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Danish experience. Best Available Techniques - BAT - in the clothing and textile industry

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Preface

This BAT-report has been prepared by the Danish Technological Institute (DTI) Clothing and Textile, and the Institute for Product Development (IPU), Technical University of Denmark, with support from the Danish Environmental Protection Agency (DEPA).

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Background
In the last 10 years numerous cleaner technology projects have been initiated in Denmark with support from the Danish Environmental Protection Agency. Special focus has been put on the textile industry because of the large potential for water and energy savings. Many Danish textile companies have been involved in the projects. Valuable experience and results have been collected.

Purpose
The purpose of this BAT-report is to present the Danish contribution to the IPPC reference document on Best Available Techniques for the textile industry based on the experience and results that have been obtained during the last 10 years of research and development in Cleaner textile technology.

Method
DTI Clothing and Textile and IPU have been involved in several cleaner textile technology projects in the last 10 years. This BAT-report presents the best results of the research done by DTI, IPU and others.

Based on the knowledge and experience collected, a long-list of potential cleaner production options were made. Then a survey was implemented in the fall 2000 in order to get an overview of the effect of the research projects. Fifteen Danish textile companies covering a wide segment of textile production were contacted. Among other things, the companies were asked what they consider to be BAT. Ten Danish companies were visited. Based on the survey and interviews, the most successful options were pointed out. The options could be grouped in four overall categories presented in this BAT-report.

Summary

This BAT-report is divided into 4 main parts:

1. Cleaner Technology in pigment printing.
2. Cleaner Technology in reactive dyeing of cotton.
3. Cleaner Technology – chemical savings and substitutions.
4. Cleaner Technology in enzymatic desizing.

In each main part, several Cleaner Technology options are described and evaluated according to the BREF-standard received from the IPPC bureau. In addition, the Cleaner Technology options are evaluated according to the definition of "Best available techniques" in the IPPC directive (Council directive 96/61/EC of 22 September 1996), Article 2 (11) and ANNEX IV.

An overall summary of the evaluation of the options can be found in Table A below.

Options that for different reasons at present have been evaluated to be a BAT are so marked in the table. Options that for different reasons at present have been evaluated to be a potential future BAT are marked under the heading Emerging-BAT.

For details, refer to the descriptions of the options in the report.

Table A Evaluation of CT-options.

Head-title	**Overall sub-titles**	**Cleaner Technology options, titles**	**Evaluation**	
			BAT	Emerging-BAT
1. Cleaner Technology in pigment printing.	1.1. Reduction in water consumption in cleaning operations.			
		A) Start/stop control of cleaning of the printing belt.	X	
		B) Mechanical removal of printing paste.	X	
		C) Reuse of the cleanest part of the rinsing water from the cleaning of the squeegees, screens and buckets.	X	
		D) Reuse of the rinsing water from the cleaning of the printing belt.	X	
	1.2. Reduction in consumption of printing paste.		X	

Table A (continued) Evaluation of CT-options.

Head-title	**Overall sub-titles**	**Cleaner Technology options, titles**	**Evaluation**	
			BAT	Emerging-BAT
2. Cleaner Technology in reactive dyeing of cotton.	2.1. Recipe optimisation.			
		A) Change from overflow rinsing to stepwise rinsing.	X	
		B) Omit the use of detergents in the rinsing after reactive dyeing of cotton.	X	
		C) Omit the use of complexing agents in the rinsing after dyeing.	X	
		D) Use only neutralisation after dyeing when using VS reactive dyestuffs.	X	
		E) Chemical-free high speed rinsing after reactive dyeing of cotton.		X
	2.2. Reclamation and reuse of chemicals, energy and water.			
		A) Reclamation and reuse of dyebath and first rinse by activated carbon.		X
		B) Reclamation and reuse of rinsing water after dyeing by membrane filtration.		X
3. Cleaner Technology – chemical savings and substitutions.				
	3.1. Implementation of a score system for sorting of chemicals and dyestuffs on Basis of Environment Data and Information on Consumption.		X	
	3.2. Chemical savings.			
		A) Collection and re-use of after-treatment chemicals in finishing.	X	
4. Cleaner Technology in enzymatic desizing.				X

1 Cleaner technology in pigment printing

In pigment printing, the printing paste is applied to the surface of the fabric through different types of screens perforated in patterns and figures – one screen for each colour. The fabric is transported under the screens on an endless belt – the printing belt – momentarily fixed with water-soluble glue to avoid dislocation of the fabric relatively to the screens. To keep the printing belt totally smooth and clean from printing paste, fluff and lint, the printing belt is rinsed with water on its way back to the start of the printing machine.

The pigments are bonded to the fibre with a bonding agent by heating and the printed fabric does not require washing or rinsing after printing.

The equipment used around the printing machine – screens, buckets (for mixing, transporting and storage) and the print paste feeding system (i.e. pumps, hoses, pipes and squeegees) needs careful cleaning before it can be used for new colours.

In pigment printing, several CT-options are related to reduction in the consumption and discharge of water and printing paste. Two options are described:

1.1 Reduction in water consumption in cleaning operations

In connection with cleaning operations, there are several possibilities to reduce the water consumption. The following CT-options are described:

A) Start/stop control of cleaning of the printing belt.
B) Mechanical removal of printing paste.
C) Reuse of the cleanest part of the rinsing water from cleaning of the squeegees, screens and buckets.
D) Reuse of the rinsing water from cleaning of the printing belt.

It should be emphasised that these options are also relevant in connection with printing with dyestuffs.

1.1.1 Description

A) Start/stop control of cleaning of the printing belt.
In many cases, water dosage for the cleaning of the printing belt continues when the fabric - and thereby the printing belt - is stopped for whatever reason. A start/stop of the water dosage can be automatically connected to the start/stop of the printing belt.

B) Mechanical removal of printing paste.
Large amounts of water for cleaning of squeegees, screens and buckets are used within the print-house. An improved printing paste removal before flushing of this equipment would lead to a reduced need for water for flushing. In Denmark, physical devices for removal of dye from buckets have been developed (e.g. scraper). Some modern printing machines have a built-in system for mechanical removal of residual printing paste from pipes and hoses.

C) Reuse of the cleanest part of the rinsing water from cleaning of the squeegees, screens and buckets.
Typically, the first half of the effluent from the washing equipment is heavily loaded with printing paste and will have to be discharged as wastewater. On the other hand, the water quality demand for reusable rinsing water in this first part of the washing process is low. In the last half of the washing process, clean water must be used, but the effluent can be collected for reuse.

D) Reuse of the rinsing water from cleaning of the printing belt.
The rinsing water from cleaning of the printing belt is only slightly coloured and contains small amount of fibres (depending on the fabric) and very small amounts of glue. The rinsing water can be mechanically filtered, collected in an overflow vessel and reused for the same purpose, if minor amounts of fresh water are added to the recycling system.

The following are common features for option 1.1.A – D unless otherwise specified.

1.1.2 Main achieved environmental benefits

The environmental benefit is a reduction in the water consumption. In a Danish pigment print-house, the implementation of all the above options has reduced the annual consumption of water by approximately 25,000 m^3 (55% reduction). For option 1.1.A alone, the savings are estimated at approximately 2 m^3 for every hour the printing machine stops and the water dosage for cleaning of the printing belt is still running for whatever reason. For option 1.1.C, 50% of the water is reused. For option 1.1.D, approximately 70% of the water is recycled.

1.1.3 Cross-media (whole environment) effects

- Reduction in water consumption.
- Ability to re-use wastewater.

1.1.4 Applicability

Option 1.1.A – D can be implemented in all types of textile companies involved in printing; new or existing, large or small. Space availability is a minor factor – the company only needs space for collection tanks (option 1.1.C and 1.1.D). However, older printing machines can probably not be retrofitted with a device for mechanical removal of the residual printing paste from pipes and hoses in the printing machine (option 1.1.B).

1.1.5 Economics

In the Danish case mentioned above, the total capital costs (tanks, mechanical filters, pumps and pipes) for all options are estimated at approximately DKK 100,000 (≈ EUR 13,500). Option 1.1.C and 1.1.D together approximately DKK 95,000 – option 1.1.A approximately DKK 5,000 – option 1.1.B negligible. Change in operating costs (before and after implementation) for all options are negligible. The costs for fresh water and wastewater discharge are DKK 9 and DKK 18 per m^3, respectively. Hence the total annual savings are approximately DKK 675,000 (≈ EUR 90,000). Payback time for all options together is estimated at about two months.

1.1.6 Driving force for implementation

High costs for fresh water and wastewater discharge.

1.1.7 References to literature and example plants

Example plants:

Danish Colour Design Textile Print A/S
Mylius Erichsensvej 52
7330 Brande
Denmark
Att: Mr Benny Hansen
Phone: + 45 97 18 19 22
Fax: + 45 97 18 19 11
E-mail: dcd@teliamail.dk

Literature:

DANCEE, 1999. Cleaner Technology Transfer to the Polish Textile Industry. Idea catalogue and selected options, 1999. Danish Ministry of Environment and Energy. Danish Environmental Protection Agency. DANCEE – Danish Co-operation for Environment in Eastern Europe.

Danish EPA, 1994. Survey of the handling of resources in the wet processing of textiles. Environmental project no. 268, 1994. Danish Ministry of Environment and Energy. Danish Environmental Protection Agency. (In Danish).

1.2 Reduction in consumption of printing paste.

1.2.1 Description

The printing paste, which is left over after printing, can be collected and reused. The optimum solution implies collecting residual printing paste from as many pieces of equipment as possible, e.g. at least from squeegees and buckets. As mentioned for option I B, some modern printing machines have a built-in system for removal of printing paste from pipes and hoses. The use of PC-based recipe formation and a database can facilitate reuse of printing paste with information on the composition of the collected printing paste including information about the durability. Normally the durability is not a problem.

1.2.2 Main achieved environmental benefits

The main environmental benefit is reduction in the quantity of hazardous waste. In a Danish pigment print-house, this option has reduced the amount of hazardous waste for special treatment by approximately 25,000 kg printing paste / year (60% reduction).

1.2.3 Cross-media (whole environment) effects

Potential effects:
- Reduction in consumption and emission of chemicals.
- Reduction in hazardous waste.
- Less particulate matter (including micro-particles and metals) in the wastewater.
- Ability to re-use printing paste.

1.2.4 Applicability

This option can be implemented in all types of textile companies involved in pigment printing - new or existing, large or small. Space availability is a minor factor. However, to achieve the maximum benefits, it is necessary to be operating with or implement a PC-based recipe formation system. In addition, the print-house needs to be operating with an automatic colour dosage system (so-called "dye-kitchen"). Furthermore, operating with modern printing machines with a built-in system for mechanical removal of printing paste from pipes and hoses in the printing machines will increase the amount of printing paste that can be collected and reused.

1.2.5 Economics

In the Danish case mentioned above, the total capital costs (extension of printing paste weighing system, software and extra buckets) are estimated at approximately DKK 80,000 (≈ EUR 10,500). Change in operating costs (before and after implementation) are negligible. The economic value of the collected and reused printing paste is approximately DKK 5 per kg (savings DKK 125,000). The costs for disposal of hazardous waste in Denmark are DKK 1,500 per tonnes (savings DKK 37,500). Hence the total annual savings are approximately DKK 160,000 (≈ EUR 21,500). Payback time is estimated at about six months.

1.2.6 Driving force for implementation

High costs for printing paste and disposal of hazardous waste.

1.2.7 References to literature and example plants

Example plants:

Danish Colour Design Textile Print A/S
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7330 Brande
Denmark
Att: Mr Benny Hansen
Phone: + 45 97 18 19 22
Fax: + 45 97 18 19 11
E-mail: dcd@teliamail.dk

2 Cleaner technology in reactive dyeing of cotton

This chapter presents Danish know-how with reclamation and re-use of process water from reactive dyeing of cotton knitwear in batch. Reactive dyeing of cotton is the most used textile dyeing process world-wide, both with regard to cotton textiles or all kinds of textiles, and the share of the market is increasing.

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

1. Process optimisations – e.g. savings in chemicals, energy and water.
2. Reclamation and re-use of chemicals, energy and water.

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

In textile dyeing the *recipe* is the fundamental specification of the processes. Water consumption, chemical consumption, temperature, salinity, pH etc. are all specified step by step in the recipe.

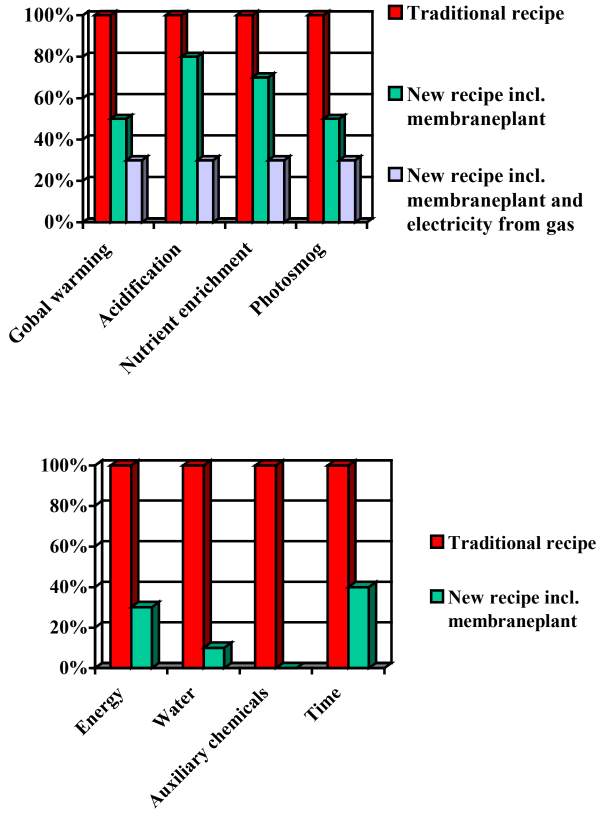
The recipe for reactive dyeing of cotton can be divided into three steps: the pre-treatment, the dye-bath and the rinsing after dyeing. Traditionally, the consumption of energy, chemicals and water in rinsing is crucial; approximately half of the total energy consumption and up to three-quarters of the total COD discharge and of the total water consumption have relation to the rinsing after the dyeing processes. The potential for environmental improvements in the rinsing procedures are in this way considerable and the process of recipe development focused on *the rinsing after dyeing*.

The advantages and limitations of different water reclamation techniques 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 dyebath* itself. The solution implies hot water reuse in rinsing, reuse of filtration remains in anaerobic digesters, and reuse of dyebath water and salts.

In this way, Danish experience includes development of new rinsing recipes and of water reclamation techniques, leading to large savings in time, water, energy, and chemicals. For reclamation and reuse of the rinsing water from the optimised rinsing recipe, a comparative study of the environmental impacts *before* and *after* rinsing water reuse has been carried out. The study concerns a reuse solution based on membrane filtration. All changes in use of water, energy, and chemicals are included in the study, also including the membrane plant, reservoirs etc. from raw material extraction, to production, use, and disposal of the equipment. This study is a so-called life-cycle assessment of the solution, performed according to international practice. The study concerns *only* environmental impacts from the rinsing process and the results are outlined in figure 2.1.

In figure 2.1, there is a column for the “before” situation and for the “after” situation, and the potential for improvements explain mostly itself. In the environmental benefits there are three columns. This is because the dye-house, where the membrane plant is implemented, has heat production on the basis of natural gas – but the membrane plant is driven by electricity based on coal. The difference in the environmental load due to different energy source blur the real environmental improvement potential – this is the reason why the third column is calculated as if the electrical power for the membrane plant was produced on natural gas.

Figure 2.1 Environmental benefits (on top) and resource savings (below) by introducing the new rinsing recipe and reuse of water and energy by membrane filtration.



A more detailed description of the research is presented in the following Chapter “2.1 Recipe optimisation” and Chapter “2.2 Reclamation and reuse of chemicals, energy and water”.

2.1 Recipe optimisation

The reactive dyeing process is outlined in table 2.1 by a representative recipe selected by one of the dye-houses included in the project. During the pre-treatment, the cotton fabric is washed and degreased, and treated with lye in order to open the fibre structure. When the pre-treatment is part of a light shade recipe, the pre-treatment process includes a bleaching. After some rinses, the dyestuff is poured into the dyebath and a diffusion of the dyestuff molecules between the cellulose fibres takes place. After some time, salt is added to obtain adsorption of the dyestuff to the cellulose fibre. After this, adjusting temperature (50-80°C) and pH (10,5-11,5) completes the reaction between the dyestuff and the cellulose. Some of the dyestuff will be hydrolysed during this dyeing process, and the adsorbed hydrolysate must be removed in the succeeding rinsing after dyeing.

Table 2.1 Original recipe, typical example. The dyeing machine is drained after each batch.

Batch no.	Process	Wastewater (l)	Temp. (°C)
1	Washing & bleaching	700	95
2	Overflow rinse	7300	10
3	Neutralisation	700	30
4	Overflow rinse	7300	10
5	Dyeing	700	50
6	Overflow rinse	7300	10
7	Warm rinse	700	50
8	Neutralisation	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	Neutralisation & softening	700	40

Traditional rinsing after dyeing processes

The rinsing traditionally consists of several rinsing baths, as in table 2.1. The large water consumption in the rinsing after dyeing 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 dyestuff producers recommend neutralisation to pH around 8, when dyestuffs with vinyl sulphone reactive groups are used. This neutralisation has, however, in some dye-houses, become usual practice for all sorts of reactive dyestuffs.

After neutralisation, the rinsing consists of a number of *soaping sequences*: hot soaping, warm rinse and overflow rinse. Table 2.1 shows a typical use of two soaping sequences. In the hot soaping – bath no. 10 and 13 in table 2.1 – »soaping« additives are used, covering surface active agents (detergents), complexing agents and dispersing agents. The reasons for the use of these auxiliary agents are protection against hardness in the water and/or the cotton, concurrently with a need for an additive to hold the dyestuff hydrolysate dispersed in the water.

The process is finalised with neutralisation to pH around 7 and treatment with softening agents, necessary for the following sewing process.

Performed investigations

Table 2.2 gives an overview of performed investigations. The dye-houses participating in the investigations have pointed out the recipes, and thus the 24 reactive dyestuffs entering the tests, as »difficult«. Criteria have either been the very accurate and sensitive balance between the used dyestuffs in light shades or problematic fastness for dark shades.

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

To assess the quality of the dyed textiles, the skilled quality assessment people at the dye-houses did the normal quality assessments: washing, water, wet rub, and dry rub fastness, evaluated on a scale from 1 to 5 with 5 as 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 2.2 Overview of performed investigations.

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

More than 50 full-scale recipes have been carried out in jets, overflow and drum batch machines. None of the performed experiments caused quality reductions in the finished lots, neither when neutralisation 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. A suggestion for a new recipe is outline in table 2.3.

Table 2.3 New water saving, chemical free, high temperature and high speed rinsing recipe.

Batch no.	Process	Wastewater (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	Neutralisation & Softening	700	40

The full-scale tests with the new recipe documented that a chemical free, high temperature rinse, using a reduced number of batch rinses, and thus saving water and process time, can be implemented in the dye-house with no adverse effect on product quality. When implementing the water saving, chemical free, high temperature and high speed rinse after reactive dyeing of cotton in batch, the following CT-options should be considered:

A) Change from overflow rinsing to stepwise rinsing.
B) Omit the use of detergents in the rinsing after reactive dyeing of cotton.
C) Omit the use of complexing agents in the rinsing after reactive dyeing of cotton.
D) Use only neutralisation after dyeing when using VS reactive dyestuffs.
E) Chemical-free high speed rinsing after reactive dyeing of cotton.

2.1.1 Description

A) Change from overflow rinsing to stepwise rinsing.
Rinsing by overflow, i.e. pouring clean cold water directly into the process water in the machine while excess water is drained out of the machine, is used both for rinsing and for cooling purposes. Overflow is quick but causes unnecessary water consumption.

Changing from overflow rinsing to a stepwise rinsing procedure as outlined in table 2.4 should be considered.

Table 2.4 Stepwise rinsing as substitute for each overflow rinse.

Stepwise rinsing	
A	Fill the machine according to liquor ratio
B	10 minutes rinsing
C	Discharge rinsing water
D	5 minutes draining

This option is in general relevant and should be investigated wherever overflow rinsing is used.

B) Omit the use of detergents in the rinsing after reactive dyeing of cotton.
Surplus and non-fixed reactive dyestuffs are highly water-soluble. Nevertheless, detergents are often used during rinsing after dyeing.

Both in international literature and in the Danish projects, it has been documented that detergents do not improve removal of hydrolysed reactive dyestuffs from the fabric. In the Danish project, 50 full-scale dyeings have been carried out at various dye-houses without the use of detergents. All have successfully proven that detergents can be omitted without negative impact on product quality.

C) Omit the use of complexing agents in the rinsing after reactive dyeing of cotton.
If soft water with a quality of below 5°dH is used, complexing agents can be omitted. In the Danish project, the 50 full-scale dyeings included dyeing without the use of complexing agents. No negative effects on the dyeing results were observed.

However, if hardness builders e.g. calcium and magnesium are present in the dyeing processes and in the rinsing after dyeing, they might have a negative effect on the dyeing result, e.g. change in shade or problems with reproducibility. For that reason, soft water is recommended as standard procedure in the dyeing processes. However, water softening in the dyeing machine by using complexing agents, forming bonds with the hardness-builders, are both economically and environmentally a bad solution.

Water softening can profitably be done in a separate plant by the ion-exchange technique or the membrane filtration technique.

D) Use only neutralisation after dyeing when using VS reactive dyestuffs.
Referring to the chemical suppliers, neutralisation in the first rinse after dyeing can be restricted to the vinyl sulphone (VS) reactive groups. Some VS dyestuffs have poor alkaline washing fastness and thus sensitive to high pH and high temperature simultaneously. Nevertheless, it is not uncommon that all recipes for reactive dyeing in a dye-house include neutralisation in the first rinse after dyeing, whether VS reactive dyestuffs are used or not.

In the Danish project, the dyeing was successfully carried out without the use of neutralisation in the first rinse after dyeing. This in spite of the fact that more than half of the dyeings were carried out with dyestuffs based on VS-groups. As it is not possible to put forward general guidelines on when to neutralise dyestuffs based on VS-groups, it is recommended always to neutralise these. There is no reason to neutralise in this step when all other sorts of reactive dyestuffs are used, e.g. based on monochlorotrazine (MCT), monofluorotriazine (MFT), dichlorotriazine (DCT), trichloropyrimidine (TCP) or difluorochloropyrimidine (DFCP).

In general, it is recommended to select dyestuffs with a superior alkaline washing fastness when selecting VS-dyestuffs for the dye-house.

E) Chemical-free high speed rinsing after reactive dyeing of cotton.
Danish tests have shown that rinsing is more effective and faster at elevated temperatures – e.g. around 30% more unfixed hydrolysed reactive dyestuff is rinsed out after 10 minutes at 95°C than at 75°C.

Danish full-scale tests using hot 90-95°C rinsing after reactive dyeing of cotton have proved that the technique has no negative effects on the dyeing results. Most often the fastness of the goods were better after the hot rinsing than after the traditional rinsing with overflow, detergents, complexing agents and neutralisation in the first rinse (referring to option 2.1.A-D). Furthermore, when using 90-95°C rinsing water, a few stepwise rinses (table 2.3) can reduce the rinsing time with around 50% compared to a standard recipe (table 2.1). The tests covered 9 different recipes and 13 different reactive dyestuffs including very bright and dark shades.

2.1.2 Main achieved environmental benefits

Option 2.1.A:
The benefit is reduction in water consumption and wastewater generation. By replacing each overflow rinse by 2-4 stepwise rinses, a reduction rate at 50-75% per overflow rinse can be achieved.

Option 2.1.B, 2.1.C and 2.1.D:
The benefit is reduction in consumption of resources for the production of chemicals and reduction in pollution load of the wastewaster. Obviously, the potential for reduction will vary according to the existing dyeing procedure at the company. The Danish project was performed at two dye-houses mainly engaged in dyeing knitted piece goods and one mainly engaged in garment dyeing. The average potential load reduction at these dye-houses was documented to be at approximately 1 kg detergent, 1 kg complexing agent and 1 kg acetic acid per 100 kg of textile.

Option 2.1.E:
Best available technology on textile dyeing should include energy reclamation – especially when using large volumes of hot process water. If the company do not operate with energy reclamation, there is a risk of enlarged environmental load due to energy production, consumption and discharge when substituting cold rinsing with hot rinsing.

Energy reclamation can be done either by heat exchange between hot outgoing process water and cold incoming clean water or by reclamation of hot water and reuse of both the energy and the water.

In addition, the environmental benefits from option 2.1. E are the combined benefits for option 2.1. A – D.

2.1.3 Cross-media (whole environment) effects

Option 2.1.A:
Reduction in water intake, consumption and discharge.

Option 2.1.B, 2.1.C and 2.1.D:
Reduction in production, consumption and discharge of chemicals.

Option 2.1.E:
To accomplish the environmental benefits when using hot process water, the company must as a minimum include reclamation of the energy by heat exchanging hot outgoing process water with incoming cold water. In this situation, the benefits are the combined effects of option 2.1.A, B, C and D. However, if this is not the situation, a negative aspect could be increased environmental load due to energy production, consumption and discharge.

The optimal situation at the dye-house would be to reclaim both energy and water by membrane filtration as described in section 2.2.B.

2.1.4 Applicability

Option 2.1.A – E:
Can be implemented in all types of textile companies involved in reactive dyeing of cotton in batch; new or existing, large or small.

Option 2.1.A:
Stepwise rinsing is somewhat slower than overflow rinsing. For a company producing at the maximum dyeing-capacity, the extra production time when changing from overflow to stepwise rinsing can be a problem.

Option 2.1.C:
Can only be implemented if the company do have availability to very soft groundwater or is operating with a soft-water system (which is normally the case).

Option 2.1.D:
It is recommended always to neutralise in the first rinse after the dyebath when dyestuffs based on VS-groups are used. There is no reason to neutralise in this step when all other sorts of reactive dyestuffs are used, e.g. based on monochlorotrazine (MCT), monofluorotriazine (MFT), dichlorotriazine (DCT), trichloropyrimidine (TCP) or difluorochloropyrimidine (DFCP).

Option 2.1.E:
In order to be environmentally and economically feasible, the company must as a minimum perform energy reclamation, as an optimum perform energy and water reclamation.

2.1.5 Economics

Option 2.1.A:
The economic feasibility is obvious - 50-70% reduction in the consumption of water for rinsing. Total savings will depend on the number of reactive dyeings at the company.

Option 2.1.B-D:
The only change in operating procedures is to omit the addition of detergents, complexing agents and acetic acid. Savings will depend on the number of reactive dyeings at the company.

Option 2.1.E:
If the company is operating with energy reclamation an additional economic benefit (on top of 2.1.A–D combined) would be the economic value of the extra dyeing capacity.

If the company is operating without energy reclamation option 2.1.E is not economically feasible. Best available technology on textile dyeing should include energy reclamation.

2.1.6 Driving force for implementation

Option 2.1.A:
High costs for water and wastewater discharge and/or low availability for water of appropriate quality.

Option 2.1.B-D:
High costs for chemicals and wastewater load.

Option 2.1.E: (assuming the company is operating with heat exchange of hot outgoing process water):
A desire for reduced operation time per lot and increased capacity per machine.
High cost for fresh water and wastewater discharge and/or low availability for water of appropriate quality.
Reduction in chemical expenses.

2.1.7 References to literature and example plants

“Cleaner Technology Transfer to the Polish Textile Industry. Idea catalogue and selected options”.
DANCEE, Danish Co-operation for Environment in Eastern Europe. ISBN 87-7909-265-9.

“Membrane filtration of textile dye-house wastewater for technological water reuse”.
Desalination 119 (1998) 1-10.

“Environmentally friendly method in reactive dyeing of cotton”.
Water Science and Technology Vol. 33, No.6, pp.17-27, 1996.

“Reclamation and reuse of process water from reactive dyeing of cotton”.
Desalination 106 (1996) 195-20

Example plants:

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7400 Herning
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E-mail: LL@martensens.dk

2.2 Reclamation and reuse of chemicals, energy and water

The strategy for the Danish water reclamation research was to introduce reclamation and re-use closely integrated in the dyeing process. This implies working upstream, where water characteristics are still process specific, and not downstream, where sub-streams 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 was found very suitable, and the Danish experience shows that it will result in the environmentally and economically optimal solution. Furthermore, and not least important, the strategy was to look for reuse not only of water but also of the energy and chemical content in the water.

Water reclamation techniques

Investigated water reclamation techniques were chemical precipitation, membrane filtration, activated carbon absorption, and counter current evaporation/ condensation. The advantages and limitations of each technique, related to the different characteristics of the process water from reactive dyeing of cotton, have been identified in lab-scale and documented in pilot-scale.

Besides the technical tests, economical estimates were given on the basis of not binding offers from suppliers. Economical estimates are expressed as EUR/m^3 of process water including both operation costs and investment costs amortised over 5 years. Only the water reclamation equipment is included, *not* buffer reservoirs, pipes etc. being equal for all solutions. Table 2.4 gives the comparison in a total overview.

Table 2.4 *Comparison of 4 water reclamation techniques in reactive dyeing of cotton.*
Signatures: "😐 = not influenced significantly", "☺ = positive influence", "☹ = negative influence", "✋ = specific compounds, e.g. cations, can influence negatively".

Waste-water characteristics	Membrane filtration	Chemical precipitation	Activated carbon	Counter current evaporation
Initial high dyestuff concentration	😐	😐	☺	😐
High salt concentration	☹	☹	☺	☹
Detergents and other COD	😐 ✋	☹	😐	😐
High temperature	☺	☹	😐	☺
pH	(2)-7-9-(10)	(2)-8-10	2-10	(2)-7-10
Costs, EUR/m³	1	1-2	10-15	10-15

Surplus costs can be expected for chemical precipitation, as heat exchange and polishing of suspended solids and excess precipitation chemicals may be necessary. The cost estimates in table 2.4 concerns the rinsing water, except for activated carbon for which it concern the dye-bath.

An overall solution has been chosen, based on the relatively cheep membrane technology for the high volume, high temperature and low salt rinsing water, and the relative expensive activated carbon adsorption technique for the exceptional high in salinity and high in dyestuff process water from the exhausted dyebath. Both solutions have been demonstrated at a Danish commission dye-house. The recycling system is connected to five Jet-dyeing (batch) machines with a capacity of 100 kg each. Results are more closely described in the two following chapters:

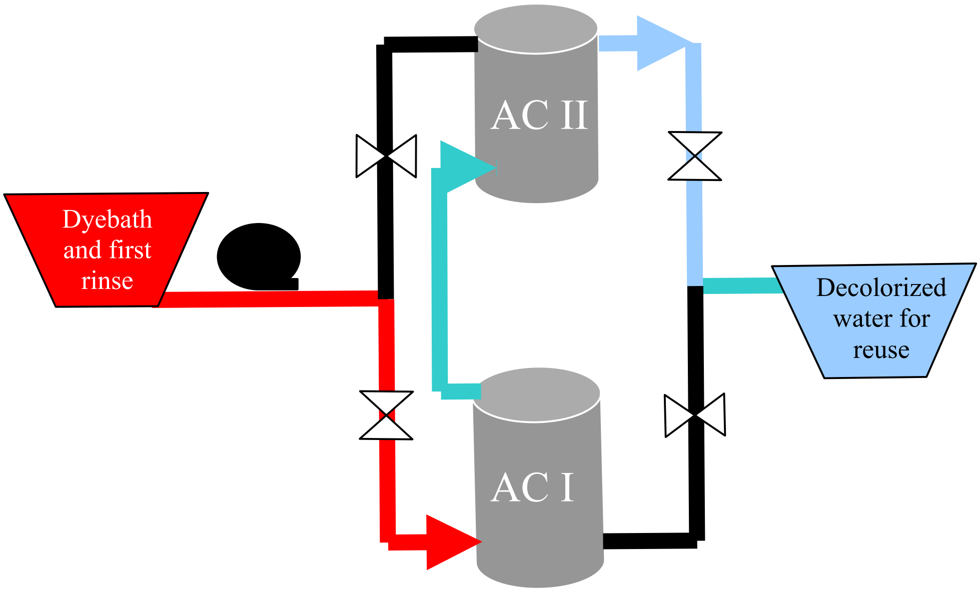
A) Reclamation and reuse of dyebath and first rinse by activated carbon.
B) Reclamation and reuse of rinsing water after dyeing by membrane filtration.

2.2.1 Description

A) Reclamation and reuse of dyebath and first rinse by activated carbon.

By treating the highly coloured and salty process water types with activated carbon, the carbon will retain the dyestuff and other organic components by adsorption. The higher the content of dyestuffs and organics, the higher the capacity of the activated carbon, and the ions from the salt significantly improves the adsorption capacity of the activated carbon.

Figure 2.2 Principle in the activated carbon demonstration plant.

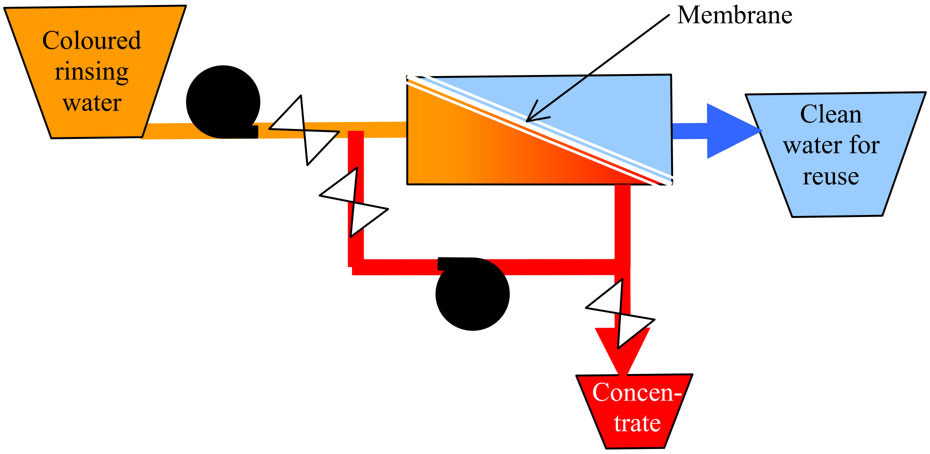


The dimensioning parameters from the test plant were a retention time of 2 hours and a consumption of 4 kg activated carbon/kg dyestuff. The used carbon type was F400 from Chemviron Carbon. A full-scale plant can consist of two columns (see figure 2.2) connected in series and with reversible flow. The flow is from the start from column 1 to column 2. When column 2 has the first break through of dyestuffs, column 1 is totally saturated and can be replaced with a new. The flow is reversed so that the flow is now from 2 to 1.

The activated carbon technique provides clear, warm water with sodium chloride and lye for reuse. Test dyeings showed that reusing warm, saline and de-coloured dye-baths as the basis for new dye-baths was possible with no adverse effects on fabric shade or fastness. Both the water, the energy content and the very high content of salts (up to 80 g sodium chloride per litre) and sodium hydroxide are utilised again by this option.

B) Reclamation and reuse of rinsing water after dyeing by membrane filtration.
By treating the large volume of coloured rinsing water by membrane filtration, the dyestuff and other components will be retained in a low volume concentrate and a large volume of clear, hot and soft permeate water for reuse is produced.

Figure 2.3 Principle in the cross flow membrane filtration demonstration plant.



The membrane technology in question will have to be nano-filtration or reverse osmosis to be able to produce to a sufficient water quality. The dimensioning parameters from the test plant based on spiral wound elements were an average production of 25 l/m^2h at 25°C and 7-10 bar. The selected elements in use were 50 mil Duratherm elements from OSMONICS DESAL. The operational parameters depend heavily and directly proportionally on the temperature of the water. Operation at 90°C will increase flux from 100% to 300% at the same pressure, but it is recommended to reduce pressure to 1/3 and save a very substantial amount of electricity.

The rinsing water reclaimed by membrane filtration was successfully tested in both standard recipes (table 2.1) and the chemical-free high-speed recipe (table 2.3 and option 2.1.E) for rinsing purposes.

2.2.2 Main achieved environmental benefits

Option 2.2.A:
Reduction in consumption and discharge of chemicals – too much salt (sodium chloride) and too high pH (sodium hydroxide) are most often the essential problems for cotton dye-houses.

Energy recovery by using warm process water for the new dye-baths gives reductions in consumption of energy.

Option 2.2.B:
Large reduction in consumption of water.
Hot water reuse gives large reduction in consumption of energy.

2.2.3 Cross-media (whole environment) effects

Option 2.2.A:
Reduction of the total emission of salt with the wastewater.
Reduction of the emission of dyestuff with the wastewater.

In Europe, an efficient line of suppliers and regeneration plants are prepared to receive the saturated carbon.

Alternatively, the saturated carbon can be incinerated and thereby the heat energy in the carbon can be utilised.

Option 2.2.B:
Reduction in consumption of water.
Reduction in consumption of energy.

An environmentally profitable solution to handle the concentrate is anaerobic degradation. The method has been successfully tested in laboratory scale.

Alternatively, the concentrate can be dried and incinerated and thereby the heat energy in the waste components can be utilised.

A detailed LCA has been worked out according to international standards by the EDIP method. The LCA compare option 2.1.E (Chemical-free high speed rinsing after dyeing) in combination with option 2.2.B (Reclamation and reuse of rinsing water by membrane filtration) with the old traditional recipe, including the use of detergents, complexing agents and overflow rinsing (table 2.1).

The results are outlined in figure 2.1 and points out the following improvements:

- Energy consumption reduced by 70%.
- Water consumption reduced by 90%.
- Chemical consumption reduced by 100%.
- Time consumption per lot reduced by 60%.
- Global warming reduced by 70%.
- Acidification reduced by 70%.
- Nutrient enrichment reduced by 70%.
- Photochemical ozone reduced by 70%.

2.2.4 Applicability

Option 2.2.A:
Activated carbon is relatively “low tech”, relatively easy to operate and relatively low in investments and can be implemented in all types of textile companies involved in reactive dyeing of cotton in batch; new or existing, large or small. Activated carbon adsorption is relatively high in operation costs and the limiting parameter is the accepted pay-back time at the dye-house – this includes of course the costs for wastewater discharge and limitations in discharge of salt and dyestuff, if any. Piping, pumps, tanks and separation plant will demand some space but rarely constitute a critical problem.

Before implementation of a activated carbon plant, it is very important to test the retention time and the capacity of the carbon type with the actual process water.

When the salt is in the process water from the very start, the process is a so-called “all-in dyeing”. The dyestuff is subsequently added on a time or flow basis. This is contrary to the ”normal” way, where the dyestuff is evenly distributed on the fabric before salt is added. Not all types of recipes have been tested, and problematic recipes may exist. Installation of chemical dosing equipment on the dyeing machines facilitates the “all-in dyeing” considerably.

Option 2.2.B:
Principally membrane filtration can be implemented in all types of textile companies involved in reactive dyeing of cotton in batch; new or existing. However, membrane filtration is relatively “high tech”, relatively high in investment and the option do involve some monitoring of the applicability of the used chemicals at the dye-house to the membrane type. The membrane filtration technique addresses in this way to dye-houses of a reasonable capacity and a reasonable critical minimum volume of water to be treated to give an acceptable pay-back time. On the other hand, membrane filtration is relatively low in operation costs.

Piping, pumps, tanks and separation plant will demand some space but rarely constitute a critical problem. Piping can advantageously be done above the dyeing machines, and the collection pumps can be the existing pumps on the machines. A major problem can be the production stop during the piping.

2.2.5 Economics

This economy assessment is based on typical prices in Ringkjøbing County in Denmark, where the majority of dye-houses in Denmark are situated.

Option 2.2.A:
Investments: 1,3 EUR/m³.
Operation and maintenance: 10 EUR/m³.
Saved expenses: 7-11 EUR/m³.
Assessed pay back time: Maximum of 5 years.

Option 2.2.B:
Investment: 0,6 EUR/m³.
Operation and maintenance: 1,3 EUR/m³.
Saved expenses: 4 EUR/m³.
Assessed pay back time: 8 months.

2.2.6 Driving force for implementation

High costs for fresh water and wastewater discharge.

2.2.7 References to literature and example plants:

Literature:

“Cleaner Technology Transfer to the Polish Textile Industry. Idea catalogue and selected options”.
DANCEE, Danish Co-operation for Environment in Eastern Europe. ISBN 87-7909-265-9.

“Membrane filtration of textile dye-house wastewater for technological water reuse”.
Desalination 119 (1998) 1-10.

“Environmentally friendly method in reactive dyeing of cotton”.
Water Science and Technology Vol. 33, No.6, pp.17-27, 1996.

“Reclamation and reuse of process water from reactive dyeing of cotton”.
Desalination 106 (1996) 195-20

Example plants:

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3 Cleaner technology – chemical savings and substitutions

The chapter is divided into two parts:

3.1 Implementation of a score system for sorting of chemicals and dyestuffs on Basis of Environment Data and Information on Consumption.
3.2 Chemical savings.

Part 3.1. deals with a score system, which is an administrative method of sorting chemicals on basis of information, especially from the specification sheets of the chemical suppliers. The sorting permits a priority selection of chemicals which, because of actual consumption and information on environmental behaviour, should be subject to closer examination.

Part 3.2. deals with the subject "Chemical savings" i.e. possibilities to eliminate or reduce the use of chemicals.

3.1 Implementation of a score system for sorting of chemicals and dyestuffs on Basis of Environment Data and Information on Consumption

3.1.1 Description

The score system is an administrative tool to indirectly control of the discharge of chemicals and dyes from the textile industry. It is a system of sorting of chemicals based on environmental data, consumption and discharge data. Sorting of various chemicals makes it possible to perform a prioritised selection of chemicals which should be examined closer due to consumption and environmental impacts. Upon the assessment of the score of a particular chemical, a company can then make management decisions on reduction of the consumption or substitution of the chemical with a compound that exerts less impact on the environment.

The score system is based on the parameters usually considered to be the most interesting in connection with characterisation of substances injurious to the industrial sewage environment:

A. Discharged amount of substance
B. Biodegradability
C. Bio-accumulation
D. Toxicity

If no information is available, the parameter is given the highest score and marked with an ”U” for unknown.

For more details refer to "Score System for Sorting of chemicals" in Annex A.

3.1.2 Main achieved environmental benefits

The score system is an in-house operational management system, which gives a very good survey of all the chemicals and dyestuffs used in the production. In addition, it gives an easy survey of the chemicals and dyestuffs without any information available about the environmental impact. When the score system is implemented, it will impose the dyeing mills to be aware of what kind of products they use and why. Furthermore, sorting of various chemicals makes it possible to perform a prioritised selection of chemicals.

3.1.3 Cross-media (whole environment) effects

Reduced amount of persistent/toxic/bio-accumulable components in wastewater.

3.1.4 Applicability

This option can be implemented in all types of textile companies; new or existing, large or small.

3.1.5 Economy

To implement the score system, the authorities and the companies have to allocate the necessary man-hours to set-up the system. Once the authorities have made the system operational, a company has to allocate approximately 100-150 man-hours for the necessary preparation to implement the system. Once the company has implemented the system, they only have to allocate approximately 25-50 man-hours every year for maintenance of the system.

3.1.6 Driving force for implementation

The first Score System for sorting of chemicals on the basis of environmental data and on information about consumption was developed by Ringkjoebing County in 1989. The system was set up because of a large number and a high amount of different chemicals and dyestuffs being used in three dyeing mills. The complex mixture of chemicals made it impossible to set-up a specific program for analysing the nature and amount of harmful substances in the wastewater. And if it were possible, such an analysis program would have been too expensive for the companies to implement.

The driving force for implementation of the system was demands from the authorities. The implementation of the score system is now a part of the environmental permits for the clothing and textile industry in Ringkjoebing County. Furthermore, several dyeing mills outside Ringkjoebing County have implemented the system voluntarily because of the advantages of the system.

3.1.7 References to literature and example plants

Literature:

Score System for Sorting of Chemicals. On basis of Environment Data and Information on Consumption. Compendium, 2nd revised edition. January 1994.

Example plants:

Kemotextil A/S
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Fax: + 45 97 12 16 62
e-mail: he@kemotextil.dk

Gabriel A/S
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9100 Aalborg
Denmark
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Fax: + 45 98 13 25 44
e-mail: tina.mai@gabriel.dk

And many more in Denmark.

3.2 Chemical savings

In connection with textile processing (especially wet treatment), many different types of chemicals are used. The following CT-options should be considered:

A. Collection and re-use of after-treatment chemicals in finishing.
B. Omit the use of detergents for rinsing after dyeing.
C. Use only neutralisation after dyeing when using VS reactive dyestuffs.
D. Omit the use of complexing agents.

Option B, C and D have been described in details in chapter 2 with the title ”2. Cleaner Technology in reactive dyeing of cotton”. It should be emphasised that option D is relevant in general in connection with textile wet processing.

3.2.1 Description

A) Collection and re-use of after-treatment chemicals in finishing.
Chemically loaded spent baths in varying amounts and compositions are produced within the textile industry. These baths are often discharged along with the wastewater leading to an impact on the environment and waste of resources. Certain baths, especially in connection with finishing, could be re-used after a simple filtration. In a printing house, for instance, it is possible to collect and reuse the softening agents. The equipment is very simple; mechanical filter, pump and hose. The filtered softening agent is returned to the dosing tank.

3.2.2 Main achieved environmental benefits

The main environmental benefit is reduction in the pollution load of wastewater. In a Danish pigment print-house, the implementation of this option for softening agents has reduced the consumption (and discharge) by approximately 20,000 kg/year.

3.2.3 Cross-media (whole environment) effects

- Reduction in consumption and emission of chemicals.
- Ability to re-use chemicals.

3.2.4 Applicability

In principal, this option can be implemented in all types of textile companies involved in finishing; new or existing, large or small.

3.2.5 Economy

In the Danish case mentioned above, the total capital costs (mechanical filter, pump and hose) are estimated at approximately 2,000 DKK (≈ 250 EUR). Change in operating costs (before and after implementation) is negligible. The economic value of softening agents is in the range of 0.5-1.25 DKK per kg (savings approximately 17,500 DKK). Hence the total annual savings are approximately 15,500 DKK (≈ 2,000 EUR). Payback time is estimated at about two months.

3.2.6 Driving force for implementation

Substantial costs for chemicals in general.

3.2.7 References to literature and example plants

Literature:

DANCEE, 1999. Cleaner Technology Transfer to the Polish Textile Industry. Idea catalogue and selected options, 1999. Danish Ministry of Environment and Energy. Danish Environmental Protection Agency. DANCEE – Danish Co-operation for Environment in Eastern Europe.

Example plants:

Danish Colour Design Textile Print A/S
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4 Cleaner technology in enzymatic desizing

Desizing is only carried out on woven material. As the size chemicals render the material water repellent, they must be removed before dyeing/printing/finishing.

Sizes made of starch and modified starch are normally removed by using enzymes (amylases), which will decompose the starch and make it water-soluble. Starch sizes can also be removed by means of an oxidation with sodium or potassium persulphate. Synthetic sizes e.g. PVA (polyvinyl alcohol) are water-soluble and can be removed by a simple washing process.

The option described in this paper is related to enzymatic desizing of starch.

4.1.1 Description

Wastewater from the desizing bath and the first rinse after desizing of starch based sizes will have a very high COD load, and it will have an elevated temperature, typically 60°C, thus being subject to heat recovery. To reduce the COD-load in the wastewater from such processes, this wastewater can be collected and treated by means of membrane filtration, either nano-filtration or reverse osmosis.

This option has been tested, evaluated and installed at a Danish dye-house, where nano-filtration and reverse osmosis membranes were used. Wastewater from nine jiggers executing desizing is collected in a holding tank, from which the wastewater is led to the membrane filtration plant. As textile wastewater contains a lot of fibres, it is very important to install mechanical filters before the membrane filters.

The permeate (cleaned water) is reused for desizing and washing purposes, where the energy content can be utilised as well. The concentrate should be handled separately. Due to its very high content of broken down starch, the concentrate can serve as a substrate for biogas production or a carbon source for denitrification. The latter option is being considered in the above-mentioned case.

Further details about the project are enclosed in Annex B.

4.1.2 Main achieved environmental benefits

The main achieved environmental benefit is reduction in water consumption. In a Danish dye-house, the implementation of the above option has reduced the daily water consumption by 17 m^3 (12%). In addition, there is a non-quantified energy saving. A reduction of COD discharge is estimated at about 70 – 90 g COD per kg textile.

4.1.3 Cross-media (whole environment) effects

- Reduction in water consumption.
- Ability to re-use wastewater.
- Reduction in energy consumption.
- Increased electricity consumption for running the membrane filtration plant.
- Reduction of COD load at wastewater treatment plant (provided concentrate could be handled separately).

4.1.4 Applicability

This option can be implemented at all dye-houses, which carry out enzymatic desizing of natural or modified starch. A membrane filtration plant with collecting tanks etc. will take up some space depending on the size of plant.

4.1.5 Economics

In the Danish case mentioned above, the total capital costs (tanks, mechanical filters, pumps, pipes and membrane filtration plant) are about DKK 800,000 (≈ EUR 105,000). Running costs are not calculated. The membrane filtration plant is designed to treat 22 m^3 per day and to produce 19 m^3 water for reuse per day. Provided the plant is utilised at its full capacity, treating wastewater at 60°C the following savings can be calculated:

Water savings: 19 m^3 per day or 4,180 m^3 per year. The costs for fresh water and wastewater discharge are approximately DKK 23.76 per m^3. Annual savings: approx. DKK 100,000 (≈ EUR 13,000).

In addition, the implementation of the system is estimated to remove the special COD-load tax at DKK 9.91 pr m^3. The tax is charged on the total water discharge at approximately 30,000 m^3 per year. Hence additional savings at about DKK 300,000 (EUR 40,000).

Energy savings: 19 m^3 per day or 4,180 m^3 per year, which must not be heated to 60°C. The gas price is DKK 3.07 per m^3. Annual savings: approx. DKK 84,000 (EUR 11,000).

The total annual savings are approx. DKK 484,000 (EUR 64,000). Simple payback time estimated at about 1.7 years.

4.1.6 Driving force for implementation

High costs for fresh water and wastewater. Extra costs for wastewater with a high COD load.

4.1.7 References to literature and example plants

Literature:

Environmental assessment of textiles, 1997. Life cycle screening of the production of textiles containing cotton, wool, viscose, polyester or acrylic fibres. Environmental project no. 369, 1997. Ministry of Environment and Energy. Danish Environmental Protection Agency.

BAT for Textile Industry, 1996. Pre-treatment, dyeing, printing and/or finishing of textile products. TemaNord 1996:558. Nordic Council of Ministers.

Membrane filtration of desizing wastewater in the textile industry. Working report no. 25, 2001. Ministry of Environment and Energy. Danish Environmental Protection Agency (In Danish).

Example plant:

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Fax: + 45 49 26 62 36
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Annex A

Score system for sorting of chemicals - Compendium, 2nd revised edition

Score System

for Sorting of Chemicals

on Basis of

Environment Data and Information on Consumption

Compendium, 2nd revised edition

Prepared in Cooperation between:

Textil- og Beklædningsindustrien
Ringkjøbing Amtskommune
Aulum-Haderup Kommune
Herning Kommune
Ikast Kommune
Videbæk Kommune

January 1994

SUMMARY

The score system is an administrative method of sorting chemicals on the basis of information especially from the chemical supplier's specification sheets. The sorting permits a priority selection of chemicals which, because of actual consumption and information on environmental behaviour, should be subject to closer examination.

The score system is based on the parameters usually considered to be the most interesting in connection with characterisation of substances injurious to the environment of industrial sewage. The parameter **A** is a score on the estimated amount of chemical, which is discharged into the environment as wastewater. **B** is a score on biodegradability, and **C** is a score on bioaccumulation. The structure of the score system appears from the table in chapter 2.

Together, **A**, **B** and **C** indicate the potential presence of the substance in the environment; (exposure); how much of, how long and how is the substance present in the aquatic environment. **A** influences the effect of **B** and **C**, while **B** influences the effect of **C**. The total score, which is obtained by multiplying the score for **A**, **B** and **C**, is called the exposure score.

Effects of chemical exposure depend on the toxicity of the chemical. The toxicity **(D)** should be evaluated concurrently in proportion to the exposure.

Each parameter is given a numerical value between 1 and 4 with 4 indicating the most critical environmental impact. Missing information involves highest score. The result is that each substance can be given a score as to exposure (A×B×C), and independent of this, a score as to toxicity (D). Subsequently, it will be possible to make a ranking of the chemicals.

Application of the system implies that the system is worked into the wastewater permits or environmental approvals of the companies. Hereafter, the companies should send in information on consumption of chemicals as well as environmental data. The first time, information on all chemicals employed should be submitted, but following, reporting of new chemicals may take place concurrently with the employment of these. At least once a year, the statement of consumption should be updated.

The Federation of Danish Textile and Clothing Industries is prepared to act as "consultant" for the individual companies, and it has established a data base management system for storing of information on chemicals and calculation of score. By means of the data base facilities, it will thus be possible to print out a list of the employed chemicals and the calculated score *(a Score Report)* specifically for each company. This list could subsequently be supplemented with a detailed analysis of the chemicals, which were given a high score.
The information now available should form the basis of the environmental authority's *(municipality/county)* evaluation as to possible "interventions".

2. DESCRIPTION OF THE SCORE SYSTEM

The score system is based on the parameters usually considered to be the most interesting in connection with characterisation of substances injurious to the environment of industrial sewage:

A Discharged amount of substance
B Biodegradability
C Bioaccumulation
D Toxicity

The structure of the score system appears from the tables overleaf.

Together the parameters **A**, **B** and **C** indicate the potential presence of the substance *(exposure)* in the environment; how much of, how long and how is the substance present in the aquatic environment. **A** influences the effect of **B** and **C**, while **B** influences the effect of **C**. Thus, the total **"exposure score"** is obtained by multiplying **A**, **B** and **C**.

As regards mixtures of substances solely consisting of inorganic compounds, the parameter "biodegradability" is without meaning. A calculation of the "exposure score" A×B×C is thus not relevant to such substances/mixtures.

The effect of the presence of a substance in the environment depends on its **toxicity**. The toxicity score should be evaluated concurrently and independently in proportion to the exposure score.

Each parameter is given a numerical value between 1 and 4 with 4 indicating the most critical environmental impact. Missing information involves highest score. The result is that each substance can be given a score as to exposure **(A×B×C)**, and independent of this, a score as to toxicity **(D)**. Subsequently, it will be possible to make a ranking of the chemicals.

Data Quality

It is advisable that the data used as score basis as far as possible have been obtained according to internationally approved methods of examination. Appendix 1 is a list of methods of examination, *which are considered approved.*

Within the parameters **B** and **C** and **D**, data on different levels are used. The highest level represents data generated on basis of examination conditions, which seen in proportion to data from lower levels are most comparable with a natural aquatic environment. As regards the parameter **C**, data obtained from standardised bioaccumulation tests with fish are thus more realistic than data from examinations based on determination of the distribution of the substance in a two-phased mixture of octanol and water (P_{ow}-data). However, P_{ow} has a more direct correlation with bioaccumulation than solubility data.

The highest level is stated at the top within each parameter. When preparing the score system, it has been taken into consideration that when data from the lowest quality level are used, the certainty will be less.

It is a prerequisite that data on the highest available level should always be used.

In order to secure the practical execution of the C score, it has been necessary to accept that the score can be established on the basis of qualitative information on solubility. With this end in view, there has been prepared a "diagram for establishment of the C score on the basis of qualitative information on solubility" (appendix 2) (enclosed).

Score System for Sorting of Chemicals on Basis of Environment Data and Information on Consumption

EXPOSURE SCORE (A×B×C)

SCORE FIGURE: PARAMETER	1	2	3	4
A **Discharged amount of substance**				
kg/week	< 1	1-10	> 10-100	> 100
kg/year	< 50	50-500	> 500-5000	> 5000
B **Biodegradability**				
Surface water (%)	> 60(50-100)	10-60	< 10	
Sludge culture (%)		> 70	20-70	< 20
BOD/COD ratio		> 0.5		≤ 0.5
C **Bioaccumulation**				
*BioconcentrationFactor (**BCF**)*	< 100			≥ 100
*or **C1**, **C2**, **C3***				
C1 *If MW > 1000 g/mol*	*			
C2 *If 500 ≤ MW ≤ 1000 g/mol*				
P_{ow}-data	< 1000	≥ 1000		
Water solubility g/l	> 10	10-2	< 2	
C3 *If MW < 500 g/mol*				
P_{ow}-data	< 1000			≥ 1000
Water solubility g/l	> 100	100-2	> 2-0.02	< 0.02
No information				*

TOXICITY SCORE (D)

SCORE FIGURE: PARAMETER	1	2	3	4
D Effect concentration divided by effluent concentration	> 1000	1000-101	100-10	< 10
No information				*

Application of the score system is described in chapter 3.

3. GUIDELINES TO THE SCORE SYSTEM

3.1 Discharged Amount of Substance (A)

The discharged amount of substance is the difference between the amount of chemical used cf. the stock list, and the part, which is expected retained in the textile. As to dyestuffs, the retention ability in the textile *(the percentage of utilisation)* is relatively high, whereas it is very poor, probably about 0%, as to accessory agents such as detergents.

If possible, accessory agents, which are converted in connection with the process, are to be scored on the basis of information of the conversion product. If no information is available, the substance is scored on the basis of the starting substance with a percentage of utilisation of 0, if no other percentage of utilisation has been detected/calculated.

As to dyestuffs, the following percentages of utilisation are presumed, if no further information is available:

Dispersing dyestuffs	90%
Acid dyestuffs	95%
Metal complex dyestuffs	95%
Cationic dyestuffs	98%
Direct dyestuffs	80%
Sulphur dyestuffs	60%
Reactive dyestuffs	50%

If the percentage of utilisation is stated as ">" x%, the actual utilisation rate is presumed to be x%.

The basis for the used percentages of utilisation is to be accepted by the surveillance authority.

If the physical/chemical qualities of the chemical related to the application method indicate a considerable outlet to the air, this should be set off in the calculated amount discharged with the wastewater. The basis for calculation of outlet to the air is to be accepted by the surveillance authority.

As to companies connected to a municipal sewage plant, A is initially calculated as starting point in proportion to the discharge to the public sewage system.

As to companies having a separate discharge of sewage, A is also initially calculated as starting point with reference to inlet of the sewage plant. If a specific documentation for removal in the sewage plant is available, this has to be taken into consideration when calculating the discharged amount.

The consumption of chemicals can be scored on basis of either the weekly or the annual consumption. Other periods of consumption (< 1 year) can be estimated by a simple conversion from the actual period into weeks.

If the consumption pattern for a substance is distinctly periodical, the consumption should in principle be scored on a weekly basis, as this will then give a more correct picture of the impact. This is especially important when calculating the D-score.

When calculating the score for new substances in the production, it will often be best to fix the amount score on basis of an expected weekly consumption. This is due to the fact that it will probably be impossible to predict the annual consumption.

In case of an experimental consumption, a weekly consumption will also be most relevant.

Information on consumption figures of products containing several substances is as a starting point stated on basis of the total product amount notwithstanding that the "active" chemical only represents a small part of the product amount. The score figure could possibly be accompanied by a note.

3.2. Biodegradability (B)

The criteria making the basis of the score are primarily the biodegradability of a substance in surface water or under more favourable conditions in sludge.

If a substance is decomposed or eliminated by a non-biological process this information will be correspondingly relevant, and after a more detailed examination, it will be possible to include it in the score (cf. below on eliminability).

The biodegradability of a substance can be described according to different degradation levels:

a) *Primary biodegradability, which means that the substance loses its chemical identity.*

b) *Functional biodegradability, which means that a specific quality of the substance disappears.*

c) *Total biodegradability, which means a complete conversion into carbon dioxide, water and other inorganic compounds.*

d) *A complete mineralization, corresponding to c), but where the inorganic compounds are found as oxides.*

The test methods, which are approved for determination of the biodegradability of a substance imply that the degradation of the substance is measured in relation to a total degradation, corresponding to item c).

Information on degradability is stated according to 3 different test levels:

Degradability in recipient water:

> *This degradability test is to refer to tests giving relatively poor conditions for biological degradation; i.e. not adapted test culture, low biomass and a relatively high concentration of the test substance, The degradation is to start before 28 days.*
>
> *Different principles according to approved methods are used. It is common for all methods that the test substance is the only carbon source.*
>
> *The results are stated as a % degradation after a fixed test period. If biodegradability data are only stated as intervals, "50-100%" is used synonymously with ">60%". This is stated in brackets after ">60" in the score system.*

Degradability in sludge

> *Degradability in sludge is to refer to tests giving relatively good conditions for biological degradation; i.e. a very large bacterial density and a high concentration of the test substance. Furthermore, the tests can be made with a longer exposure time, which secures better possibilities for adaptation. Active sludge is used as inoculum.*

BOD/COD-conditions

> *This parameter may only be used in cases where data from degradability tests are not available. BOD refers to the biological oxygen consumption after 5 days. COD is the chemical oxygen consumption.*

Eliminability

> *A substance can be eliminated from the water phase by degradation, sorption or evaporation. The concept "eliminability" covers all 3 of the processes. Some data sheets only list information on eliminability.* Determination of the score on basis of information on eliminability can take place according to the "scale" for "degradability in sludge cultures".

Degradability of mixtures of substances

> *Degradability of products, which are mixtures of several substances, should in principle be estimated in relation to each individual substance. If such information is not available, the score is made on basis of the stated degradability of the product supplemented with a note indicating that it is a mixed product.*

3.3. Bioaccumulability (C)

The bioconcentration factor (**BCF**) conveys for a given substance and a given aquatic organism the relation between the concentration of the substance in the organism and the water phase, i.e. the tendency of the substance to accumulation in organic tissue.

Bioconcentration data can be obtained on 3 "levels". The highest level is a direct determination by tests on fish. The medium level is a determination of the distribution ratio of the substance in an octanol-water "mixture". This ratio is described by a distribution coefficient called $\mathbf{P_{ow}}$.

The lowest level is based on information on solubility ($\mathbf{C_s}$, measured or estimated).

The assessment of bioaccumulability according to the lower levels is based on basis of the correlation existing between **BCF and** $\mathbf{P_{ow}}$ or $\mathbf{C_s}$.

It has been proved *in /8/* that the presumed correlation between $\mathbf{P_{ow}}$ and **BCF** disregards the fact that the possibility of a substance for bioaccumulation in tissue will be strongly limited for substances which have an extremely low fat and water solubility *(e.g. pigment dyestuffs).*

The same is in evidence as to large-molecular compounds (actually the steric configuration) where the molecular size can constitute a barrier to the possible absorption through cell membranes.

In order to obviate the above limitations, the score system has been drawn up with 3 subscales (C1, C2 and C3) for biodegradability. The molar weight (**MW**) of the chemical is decisive for what sub-scale one should use.

For chemicals with MW > 1000 g/mol the score figure is fixed to be 1 unless information on stable degradation products with MW < 1 000g/mol, or research indicating that the substance is bioaccumulated is available.

The working group has decided, that if exact information corresponding to the conditions for C1, C2 or C3 is not available, the score can temporarily be made on basis of qualitative information on solubility (dispersing ability, miscibility, emulsion etc.). Qualitative information is interpreted in accordance with the diagram in appendix 2.

Products containing several substances are scored according to the same principles, which apply to the B-score.

3.4 Toxicity (D)

The D-score is fixed in relation to the difference between the concentration which gives a toxic effect, and the concentration which is calculable to be found in the waste water.

The score can be calculated according to different conditions. It is thus important that the score is not stated without reference to the conditions.

The concentration in wastewater can be considered from two points of view:

- ***The average concentration*** *which refers to the annual loss of chemical to the wastewater divided by the annual water volume consumption.*

  As to a substance, which is used steadily throughout the total calculation period, the actual wastewater concentration will be reasonably described by calculation of the average concentration.

  As to substances, which are used for short campaigns, the average concentration will "underestimate" the actual wastewater concentration.

- ***The extreme concentration*** *which refers to the annual chemical loss to the wastewater divided by 24 hours' water volume consumption.*

Two different test categories are considered:

- *Test on* ***fresh-water fauna or on algae****, e.g. acute toxicity in fresh-water fish, crayfish or microalgae. The result should be stated as* LC_0 *(algae test* EC_0*), which is the highest concentration that does not give any toxic effect.*

  In cases where only LC_{50}*, is available, it is possible in the case of* LC_{50} *~100 mg/l to convert from* LC_{50}*, to* LC_0 *by dividing by 3. In the case of* LC_{50}*>100 mg/l, no conversion is made.*

- ***Test on sludge culture****. The effect concentration (*EC_{20} *in sludge organisms, either activated sludge or Pseudomonas putida, a bacterium which can be found in wastewater treatment plant sludge.*

According to the above, the different conditions can be placed together in 4 combination possibilities stated as **Dl**, **D2**, **D3** and **D4**.

Dl = Effect level for fresh-water fauna or algae divided by the average concentration.

D2 = Effect level for fresh-water fauna or algae divided by the extreme concentration.

D3 = Effect level for sludge culture or bacterium divided by the average concentration.

D4 = Effect level for sludge culture or bacterium divided by the extreme concentration.

Dl and **D2** represent data on higher quality levels than **D3** and **D4**.

D-score for different substances are only comparable within the same data level.

As it appears from the score system, the toxicity should be measured concurrently in relation to the exposure. If the actual consumption pattern is best described as periodical, D2 or D4 should be basis for the assessment.

In general, a low score in D2 or D4 may indicate that the toxicity is of secondary importance in relation to the exposure score.

4. COMMENTS TO THE SCORE PARAMETERS

It should be noted that the score system should not be used to inorganic compounds. These substances should primarily be assessed on basis of a toxicity criterion related to the amount discharged.

AMOUNT

The score levels 1 - 4 have been fixed on the basis of the consumption pattern in 1987 so that "1 " reflects a small consumption, whereas "4" reflects a big consumption.

The levels 1 - 4 should possibly be revised concurrently with changes of the raw materials consumption of the company.

When calculating the discharged amount, a deduction of the part which is removed in the sewage plant should in principle be made. In practise, however, sufficient documentation of the degrees of treatment in the sewage plant are usually not yet available. Therefore, an approved basis for making any deduction for removal in the sewage plant is still not available.

One cannot preclude that different trade names cover products which are approximately identical as regards the chemical composition. It is not the intention that the A-score is minimised by deliberately using such alternative products. In principle, these product groups should be pooled to a common A-score.

DEGRADABILITY - Surface Water

A substance is described as **"readily degradable"** if the degradation results in an elimination of 70% of the resolved organic carbon, 60% of the theoretic oxygen consumption or formation of 60% of the theoretic quantity of carbon dioxide. Moreover, the substance is considered to be readily degradable if other scientifically well-researched tests have shown that the substance is decomposed biologically or non-biologically to a level > 70%. The degradation is to take place within 1 0 days of a 28 days' test period.

To avoid more score levels and a sharp distinction between choice of method, 60% has been chosen as a general limit.

Most of the data sheets state biodegradability according to the intervals < 10%, 10-25% and 50-100%. By means of the applied intervals for the degradation score it will therefore not be possible to give a lower score than "2". This is, however, in bad accordance with the intentions to secure that unproblematic substances are sorted out. The chosen "alternative", score 1 at 50-100", is therefore a reasonable compromise.

If degradation data based an proper degradation tests are not available, the quantity BOD/COD > 0.5 can be applied as criterion for easy degradation /14/. Compared to the 1st edition of the score system, there has been made a change of the score scale for the BOD/COD criterion. The lowest score has been changed from 1 to 2. This is due to the principle that there must be accordance between data quality and "certainty" (see page 3). In the first edition there thus was a disproportion between the score according to the sludge test and the score according to BOD/COD.

It should be noted that data sheets generally state the degradability of a compound product (mixture of substances) as the sum of the degradability of the single components multiplied by the proportional part with which the component enters into the compound. Inorganic components are estimated to be 100% decomposable.

Scoring on basis of "product" information implies a risk to "overlook" the presence of non-degradable or not readily decomposable substances, which form part of products. This risk is partly neutralised by the fact that the amount score has been fixed on basis of the total amount of the product compound.

DEGRADABILITY - Sludge

Tests based on degradation in sludge cultures are not comparable with the proportions in the recipient. In principle, the tests can only be applied to predict the indegradability of a substance, but not its possible degradability in the recipient.

Substances which are decomposed by less than 20% by using methods based on sludge culture, are considered to be "not readily decomposable or slowly decomposable", and they are often described as persistent. Substances, which are decomposed by more than 70% are described as "potentially decomposable" (inherent biodegradability). Substances, which are decomposed by between 20% and 70%, are generally considered to be decomposable, but it is likely that there will be generated stable metabolites by this degradation.

It is not possible to "interpret" degradability in surface water exactly to degradability in sludge culture. One can only establish that the degradation in sludge will usually be bigger than the degradation in the water phase. This is reflected in the chosen levels of the score.

BIOACCUMULABILITY

/10/ has put forward some criteria as to when bioaccumulation tests with fish should be considered unnecessary:

- *Pigments which have a very poor solubility in both the water phase ($C_s < 0.1$ mg/l) and the organic phase ($C_s < 10$ mg/l) are considered to be "non- accumulative".*
- *Dyestuffs, which are highly water-soluble ($C_s > 2$ g/l), are supposed to have so little affinity to biological tissue that they are considered to be "non-accumulative".*
- *Dyestuffs having a molecular weight (MW) higher than 450 g/mol and a cross section bigger than 1.05 nm are supposed to be too bulky to be absorbed into biological tissue. The consideration is "little probability of accumulability".*

The molecular weight is the most simple parameter describing the molecular size. In general, information on more directly describing parameters will not be available.

A score system proposed by the Nordic Council of Ministers (MST-environment project 153, 1990) suggests that MW = 1000 g/mol is used as limit for bio-accessibility, and uses the character as a score parameter together with e.g. bioaccumulation at P_{ow}-value and degradability.

Chemicals with a Molecular Weight higher than 1000 g/mol

On basis of the information that large molecules will most probably not be bio-accessible, it is reasonable to sort out big dyestuff molecules, which usually represent very molecular weight stable molecules. Possible changes of the radical structure will be of small importance for the size of the molecule. By choosing MW = 1000 g/mol as limit for this sorting, there is accordance with the Nordic Council of Ministers' score system. At the same time there is a good margin to the limit of 450 g/mol proposed by /10/. However, it should be noted that /10/ connects the molar weight criterion with molecular cross section and fat-solubility etc.

In fact, the precondition to "acquit" chemicals with a molecular weight of more than 1 000 g/mol is that no stable products of decomposition with accumulative qualities are generated during a possible degradation. Often, this information will not be available. To make the system operative, the criterion "unless information on stable degradation products with a MW < 1000.

The probability that bioaceumulation data from tests on fish are available is little. If so, the substance is to be evaluated on basis of these data.

Chemicals with a Molecular Weight between 1000 and 500 g/mol

The probability that the chemical is bio-accessible is small. It is, however, bigger than it is the case for the above group.

The probability that bioaccumulation data from tests on fish are available is little, cf. the priority proposed in /10/.

It is an accepted fact that the critical BCF-value is 100. It is among other things applied in the EC Commission's proposal for classification and marking of substances harmful to the environment.

As to P_{ow} data, the critical value has been fixed on basis of the theory that if $P_{ow} < 1000$, then the BCF will be < 100 /7/. This quantity is recommended as criterion as to whether it is recommended to make accumulation tests on fish.

The grading for $P_{ow} > 1000$ is rather gentle as the molecule size only gives little probability of accumulation. However, compared with the score for amount and biodegradability, the grading secures that the substance will be taken into consideration, if the substance is not easily degradable, and is used to a considerable extent.

As to solubility data, the critical values have been fixed on the basis in 1101 and the mathematical connection between solubility and P(ow). It is possible to obtain a higher score than it is the case for P_{ow} data on the background that "solubility" is a weaker parameter than P_{ow}.

Chemicals with a Molecular Weight smaller than 500 g/mol

In this group most of the data are expected to come from accumulative tests on fish. The grading of the score for BCF-data is identical with the above score module.

As regards P_{ow} data, the same critical value as mentioned above is applied, but $P_{ow} > 1000$ is evaluated on a par with BCF > 100. In these cases, there is a considerable indication of bioaccumulation.

As to solubility data, the critical values have been made more stringent. Roughly, the same classification as proposed in the original score system /2/ has been applied.

TOXICITY

The toxicity of composite wastewater is notoriously difficult to characterise on basis of the information on the single substances. The reason is that the effect from the coexistence of the substances often cause that toxicity of the single substances cannot be considered as additive. Some substances may react mutually, and by this, the toxicity may be reduced or possibly increased.

Thus, the toxicity should above all be controlled by a "whole effluent" toxicity control and by establishment of a fixed permit limit regarding the total toxicity of the wastewater. By this, possible synergistic effects would be included.

Information on the toxicity of the individual substances is, however, still relevant, as this information can at least be used for a guideline estimation of the potential contribution of a substance to the toxicity of the wastewater. It will always be desirable to avoid using toxic substances. The score renders potentially problematic substances visible.

In general, treatment in sewage plants will be able to reduce the toxicity of the wastewater either as a result of a degradation of the substances or because of the retention in sludge. The actual reduction can only be determined on basis of toxicity tests on corresponding samples of head water, sewage water and sludge from the sewage plant in question.

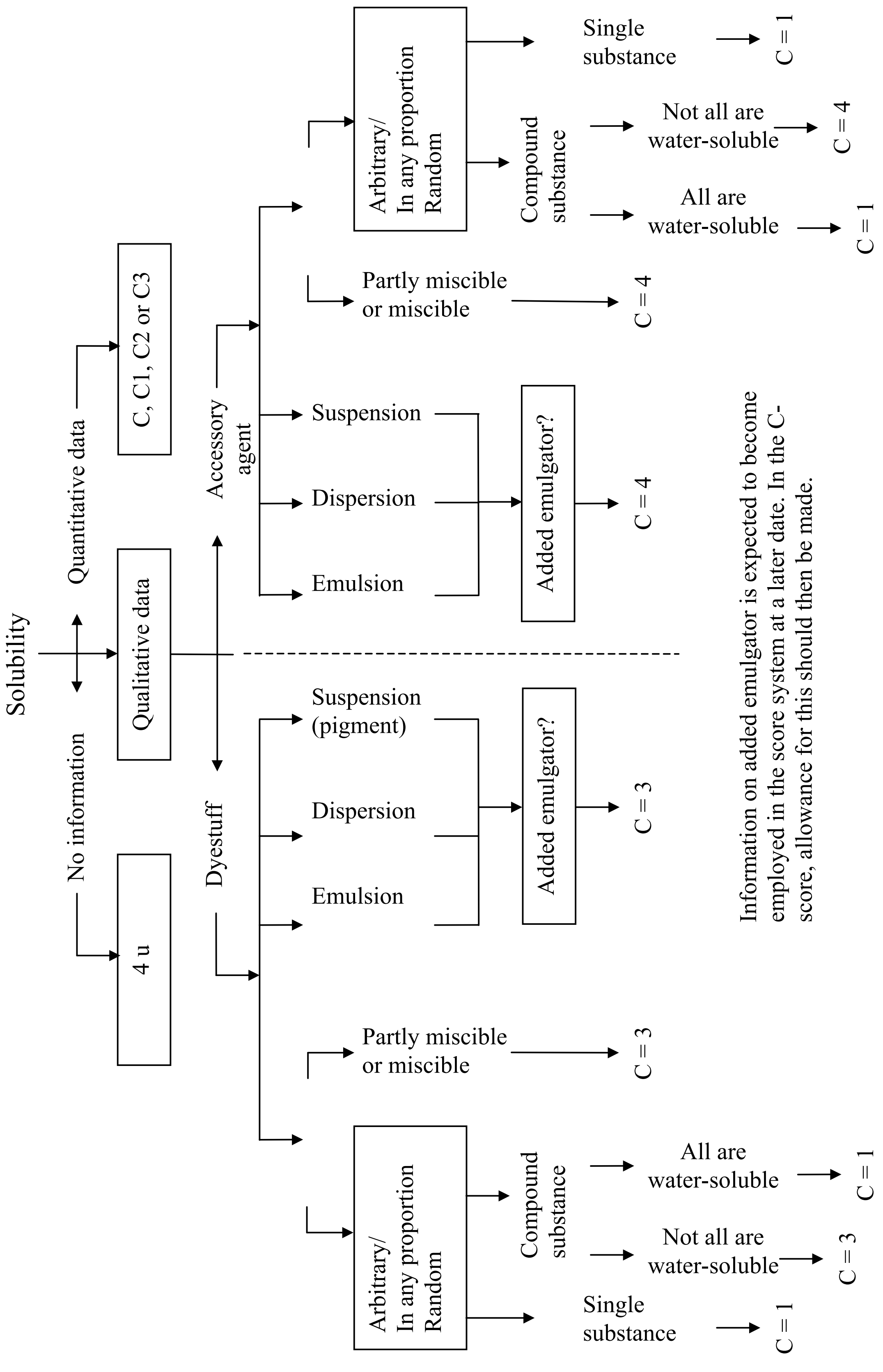
The basis for the conversion from LC_{50} to LC_0 by dividing by 3 are experience figures (The Water Quality lnstitute). The conversion is in reasonable accordance with EPA's "Criteria Maximum Concentration", which is defined as 0,3 times the lowest LC_{50} value for acute toxicity towards at least 3 species. /16/.

As regards LC_{50} >100 mg/l no conversion is made. The reason is that many toxicity tests cannot be continued beyond the concentration 100 mg/l. If ">100" is used as "absolute 100" there will therefore in most cases occur a distorted weighting of the result in connection with a possible conversion (division by 3) to LC_0.

Appendix 2

C-parameter

(qualitative data)



Information on added emulgator is expected to become employed in the score system at a later date. In the C-score, allowance for this should then be made.

Temporary score for the C-parameter when only qualitative information on solubility is available.

Membrane filtration of desizing wastewater in the textile industry

Working report no. 25, 2001. Ministry of Environment and Energy. Danish Environmental Protection Agency.

The basis for the project was the fact that desizing of woven textiles generates wastewater with a high content of COD. It must, however, be expected that the partially decomposed sizing chemicals relatively easily can be removed through an appropriate filtration process, and afterwards the water, containing energy and possible auxiliary chemicals, can be reused.

Therefore, the purpose of the project was to find the most suitable process of filtration of desizing wastewater through testing in laboratory and pilot scale as well as testing in full-scale. The economical and environmental consequences with this process should be covered at the same time. The pilot scale and full-scale tests have been implemented at Nordisk Blege- og Farveri in Helsingør. The desizing is carried out partly by oxidation and partly enzymatic.

Quickly, we could state that purification and recycling of wastewater from synthetic sizing chemicals already have been subject to extensive investigations. Therefore, it was decided that the project should concentrate on natural sizing chemicals – usually natural starch or modified starches, which at the same time exist most frequently at the company.

A number of membrane types were tested in the laboratory with the actual wastewater, and the tests resulted in the first selections of membranes to the pilot scale tests.

Two series of the pilot scale tests were carried out. In the first series, focus was primarily on the oxidation process. However, it turned out to give some practical problems, especially in connection with the risk of re-precipitation of size in the membranes. Therefore, the other series only tested the enzymatic decomposed size, and here it turned out that both nano and reverse osmosis membranes can be used for the purpose.

A full-scale plant was afterwards designed and delivered to the company. It was designed to treat the wastewater from enzymatic desizing from the company's 9 jiggers. Nano-filtration was selected with a capacity of 21 m^3 during 24 hours.

The plant has been running for a period with current adjustments, and some plant components have been changed. Experience from 6 to 7 months running time exist, but this period is too short to give reliable knowledge about the lifetime of membrane elements and optimum cleaning procedures. The purified water has been reused without any problems.

However, we have outlined a financial potential, which shows that the plant in question will have a simple payback time of between two and three years, if it is fully run. We have not included any expenses for possible changes of membranes, purification chemicals, electricity and removal of concentrate.

The removal of concentrate has not been finally clarified. Tests show that concentrate will be suitable for biogas production and as carbon source in connection with denitrification. Negotiations are conducted with Helsingør Municipality about delivery of the concentrate to one of the treatment plants, which carries out denitrification.

Therefore, we can conclude that membrane filtration can be used for separation of wastewater from desizing in clean water for reuse and concentrate, which can be utilised. The financial circumstances have not yet been finally clarified.