecting the environment against the impact from industrial exploitation of resources as well as production has, among other things, implied the creation of a number of labelling systems for consumer products.

One of the first was the »Blue Angel« in Germany, although no textile products have been given this label, as textile products have been considered too complicated.

Labelling systems also exist in a number of countries such as Japan, Canada and Austria. The Nordic Council of Ministers in 1990 adopted a voluntary environmental labelling system, known as the »Swan label«.

This paper will briefly present a number of labelling systems, introduced either by companies, associations or nations. Finally the EU eco-labelling scheme will be presented.

Company-based labelling systems

Today a large number of company-based labelling systems exist and new ones are introduced regularly. Only a few will be mentioned here.

In Denmark, the company Novotex some years ago introduced their »Green Cotton« concept, for which they have been awarded several national and international environmental prizes.

The company Steilmann in Germany has been working with environmental labelling of their products.

The American company Esprit introduced in 1991 an »ecollection«.

These company-based systems, thus introduced a more overall way of looking at textile production – the so-called cradle-to-grave concept or Life-Cycle Assessment (LCA) – instead of just looking at a few aspects for a given product.

Association-based labelling systems

A number of association-based systems have been introduced within the last 4-5 years.

For textile floor coverings (carpets) the Association for Environmentally Friendly Carpets, GuT (Gemeinschaft umweitfreundlicher Teppichboden), was established in Germany in 1990.

Up until now about 84 carpet manufacturers from most of Europe have become members, and about 48 companies supplying raw materials to the industry are supporting members.

To become a member, a manufaturer must apply for membership. Then a controller will look over the production, which has to live up to certain standards.

To be able to use the GuT-label the carpets have to pass the following tests:

- Test for content of pollutants:

Pentachlorophenol content
Formaldehyde emission
Pesticide content
Butadiene emission
Vinyl chloride emission

- Test for emissions of odoriferous components:

Toluene
Styrene
Vinyl cyclohexene
4-Phenyl cyclohexene
Aromatic hydrocarbons
Volatile organic substances

- Odour test

More information can be given by the GuT-secretariat:

GuT
Hergelsbendenstrasse 49
D-52080 Aachen
phone: +49 241 96 7901 fax: +49 241 96 79222

A more general labelling system for textile products has been established by the Austrian Texile Institute (ÖTI) together with Research Institute Hohenstein (FIH) in Germany. They have created Oeko-Tex (International Association for Research and Testing in the Field of Textile Ecology). A number of standards relating to different textile products have been published:

- 101 Textile fabrics for clothing with the exception of baby clothing
- 102 Accessories for clothing with the exception of baby clothing
- 103 Clothing with the exception of baby clothing
- 104 Textile fabrics for baby clothing
- 105 Accessories for baby clothing
- 106 Baby clothing
- 107 Textile floor coverings
- 108 Textile wall coverings (tapestry)
- 109 Furnishing fabrics and curtains
- 110 Upholstery fabrics
- 111 Textile blankets and cushions
- 112 Textile fabrics for bed clothes
- 113 Mattresses
- 114 Household textiles
- 115 Spun fibres and initial products used for manufacturing of textile fabrics in industry and trade
- 116 Leather clothing with the exception of baby clothing
- 200 Test methods

The products to be labelled with the Oeko-Tex label have to meet certain requirements for the following parameters:

- pH
- Formaldehyde release
- Heavy metal content (Hg, Cu, Cr, Co and Ni)
- Pesticide content
- PCP content
- Content of certain carcinogenic dye-stuffs
- Colour fastness

It must be emphasized that the Oeko-Tex criteria primarily provide consumer safety and only indirectly improve environmental relations.

Today 12 textile institutes all over Europe are members of Oeko-Tex. More information can be given by one of the institutes or by the secretariat:

Testex
Gotthardstrasse 6l
Postfach 585
CH-8027 Zürich
phone: +41 1 201 17 18 fax: +41 1 202 55 27

A number of similar systems, MST and MUT, have lately merged with Oeko-Tex, which for the moment, clearly is the dominating system. Moreover the founding members have launched the Eco-Tex Consortium, which will establish an Oeko-Tex standard 1.000 for certifying processes instead of products. This system will, when operational, have large positive environmental impact, as it deals with limits for discharges in the form of waste-water, exhaust-air and solid waste.

The American Textile Manufacturers Institute (ATMI) has since 1992 been running a voluntary eco-label/eco-audit scheme, entitled Encouraging Environmental Excellence (E3). This system is however restricted to members of ATMI.

National labelling systems
The Nordic »Swan label« in 1994 issued 2 sets of criteria for textile products, one for floor coverings, and one for textiles in general.

The Swedish Society for Nature Conservation in 1995 issued a criteria document for an eco-label for »Good Environmental Choice« (Bra Miljöval) for textiles.

The Dutch Department for the Environment (Stichting Milieukeur) in 1995 issued a certification schedule for textiles/clothes.

The EU eco-label award scheme
In Brussels, on March 23rd 1992, the EEC Council of Ministers adopted a regulation for a community eco-label award scheme.

The regulation states, that the specific ecological criteria for a product group shall be established using a cradle-to-grave approach.

In 1992 the Danish Environmental Protection Agency offered to convene the establishment of criteria for some textile products.

After consultations with industry, it was decided to work with two concrete product groups: T-shirts and bed linen. The first part of the work considered a very stringent definition of the product groups, also including the types of fibres to be included. Based upon a market analysis, both product groups were restricted to include cotton and polyester/cotton products.

The next part of the work considered a very detailed inventory regarding the product groups, that is, a description of all the different production stages from cotton growing and polyester production over yarn spinning to knitting or weaving, dyeing, finishing, use (including washing/drying) and final disposal. For the different production stages, all possible environmental impacts are outlined, as stated in the Regulation through its Indicative Assessment Matrix.

The inventory was used to identify key features from which a set of draft criteria were issued. These draft criteria have been intensively discussed and altered during the last 2 years, and a final criteria document was circulated for voting by the Member States in 1996. The criteria were formally approved at a meeting of the Eco-label Regulatory Committee and published as a Commission Decision on 22 April 1996, in the Official Journal No L 116/30.

Environmental management systems

In 1992 British Standards Institution (BSI) issued a specification for Environmental Management Systems, BS 7750:1992. The standard shares common management system principles with BS 5750 (EN 29000, ISO 9000), the European and internationally recognized quality systems standard.

At the same time the European Commission was preparing an eco-audit scheme, which was formally adopted in June 1993. Sometimes known as EMAS, the voluntary scheme has been in force for more than 3 years, and a number of companies are working towards establishing a system which can be certified. As an example, it can be mentioned, that two Danish textile companies already have received a certificate.

Within ISO, work has just been finallized with the aim of creating a standard (ISO 14000) based upon BS 7750, as also was the case for ISO 9000 and BS 5750.

As BS 7750 is a very general standard, it could be recommendable to have sector application guides. The Commission have supported such work in a number of cases, e.g. work is, for the moment, going on regarding the carpet industry, led by GuT. The draft guide-lines are currently being tested at selected carpet mills. Euratex are having similar plans for other sectors of the textile and clothing industry.

It can be foreseen, that environmental labelling and environmental management, including published environmental audits, will become a major demand on our industry in the years to come, both from customers and authorities.

3.9 Improvement of the rinsing efficiency in batch processing in the textile industry

Mr. Erik Henningsen, Vald. Henriksen AIS, Denmark and Mr. Aage Jensen, Vald. Henriksen A/S, Denmark

For the widely used batch dyeing machines, jigger and jet, it has theoretically been possible to achieve savings in water consumption and process time. With support from the Danish Environmental Protection Agency, Vald. Henriksen A/S has investigated the possibilities. The project was carried out in co-operation with IPU and DTI in connection with the programme for cleaner technology in the textile and clothing industry, whose goal is to reduce the outlet of polluted water with 30% before the year 2000.

Background

By far, the largest amount of water is used in connection with rinsing after washing or dyeing. Theoretically, great potential for savings exists, but so far it has only been possible in continuous processing and the trend is towards batch processing – also in Denmark.

A combination of the two systems – batch/continuous – is used to a certain extent, for instance, continuous pre-treatment within jigger dyeing and continuous washing after jet dyeing, but this implies a lot of handling, considerable investments, and planning is rendered difficult. The most common batch dyeing machines are jigger and jet, and for both types of machines, great savings were proved in the project »Nordtextil« when using rinsing in steps instead of by overflow. For jiggers, the most favourable method was spray rinsing.

Since then, the removal of liquid by suction has become a much used technique, and the advantages of a combination of spray rinsing/suction seem evident.

The jet dyeing machines are primarily used for the dyeing of knitwear in rope form. The advantages of liquor removal are obvious, due to the large amount of water which is contained in the fabric. However, the method is not appropriate, as knitwear in rope form cannot support neither squeezing, nor suction. However, in the known continuous washing machines for fabric in rope form, good results are achieved when the fabric in rope form is spread out by air before the squeezing. In jet winches today, a spreading device by air is used for expanding, to avoid crease marks and to obtain a nice looking fabric. It is, therefore obvious to fit such a jet winch with a suitable squeezing device, and to combine it with a spray rinsing system.

Purpose

The purpose of the project was to develop and manufacture a jigger with suction and spray rinsing, and to fit a jet winch with a squeezing device.

The machines were to be installed in a Danish dye-house and realistic trials were to be performed to document the possible savings when using the present technology.

Jigger

In 1995, the trial machine was installed in a dye-house, and extensive investigations were done by two engineer students as a graduate project. The principle provided the expected savings, and based on the good results, the machine was modified in such a way that further improvements could be achieved in respect to the rinsing efficiency and productivity.

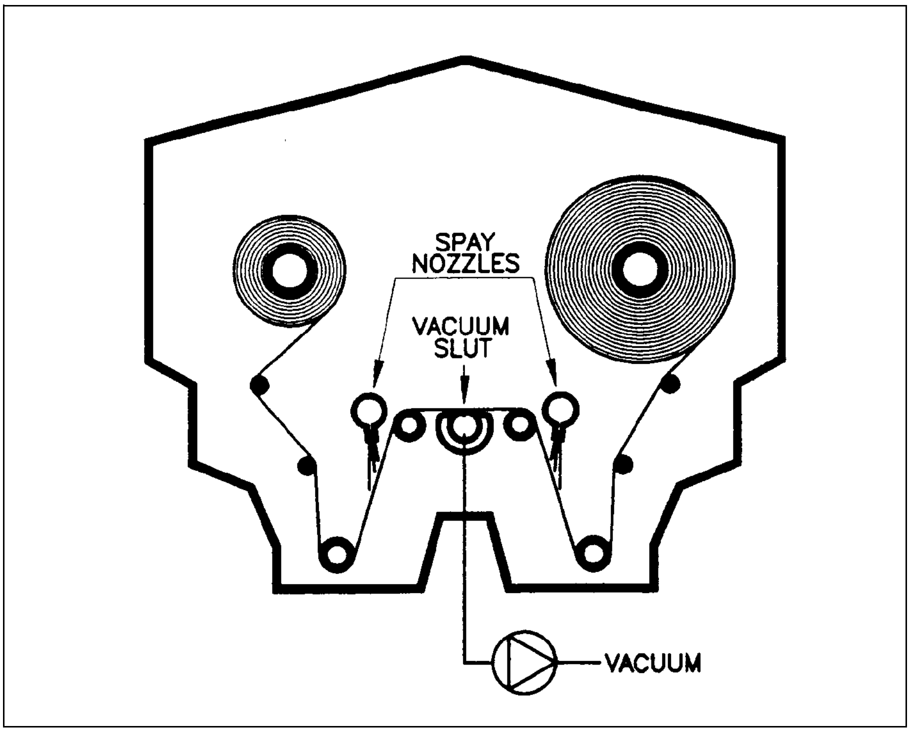


Figure 1.
Drawing of a jigger,
© Valdm. Henriksen A/S.

Result – Jigger

Upon completion of the modification of the machine DTI Clothing and Textile carried out trials dated 95.10.03 and 95.10.05, report no. 350-4-0220.

Table 1.
Documentation of savings in water consumption and process time on VH VACU-JIG 1200/2000 compared to conventional jiggers.

Improved procedure	**Standard procedure**
Neutralization, 1 pass suction, spraying. Water consumption: 1030 L or 1,6 L/kg Time consumption: 17 min.	Neutralization, 1 pass. Water consumption: 1560 L or 2,5 L/kg Time consumption: 17 min.
Soaping 80°C, 1 pass suction, spraying. Water consumption: 820 L or 1,3 L/kg Time consumption: 20 min.	Neutralization, 1 pass. Water consumption: 1560 L or 2,5 L/kg Time consumption: 17 min.
Soaping 80°C, 1 pass suction, spraying. Water consumption: 470 L or 0,8 L/kg Time consumption: 19 min.	Soaping 95°C, 2 passes. Water consumption: 1560 L or 2,5 L/kg Time consumption: 35 min.
Soaping 80°C, 1 pass suction, spraying. Water consumption: 80 L or 0,8 L/kg Time consumption: 19 min.	Soaping 95°C, 2 passes. Water consumption: 1560 L or 2,5 L/kg Time consumption: 35 min.
Cold rinse, 1 pass suction, spraying. Water consumption: 740 L or 1,2 L/kg Time consumption: 18 min.	Cold overflow rinse, 2 passes. Water consumption: 1400 L or 22,4 L/kg Time consumption: 35 min.
Water consumption: 3540 L or 5,7 L/kg.	**Water consumption: 20240 L or 32,4 L/kg.**
Time consumption: 93 min.	**Time consumption: 139 min.**

As can be seen, the test passes resulted in water savings of 16.700 L or 82,5%. At the same time 3 passes were saved or 46 minutes or 33%. A copy of the report is available with Vald. Henriksen A/S.

Jet
A Dynawin jet was bought from Fong's Nat. Eng. Co. Ltd. After fitting of a squeezing device at Vald. Henriksen A/S, the machine was installed in a dye-house and trials were carried out.

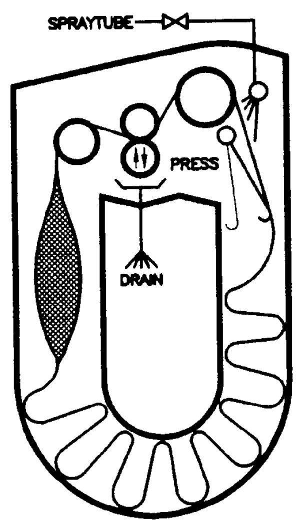


Figure 2.
Drawing of a jet.
© Valdm. Henriksen A/S.

Result – Jet
Trials were performed by DTI Clothing and Textile dated 95. 10. 10 report no. 350-4-0220.

Table 2.
Documentation of savings in water consumption and process time on Henriksen/Fong's Dynawash 1T2 compared to conventional jets or winches.

Improved procedure	**Standard procedure**
Cold rinse, squeeze, spray. Water consumption: 2000 L or 19,6 L/kg Time consumption: 15 min.	Cold overflow rinse. Water consumption: 3000 L or 30 L/kg Time consumption: 10 min.
Neutralization 40°C. Water consumption: 600 L or 6 L/kg Time consumption: 10 min.	Cold overflow rinse. Water consumption: 3000 L or 30 L/kg Time consumption: 10 min.
Cold rinse, squeeze, spray. Water consumption: 1200 L or 12 L/kg Time consumption 10 min.	Neutralization 40°C. Water consumption: 1000 L or 10 L/kg Time consumption: 25 min.
80°C rinse. Water consumption: 600 L or 6 L/kg Time consumption: 10 min.	Cold overflow rinse. Water consumption: 3000 L or 30 L/kg Time consumption: 10 min.
Soaping 95°C. Water consumption: 600 L or 6 L/kg Time consumption: 30 min.	80°C rinse. Water consumption: 1000 L or 10 L/kg Time consumption: 15 min.
Cold rinse, squeeze, spray. Water consumption: 1300 L or 13 L/kg Time consumption: 10 min.	Soaping 95°C. Water consumption: 1000 L or 10 L/kg Time consumption: 25 min.
80°C rinse. Water consumption: 600 L or 6 L/kg Time consumption: 10 min	Soaping 95°C. Water consumption: 1000 L or 10 L/kg Time consumption: 25 min.
Softening 40°C Water consumption: 600 L or 6 L/kg Time consumption: 20 min.	Cold overflow rinse Water consumption: 3000 L or 30 L/kg Time consumption: 10 min.
	80°C rinse Water consumption: 1000 L or 10 L/kg Time consumption: 15 min.
	Softening 40°C Water consumption: 1000 L or 10 L/kg Time consumption: 20 min.
Water consumption: 7500 L or 75 L/kg	**Water consumption: 18000 L or 180 L/kg**
Time consumption: 115 min.	**Time consumption: 165 min.**

As it can be seen, the new process results in water savings of 10.500 L or 58%, as well as a time saving of 50 min. or 30%.

Futher development
Both machines were presented at ITMA'95 and were the focus of great interest. The Vacu-Jigger was presented in a 2 baths version, which gives further process possibilities.

With the carrying out of this project it is proven that extensive savings in water are possible when dyeing in batch on jet and jigger. With our Vacu-Jigger Henriksen can add another machine to our jigger programme which also includes a patented dosing system and a patented HighSpeed process.

Part 4.
Implementation projects

4.1 Introduction

On the basis of the surveys and on the expressed preferences by industry on the seminars, three demonstration projects have been selected and started:

- Extended Counter Current Operation in Continuous Processes
- Implementation of Cleaner Technology in Batch Dyeing of Cotton
- Savings and Substitutions of Hazardous Chemicals

The three projects contain some of the most promising cleaner technology options and they all represent a very high probability of success. They are selected to spread the possibilities for technology transfer as far out in the textile and other related industries as possible. The three projects include and affect both the textile industry, the industry which supplies the textile industry with machines and chemicals and the public authorities being responsible for environmental protection.

The first project has at this time successfully been carried through at the factory Z.P.B. Bielbaw S.A. by an independent grant from the Danish Environmental Protection Agency (EPA). The project were finalized in 1996 and the results are accessible in a report from the Danish EPA called »Extended Counter Current Operation in Continuous Processes«.

The second project has been granted from the Danish EPA in May 1995. The title is »Cotton dye-house, Teofilow, Poland. Implementation of Cleaner Technology and Water Re-use«. The project is ongoing with very promising results, and is planned to end in 1997.

The project »Savings and Substitutions of Hazardous Chemicals« has been applied for, and concession has been given by the Danish EPA in 1997.

For all three projects contents and status are described in the following papers.

4.2 Extended Counter Current Operation in Continuous Processes

Z.P.B. Bielbaw S.A., Poland

Henrik Birch[1] and Henrik Wenzel, Institute for Product Development, Denmark,[1)] now employed at VKI-Institute for the Water Environment, Denmark.

Background description

The present project technology has been developed and implemented to establish counter current operation in a continuous machine at the company Z.P.B. Bielbaw S.A. In this continuous machine, textile fabric is continuously treated by passing it in a row of consecutive, water containing compartments. The fabric is guided through the machine by rollers in a way that fabric is submerged several times in each compartment, with an intermediate squeezing out of water.

Different processes may take place in continuous machines, all of which are usually followed by a rinse process as a last or intermediate process to remove unwanted components in the fabric. Rinse water is continuously added to maintain a satisfying fabric and rinse water quality in the compartment, and as a consequence, an according discharge of spent rinse water is let out of the compartment.

A rinse process in a continuous machine typically takes place in more consecutive compartments, and the way of adding rinse water has been of special interest for this project. In all new machines the entire amount of rinse water is added to the compartment in which fabric is finally rinsed. Spent rinse water effluent from this compartment is then fed to the preceding rinse compartment and so forth. A rinse process operated this way is called counter current rinse, because the rinse water flow is opposite to the direction of fabric movement.

In older machines, however, rinse water is added and discharged separately to and from each rinse compartment, as these are all situated at the same horizontal level. This rinse procedure is much more water consuming than counter current rinse.

Counter current rinse in modern machines is mostly achieved by a simple gravitational flow, the rinse compartments being vertically displaced to each other. Reconstruction of older machines to operate in counter current mode by gravitational flow is considered technically unrealistic, because the entire machine has to be reconstructed if existing horizontal compartments have to be vertically displaced.

The cleaner technology principle

To implement counter current operation in older machines, some kind of pumping from compartment to compartment has to be made. Pumping by conventional technology, however, did not seem immediately applicable (price, means of control, operational reliability, dry running, clogging). Thus, it was decided to develop and implement so called air lift pumps, which in theory from many points of view seemed advantageous. The principle of operation for an air lift pump is simply, that by injecting air to a water filled vertical pipe, the water column will expand. Water will flow out of the upper end of the pipe, and a continued pumping is achieved when displaced water is replaced by more water going in to the lower, submerged end of the pumping pipe.

Implementation and tests

After an initial visit to the Polish case company Bielbaw, dimensional criteria for a pump were agreed (pump capacity, lifting heights etc.). On this background, a prototype pump was developed and tested in Denmark, followed by a successful hydraulic test on the Bielbaw machine.

Subsequently, five more pumps were constructed in Denmark, and technicians at Bielbaw prepared the machine for the implementation of the first six pumps. This preparation – especially construction of the air supply system – did not interfere with normal production, and welding on outlet manifolds to compartments could take place at ordinary productional stops.

The six air lift pumps were installed in a single day, and the machine was ready for a counter current test in 7 out of 15 compartinents. A series of tests were made, each concerning different recipes (textile type, type of process). In each test the water flow was gradually reduced until the limit at which a satisfactory fabric quality was still met. It was observed, that only one quarter of the normal rinse water amount was necessary to obtain usual textile quality, when operating in counter current.

After this successful full-scale test, technicians at Bielbaw constructed and implemented the remaining number of pumps for complete counter current operation. From that time (August 1995), the machine has solely been operated in counter current mode, and the implemented pump system has in this period proven highly operationally reliable. Thus, no maintenance at all has taken place, except from a periodical exchange of an air filter on the suction side of the air fan.

Environmental and economic benefits

From operational data before and after the change to counter current mode, savings in water and energy have been estimated to 100.000 m^3 of water and 2.600 tons of coal per year on this machine alone. These savings correspond to value of approximately 1.4 mio. DKK per year. These savings are to be compared to a total investment cost of approximately 0.1 mio. DKK, thus giving a simple pay-back time of less than one month. Bielbaw has subsequently started reconstruction of another machine having approximately twice the saving potential as the case machine, implying a possible annual saving of 200.000 m^3 of water and 5.000 tons of coal, corresponding to a value of approximately 2.8 mio. DKK per year.

The obtained savings imply several environmental improvements. The obtained fresh water saving has reduced exploitation of scarce ground water resources, the reduced combustion of low quality coal has implied better local air quality and a reduction in emission of carbondioxide (greenhouse gas). Furthermore, a reduction in the amount of discharged waste-water may improve the performance of the municipal waste-water treatment plant.

Dissemination potential

As a final activity in this project, a seminar at Bielbaw was organized and companies with machines similar to the Bielbaw machine were invited. After the seminar it was accounted from questionnaires, that in 8 out of 10 companies a total of 19 machines with a reconstruction potential exist.

4.3 Cotton Dye-house Teofilów, Poland. Implementation of Cleaner Technology and Water Re-use

Claus Christensen, RINSE, Industrial Water Management, Denmark

This project was established based on experiences with similar Danish projects, and it is based on a cleaner technology approach. According to this way of thinking, the possibilities of reducing material consumption and load on the environment, e.g. by choice of recipes and equipment, should be examined before installation of equipment for water re-use. The projects are, therefore carried through according to the following strategy for seeking improvements:

- Optimisation
- Modernisation
- Chemical savings and substitution
- Water treatment for re-use

Project decription

Project partners

The project partners are RINSE ApS (project leader), Institute for Product Development, Denmark, VKI-Institute for the Water Environment. Denmark, DTI Clothing and Textile, Denmark and Textile Research Institute, Poland. Financing of the project was granted by the Division for Environmental Assistance to Eastern Europe of the Danish Environmental Protection Agency in May 1995.

The project is divided into the following main phases based on the strategy above:

Project phases

Phase 1. Recipes
Phase 2. Modernisation of equipment
Phase 3. Water treatment and re-use
Phase 4. Evaluation and reporting
Phase 5. Demonstration seminar
Phase 6. Full-scale membrane plant

Below is given a short presentation of the phases and the preliminary results.

Phase 1

A number of typical dyeing recipes were collected in order to evaluate if unnecessary or unnecessarily hazardous chemicals were used and if the physical parameters, e.g. rinsing method and temperature, were optimal.

Based on this, two proposals for alternative recipes were elaborated to avoid these hazardous chemicals, to optimise the process and to regard the fact that it must be possible subsequently to treat the water in a membrane filter in order for the water to be re-used.

The new recipes were tested in a laboratory scale at the Textile Research Institute, and the results were tested with respect to colour, shade and fastness. The results were satisfactory.

Besides the dyeings themselves, tests were made for neutralisation with other agents than the most commonly used acetic acid.

Selected recipes were then tested in full-scale in the dye-house of Teofilów, and the results were to a high extent in accordance with the laboratory results.

Phase 2

As preparation to the pilot-scale testing of Phase 4, the existing dyeing equipment was examined and an extra outlet was mounted in order to tap rinsing water for treatment in a pilot plant with membrane filter.

The dye-house is divided into an old and a new section. At project start it was expected that the old machines in the old dye-house would be replaced by modern machines due to an expected increase in production. This has, however, not happened yet, and a disproportionate level of water is used in the old ineffective machines. The old machines ought to be replaced by new ones, however, it is being evaluated if it would be more profitable to build a larger membrane filter plant for the rinsing water in order to reduce the water consumption until the financial situation allows a replacement of machines.

The machines within the new sector are top modern, however, they are not all being used optimally. We are trying to solve this problem.

Phase 3a-3c

After going through the recipes, a number of typical rinsing water types were selected. A laboratory membrane filter was used in tests of these water types of filtration on different membranes, with both nano-filters and reverse osmosis-filters. The choice of membrane was based on Danish experiences from a similar project.

The results were satisfactory. No surprises were discovered in respect of destroyed membranes due to the chemicals used and flux rates as a function of pressure, temperature and degree of concentration were satisfactory,

A pilot-scale membrane filter using standard membrane filter cartridges was installed at the company. A series of tests with rinsing water from different cotton dyeings, with the use of different types of membranes at different pressures and temperatures was made. The results are satisfactory and will be used for dimensioning a full-scale membrane filter for the dye-house.

At the beginning of the project it was expected that dyeing of polyester and mix of cotton-polyester would be strongly reduced during the coming years so that these products would amount to less than 20% of the total production. This has turned out not to be the case at least till now. Todays production is divided in 50% cotton, 30% cotton-polyester and 20% polyester. It has, therefore, been urgent to investigate the possibility of re-using rinsing water from the polyester dyeings, even though this is not included in the original project definition, which covered only cotton dyeings. After finishing the planned pilot tests with rinsing water from cotton, the employees from Teofilów have continued making pilot tests with guidance from the Textile Research Institute. The preliminary results are promising, and we soon expect to be able to decide if the full-scale membrane filter should also be dimensioned to handle this water type.

Phase 3d

While Phase 1 and 2 are directed towards reduction of both water and chemical consumption, the membrane filtration is directed towards reduction of the remaining water and energy consumption. The membrane filter separates the rinsing water in water, which can be re-used and in a concentrate which contains the same amount of dry matter, only more concentrated. The dry matter will not be degraded or eliminated during membrane filtration.

The project does include only limited resources for investigating the possibilities for disposal of this concentrate.

When the projects were elaborated, it was known that the concentrate of dye-stuff used could be digested biologically in an anaerobic digester. Such a digester was under establishment at the municipal waste-water treatment plant in Lodz. In order not to depend solely on this solution, we investigate the possibility of using the so called »Advanced Oxidation Process« (AOP), which is based on the use of combination of ozone, hydrogen peroxide and UV-light, to oxidize the waste material partially or completely. In literature we find good results with partial destruction of the exhausted dye-stuff, before the water is led to an aerobic biological treatment plant.

Phase 4

The results will be included in a total evaluation, along with a technical-financial calculation of the consequences of installing a membrane filter plant with necessary auxiliary equipment for re-use of rinsing water from the dyeing processes. This phase is expected to be finished during December 1996 and it should then be decided if Phase 7: Full-scale Membrane Plant should be implemented.

According to the project agreement with Teofilów, the dye-house is obliged to finance half of the membrane plant (limited by a maximum amount however), if the result of the report will be that the plant is profitable.

Phase 5

The results have been presented to the Polish textile dyeing-houses at a demonstration seminar, which was held at the Teofilów factory on 22-23 January, 1997. At this seminar, the pilot plant was demonstrated in operation.

4.4 Savings and substitution of environmentally hazardous chemicals

Technology Transfer to Polish Chemical Producers and Demonstration of New Recipies in Polish Dye-houses

John Hansen, DTI, Clothing and Textile, Denmark

During the technology transfer programme a number of cases has been revealed, where chemicals are used which are harmful to the environment.

These are used because of their technical performance and the low price. The chemicals are often produced by Polish chemical producers, and are in some cases of a type which have an environmentally bad reputation, i.e. detergents based on APEO, fixation agents for direct dyes based on formaldehyde, reactive dyes with relatively low fixation rates.

For the textile finishing companies questions about water are of major concern – rational use of water and waste-water treatment. Textile waste-water can contain a large number of environmentally harmful substances, such as:

- inorganic ions (chloride, sulfate, sulfite and sulfide)
- heavy metal ions
- detergents
- dye-stuffs
- acids and bases
- reduction and oxidation chemicals
- certain finishing chemicals

Below, a number of possible substitution projects is listed, which have been discussed with the participating companies and agreed upon at the seminar and later.

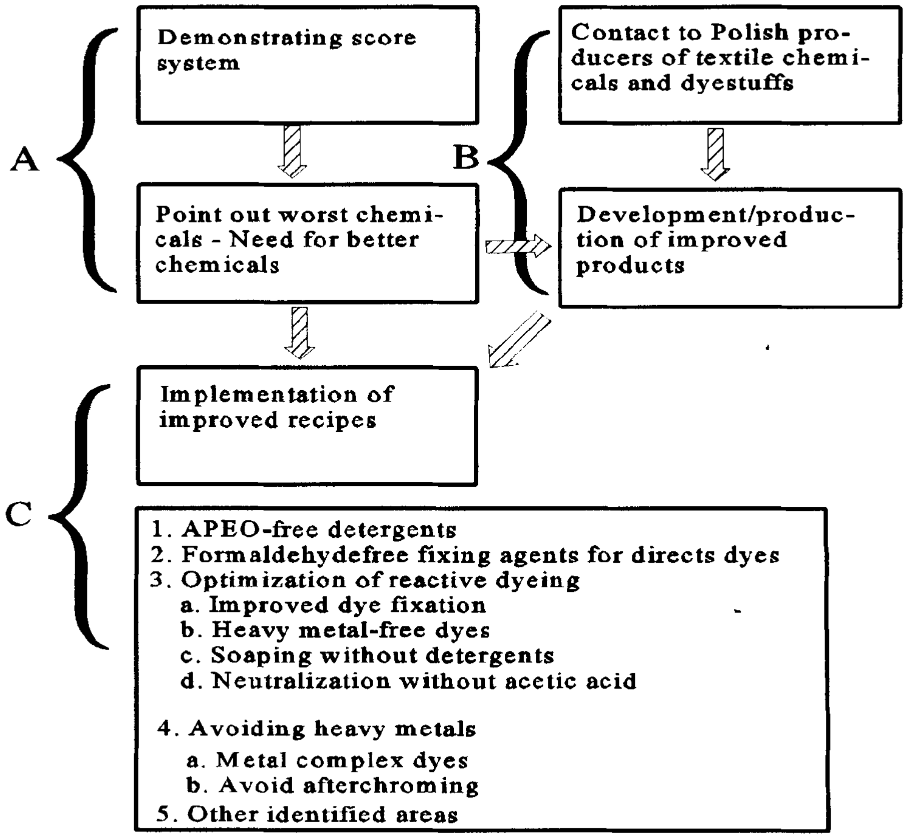
Project content
The programme falls into three groups, which are linked together as indicated in the figure next page.

A: Demonstration of substitution tool in Polish dye-houses (score system).

B: Supporting Polish production of more environmentally friendly textile chemicals and dye-stuffs.

C: Specific demonstration projects on savings and substitutions.

The following partners are expected to participate in the project:



From Poland:

The Textile Research Institute, Lodz
5-8 Polish dye-houses (these have been appointed)
2-3 producers of textile dye-stuffs and/or auxilliaries (these have been appointed)

From Denmark:

DTI Clothing and Textile
Institute for Product Development
VKI-Institute for the Water Environment

Expected environmental improvements
The introduction of improved recipes, processes, chemicals and dye-stuffs will lead to a major improvement of the environmental impact from the Polish textile industry.

Special focus will be put upon substances such as:

- Dye-stuffs containing heavy metals
- Dye-stuffs with low fixation rate
- After chroming processes
- APEO containing detergents
- Formaldehyde containing chemicals
- Cationic surface active agents

To illustrate the order of magnitude of the problems, figures from 13 of the companies visited during the technology transfer programme, showed a mean consumption per company of 49 tons of dye-stuffs, of which around 40% ends up in the waste-water, and 24 tons of detergents, of which the major part was revealed to be APEO-based, and which all ends up in the waste-water.

Although it is the aim of the project to improve these and other figures considerably, a quantification is however not possible at present.

Project status

The project application was filed late 1995 and for different reasons, was delayed until 1997. It was approved in 1997 by the Danish Environmental Protection Agency. The project is expected to commence in 1997.

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Fokus for dette initiativ har været muligheder for implementering afrenere teknologiløsninger, som både er miljømæssigt og økonomisk bæredygtige. Initiativet har været finansieret af DANCEE, Miljøstyrelsen

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Forsidefoto: VH-jet farvemaskine på tekstilfarveriet ZTK Teofilów, Lódz, Polen. Taget af Claus Christensen ApS.

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Abstract: This report presents the results of an environmental survey of dyehouses within the Polish textile industry and the identification of options for pollution prevention and resource savings. The main focus of the initiative has been possibilities for implementation of cleaner technology solutions being environmentally and economically friendly at the same time. The initiative has been financied by the Danish Cooperation for Environment in Eastern Europe (DANCEE).

Terms: textile industry; Poland; cleaner technology

Supplementary notes: VH-jet dyeing machine at textile dyehouse ZTK Teofilów, Lódz, Poland.

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