Survey of chemicals in consumer products

Survey no. 21, 2003

Mapping of chemicals in dry-cleaned textiles from Rynex and hydrocarbon dry-cleaning shops

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Foreword

This project forms part of a major investigation of different consumer products with the title: Mapping of chemicals in consumer products.

The investigations were initiated in order to map the above field and to examine the exposure of the population to chemicals in consumer products as well as the risk involved.

The project work was carried out by an interdisciplinary team consisting of employees from Eurofins Denmark A/S and Kampsax A/S. These employees are as follows:

- Eurofins Denmark A/S: Peter Mortensen and Kurt Borch Christensen
- COWI A/S, (previously Kampsax A/S): Dorte Glensvig, Jan Dam Christensen and Ninna Dahl Ravnsbæk. Ninna Dahl Ravnsbæk has carried out internal quality control of the project report.

The success of the project has been fully dependent on information from dry-cleaning shops and their suppliers. We would therefore like to express our sincere gratitude to the 6 Danish dry-cleaning shops and the 4 suppliers that have provided us with responses, safety product sheets and samples of chemical products, etc. Furthermore, we would like to thank Flemming Gordon Olsen, Sober Rens ApS - Texpert Allerød, who assisted us to work out section 3.

This project has been followed by a team consisting of:

- Lea Frimann Hansen, the Danish Environmental Protection Agency
- Anette Ejersted, the Danish Environmental Protection Agency
- Lisbet Heerfordt, the Danish Environmental Protection Agency
- Peter Mortensen, Eurofins Denmark A/S
- Dorte Glensvig, COWI A/S

The primary target group of the project is the Danish Environmental Protection Agency and consumers who have their textiles dry-cleaned, using hydrocarbon or Rynex cleaning fluid. The results of the project will also be of interest to Danish counties, municipalities, consultancy firms, health institutions and others dealing with administration or consultancy in relation to the chemical substances used in the dry-cleaning trade.

Summary and conclusion

This consumer project deals with the use of chemicals in alternative dry-cleaning shops using either hydrocarbon compounds or or glycolether compounds (Rynex) as cleaning fluid. The purpose of the project is to map the chemicals used in the alternative dry-cleaning shops, including the composition of the chemicals, to determine the concentration of residues in selected textiles (residual content) dry-cleaned in alternative dry-cleaning shops and to evaluate the potential influence of the residues on the indoor climate by introducing the textiles into residences.

A questionnaire was sent to 2 Rynex dry-cleaning shops and 5 hydrocarbon dry-cleaning shops, whereby 17 and 19 chemical products were identified respectively. Safety data sheets were provided from the suppliers of the chemical products and a gross list was prepared, stating the declared substances, product numbers and producers, etc. From the gross list, it appears that some of the chemicals are used in several products, e.g. 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5), poly(oxy-1,2-ethanediyl) (CAS number 69011-36-5) and a number of hydrocarbon compounds (isoalkanes and isoparaffins).

It was analysed if samples of the chemical products Toptrel HP, Actrel 3365-D, Frankotex KW, Rynex 2 , Cetox KWI, Prenett Pur, Solxex 1, Solvex 2, Solvex 3, ClipComfort, Polysol, Preclin Odosorb and TempoRyn contained volatile components, nonyl and octyl phenol polyethoxylates. Generally, there was coincidence between the declared substances in the safety data sheets and the components found during the analyses. All the investigated products did meet the rules of the Danish Environmental Protection Agency with regard to information about substances in connection with classification and marking.

The investigation showed that the products for this trade typically contain hydrocarbons or glycolethers as dominant components. The product analyses showed that 5 of 13 products contained octyl- or nonylphenolpolyethoxylates in a quantity of 0.1 to 47 percentage by weight. Tetrachlorethylene was demonstrated in Rynex 2 in a concentration of 0.01 % (percentage by weight). The analyses have shown a considerate number of volatile/semi-volatile substances. These substances do not have to be marked according to law or their concentrations are so low that they do not have to be marked.

Futhermore a sample of contact water was analysed. The contact water contained glycolethere in a concentration of 1.1 % (percentage by weight) and nonylphenolethoxylates in a concentration of less than 0.001 % (percentage by weight). Hydrocarbons or tetrachlorethylene was not detected (detection limit was 0,01 percentage by weight).

Two sets of identical textiles consisting of coat, trousers and dress were dry-cleaned in a Rynex dry-cleaning shop and a hydrocarbon dry-cleaning shop respectively. The residual content of selected chemicals was determined via emission in a climatic chamber and via extraction of the components from the textiles.

The residual content in textiles dry-cleaned in the hydrocarbon dry-cleaning shop was generally much lower than the residual content in textiles dry-cleaned in the Rynex dry-cleaning shop. Residues of tetrachlorethylene were demonstrated in textiles from the Rynex dry-cleaning.

The results from the measurements in the climatic chamber were used in a mathematical model for determination of the resulting concentration of the volatile substances in the indoor climate in a poorly ventilated apartment and in a well-ventilated single-family house respectively. The calculations were made by introducing common quantities of textiles into private homes. Based on the results of the model calculations, it is estimated that there may be a risk of indoor problems in connection with textiles with a similar residual content due to emission of glycolether from Rynex dry-cleaned textile. No unacceptable influence on the indoor climate could be demonstrated via the model calculations when the hydrocarbon dry-cleaned textile was introduced into the residence.

It was analysed if distillates from dry-cleaning machines in hydrocarbon and Rynex dry-cleaning shops contained volatile components. Besides the expected content of hydrocarbons and glycolethers, the results showed tetrachlorethylene in quantities of 0.01 and 0.04 percentage by weight.

The chemicals in the cleaning fluids may end as residue in the finally treated textile and thereby influence the consumers. At the same time, the content of for instance chlorinated solvents in the products can be a reliability problem for this part of the trade, as several of the alternative dry-cleaning shops advertise their shops as being "chlorine-free". For these reasons, the suppliers of chemical products ought to introduce an improved declaration of the content of critical substances like for instance tetrachlorethylene in the products - also in the cases where the content is below the level requiring marking in accordance with the rules of the authorities.

Part-results of the investigation have shown that the residue in textiles may be reduced considerably after the dry-cleaning by using an improved drying technique.

1 Background and objective

1.1 Background

The Danish Environmental Protection Agency has invited tenders for a number of consumer projects the purpose of which is to map chemical substances in ordinary consumer products.

One of the projects includes mapping of chemical substances in dry-cleaned textile. The project focuses on the dry-cleaning shops in Denmark using alternative cleaning fluids such as hydrocarbon cleaning fluid and Rynex cleaning fluid.

The reason for the project is a wish to increase the knowledge of the chemicals used in the dry-cleaning process and which may be found in the textiles after dry-cleaning and final treatment.

Based on the tender documentation dated 6 May 2002 of the Danish Environmental Protection Agency, the project group, consisting of Kampsax A/S and Eurofins Denmark A/S, has prepared a project proposal dated 30 May 2002.

On 20 June 2002, a meeting was held between the Danish Environmental Protection Agency, Kampsax A/S and Eurofins Denmark A/S where further project adaptations were agreed on.

1.2 Objective

The objective of this project is:

- To map the chemical products used in hydrocarbon and Rynex dry-cleaning shops by making inquiries at dry-cleaning shops and suppliers/producers.
- To map which chemicals are included in the products, both by making inquiries at suppliers and/or producers and by carrying out chemical analyses of selected chemical products.
- To investigate the concentration of residual substances in selected textiles upon dry-cleaning using the alternative cleaning fluids.
- To estimate the potential influence on the indoor climate by introducing dry-cleaned textile into residences.

Both in the above text and in the remaining part of the report, ”dry-cleaning shop” means a dry-cleaning shop using hydrocarbon or Rynex as cleaning fluid.

2 The contents and reading instructions of the project

In section 3, there is a short introduction to the processes in the dry-cleaning shops, including an introduction to the chemical products used.

The project consists of four phases with the following main contents:

- **Phase 1: Creation of a gross list of the used products**
  In phase 1, a questionnaire investigation was carried out in selected dry-cleaning shops with regard to their consumption of chemical products. Based on the responses to the questionnaires, the suppliers were contacted in order to get safety data sheets or other information about the composition of the products. This information was used for creation of a gross list of the used products (kind and quantity) and the chemicals in the hydrocarbon and Rynex dry-cleaning shops.

  Please see section 4 for a detailed description of the investigations and the results.

- **Phase 2: Screening analyses of selected products**
  On the basis of the gross list, 13 products and 1 sample of contact water were selected for chemical analysis. The analyses were carried out as specific analyses of selected substances and as screening for selected groups of substances – especially volatile organic compounds.

  Please see section 5 for information about the selected products, the analysis methods used as well as the results.

- **Phase 3: Dry-cleaning of textiles and determination of the residual content**

  At the same time the analysis of the products was carried out, a number of selected textiles were dry-cleaned in a dry-cleaning shop using hydrocarbon-based cleaning fluid and in a dry-cleaning shop using Rynex cleaning fluid. The purpose of this part of the project was to determine the emission of volatile substances from the dry-cleaned textiles and to determine the residue of selected non-volatile substances after dry-cleaning.

  Before dry-cleaning the textiles, they were provided with a number of spots to make sure that the dry-cleaning shops did use spot removers.

  The textiles and spots were selected on the basis of inquiries made at the dry-cleaning shops. Please also see section 6.

  The investigation of emission of volatile substances was made as a climatic chamber test over a period of 14 days under controlled laboratory conditions. The analysis of the residue of non-volatile sub-

stances was made after the end of the emission period. At the same time, the residue of volatile substances in the textiles was determined.

On the basis of the results of the tests carried out in the climatic chambers, the controlling parameters for the emission were determined (emission constants and residual content).

Please see section 6 for a detailed description of the test conditions, the selected textiles and spots as well as the analysis results and calculated parameters.

- **Phase 4: Modelling of the indoor climate influence from dry-cleaned textile**
  The emission constants were subsequently used for modelling of the resultant indoor climate concentration upon introduction of different quantities of newly dry-cleaned textile into a poorly ventilated apartment and a large well-ventilated single-family house respectively.

  The mathematical model, its assumptions and the results appear from section 7.

The results of the projects are discussed in section 8.

3 Introduction to processes in dry-cleaning shops

In Denmark, there are 285 dry-cleaning shops, some of them may only be for handing in (registered as ”dry-cleaning shops” under www.dgs.dk). It is estimated that approximately 225 dry-cleaning shops have their own production. Approximately 25 of these dry-cleaning shops use hydrocarbon cleaning fluid (October 2002). Some of the dry-cleaning shops have both tetrachlorethylene and hydrocarbon dry-cleaning machines. 4 of the dry-cleaning shops are using Rynex cleaning fluid. Please note that according to the company installing the Rynex cleaning machines, it has been decided to convert the above 4 machines into machines using hydrocarbon cleaning fluid due to a risk of mechanical engineering problems in the future (HJM-Teknik A/S, 2002)

The work procedure in the dry-cleaning shops typically includes the following activities:

- Goods reception and storage
- Spot removal
- Basic dry-cleaning in dry-cleaning machine
- Shaping (e.g. pressing) and/or final treatment
- Goods control and storage
- Delivery of goods

The basic dry-cleaning in the dry-cleaning machine typically consists of a pre-rinse, a filter rinse and subsequent drying. If you compare the dry-cleaning process with the washing process in an ordinary washing machine, the pre-rinse can be compared with the pre-wash and the filter rinse can be compared with the basic washing programme and subsequent rinsing.

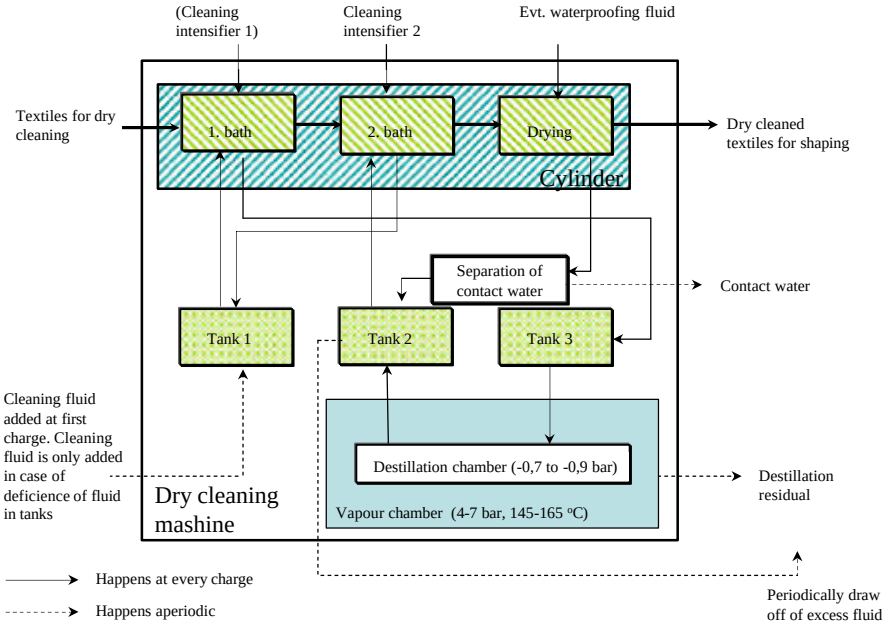
Besides the cleaning fluid, a number of chemical products, such as spot removers, cleaning intensifiers, antistatica, etc., are used for the treatment of the textiles. These chemical product types are listed in table 3.1 below, the product types being used to a larger or smaller extent in both hydrocarbon and Rynex dry-cleaning shops. For some of the chemical products, more functions can be included in one product.

Table 3.1: Types of chemical products used in dry-cleaning shops

Product type	**Function/use**
Pre-brushing fluid/spot remover	Spot cleaning before the basic dry-cleaning
Cleaning fluid	Basic dry-cleaning
Cleaning intensifier	Product containing tensides. To be used during the basic dry-cleaning (first bath) and in the second bath
Starching fluid	To be added to the second bath
Antistatica	Removes statical electricity. To be added to the second bath
Waterproofing fluid	Extra treatment: Protects the textile against water. To be used after the second bath, but before the drying
Dubbin	For special cleaning of leather. To be added to the cleaning bath. Cleaning of leather typically takes place in a special dry-cleaning shop
Spotting fluid	Spot cleaning before/after the basic dry-cleaning
Other products	Filter powder, active carbon for air cleaning, etc.

The processes in the hydrocarbon and Rynex machines used in Denmark can be illustrated by the flow diagram in figure 3.1.

Figure 3.1: Schematic description of the typical processes in the hydrocarbon and Rynex dry-cleaning machines



After the first bath, the cleaning fluid is diverted for distillation. The distillate is collected after distillation and condensation in tank 2. The fluid from tank 2 is used for the second bath, whereupon it is pumped into tank 1. This means that there is a constant re-circulation with intermediate distillation of the cleaning fluid.

The dry-cleaning shop is adding cleaning intensifier to the first and/or second bath. Waterproofing fluid is added after the second bath, but before the drying.

When a new dry-cleaning machine is started, cleaning fluid is added. Hereafter, cleaning fluid is only added in case of deficiency of fluid in the tanks. Often, the continuos addition of cleaning intensifier, which typically contains some of the same components as the cleaning fluids, is sufficient to compensate for the loss of cleaning fluid via the clothes, cylinder air and distillation process. In some cases, dry-cleaning shops using the latest technology periodically draw off excess fluid from the machine.

4 Phase 1 – Creation of gross list of used products

4.1 Selection of dry-cleaning shops for questionnaire round

Contact has been taken to many of the Danish Rynex and hydrocarbon dry-cleaning shops. Of these, 5 hydrocarbon dry-cleaning shops and 2 Rynex dry-cleaning shops have agreed to take part in the project. Please note that most of the inquired dry-cleaning shops form part of the same interest group, viz. Texpert.

The dry-cleaning shops are called dry-cleaning shops A to G, dry-cleaning shops A and B being Rynex dry-cleaning shops and dry-cleaning shops C to G being hydrocarbon dry-cleaning shops.

4.2 Sending out questionnaires to the dry-cleaning shops

In July 2002, a questionnaire was sent to all selected cleaning firms. Please find a non-completed questionnaire in appendix 1.

The responses to the questionnaires were collected and studied and contact was taken to the owners of the dry-cleaning shops in order to go into details about the answers.

Please see the responses to the questionnaires in appendix 2. The responses have been made anonymous.

4.3 Result of questionnaire round

This project does not include waterproofing fluids. However, the information that came to light about waterproofing fluids during the questionnaire round has been included in appendix 2. This will not be discussed any further in this report.

As it appears from the responses to the questionnaires (please also see appendix 2), there is a relatively great variation from dry-cleaning shop to dry-cleaning shop with regard to the chemical products used. The dry-cleaning shops informed about use of 30 chemical products in total, 13 products being used in the 5 hydrocarbon dry-cleaning shops and 17 products being used in the 2 Rynex dry-cleaning shops. Furthermore, one of the Rynex dry-cleaning shops informed about 2 products that are not being used any longer by the dry-cleaning shop in question.

As to the hydrocarbon dry-cleaning shops, almost 70% of the identified products were used in more than one dry-cleaning shop. As regards the Rynex dry-cleaning shops, there was coincidence between the cleaning fluid and the cleaning intensifier used, whereas different spot removers were used.

From the responses to the questionnaires, it appears that the chemicals used in the relatively largest quantities are cleaning intensifiers and cleaning fluids. The consumption of these chemicals appears from table 4.1. The quantity of dry-cleaned textile on an annual basis is also specified in this table.

Table 4.1: Consumption of cleaning fluid and cleaning intensifier. Please also see appendix 2.
[A]: Specified as 1% of the quantity of dry-cleaned clothes.
[B]: It is assumed that the specific gravity is 1.
c: Please note that this is not pure cleaning fluid, but a distillate. Minus states that distillate is drawn off from the machine.
-: Not known by the owner of the dry-cleaning shop

Dry-cleaning shop	**A**	**B**	**C**	**D**	**E**	**F**	**G**
Cleaning fluid	**Rynex**		**Hydrocarbons**				
Dry-cleaned textile quantity, kg/year	9,500	6,000	22,000	40,000	-	25,000	14,000
Consumption of cleaning fluid, litres/year	-	60[A, B]	-	-100[C]	-	50	80
Consumption of cleaning intensifier, litres/year	150	20[B]	150	425	-	350[B]	45

As dry-cleaning shop D does not add cleaning fluid but draws off distillate from the machine, the negative consumption of cleaning fluid is not pure cleaning fluid but a distilled mixture of cleaning fluid, cleaning intensifiers and other chemical products.

It is interesting to see (please also see table 4.1 and appendix 2) that the consumption of cleaning intensifier in more cases is higher than the consumption of cleaning fluid. According to the owners of the dry-cleaning shops, the consumption of cleaning intensifiers in the hydrocarbon dry-cleaning shops is almost at the same level as when they used tetrachlorethylene.

The other chemical types are typically used in quantities of less than 120 litres per year at a dry-cleaned textile quantity of up to 40,000 kg per year.

Both the owners of the hydrocarbon dry-cleaning shops and the owners of the Rynex dry-cleaning shops informed that they found the dry-cleaning satisfactory. Nothing was informed about obnoxious smells or complaints from customers due to the cleaning fluid and/or helping agents and additives used. Only one of the inquired Rynex dry-cleaning shops informed about operation problems due to the cleaning fluid(s) and helping agent(s) used: This dry-cleaning shop found the drying time too long.

When asked about other advantages or disadvantages in relation to the cleaning fluid and the helping agents and additives, the owners of the dry-cleaning shops answered as follows:

The Rynex dry-cleaning shops:

- The customer satisfaction has increased after changing to the Rynex cleaning fluid. The customers appreciate that the dry-cleaning shop is not using chlorine.

The hydrocarbon dry-cleaning shops:

- More comfortable smell in the dry-cleaning shop.

- Very satisfied with the non-smelling cleaning fluid.
- The dry-cleaning shops have received positive feedback from the costumers because they are using hydrocarbon cleaning fluid.

4.4 Providing information from suppliers

The suppliers of the chemical products used appear from the responses of the dry-cleaning shops to the quesionnaires.

The suppliers of the chemical products were contacted subsequently, a list of the chemical products that appeared during the questionnaire investigation being enclosed with the enquiry. The supplier was asked if the information from the dry-cleaning shops was correct and adequate of the products he is selling to the Rynex and hydrocarbon dry-cleaning shops. In this way, it was ensured that, wherever possible, the gross list covers all the components that are sold to the dry-cleaning shops.

Inquiries were sent to 4 suppliers in total. The inquiry resulted in identification of 4 additional products that are sold to the hydrocarbon dry-cleaning shops, but which did not appear from the product lists from the inquired dry-cleaning shops. Please also see appendix 2.

The suppliers' updated lists were included in a gross list of chemical products used in Rynex and hydrocarbon dry-cleaning shops respectively. The gross list appears from appendix 3.

Tables 4.2 and 4.3 below list the chemicals declared in the safety data sheets of the products. It is also stated in how many products the chemical is included.

Table 4.2: Chemicals including CAS number declared in safety data sheet for products sold to Rynex dry-cleaning shops, dry-cleaning shops A and B. The frequency of the chemical in the identified products is also stated (N = 19 chemical products)

CAS number	Name of chemical	Name used in safety data sheet	Used in number of products
112-34-5	2-(2-butoxyethoxy)ethanol	2-(2-butoxyethoxy)ethanol	13
69011-36-5	Poly(oxy-1,2-ethanediyl)	Fettalkoholethoxylat	10
577-11-7	Di(2-ethylhexyl) sulfosuccinat, natrium salt	Diisooctylsulfosuccinat, Natriumsalz	8
68425-47-8	Fatty acid diethanolamide	Fettsäurediethanolamid	7
68411-30-3	C_{10}-C_{13} Alkyl benzene sulfonic acid (LAS)	Alkylbenzolsulfonate	5
64742-48-9 or 90622-57-4	Hydrocarbon compounds	Isoparaffins/isoalkanes	5
100-51-6	Benzoyl alcohol	Benzoyl alcohol	2
22-99-6	2-Phenoxyethanol	Phenyl monoethylene glycolether	2
1341-49-7	Ammonium hydrogen flouride	Ammonium hydrogen flouride	2
7664-38-2	Phosphoric acid	Phosphoric acid	2
61790-12-3	Fatty acid	Oleic fatty acid	1
-	"Propane diolether"	Propane diolether	1
141-43-5	Ethanol amine	2-aminoethanol	1
50-21-5	Lactic acid	2-Hydroxypropiionsäure	1
107-41-5	2-methyl-2,4 pentandiol	2-methyl-2,4 pentandiol	1
34590-94-8	Dipropylene glycol monomethyl ether	Dipropylene glycol methyl ether	1
848-0103	n-butylacetate	Dipropylene glycol methylether	1
123-86-4	n-butylacetate	n-butylacetate	1
872-50-4	N-methyl-2-pyrrolidon	N-methyl-2-pyrrolidon	1

Table 4.3: Chemicals declared in safety data sheet for products sold to hydrocarbon dry-cleaning shops, dry-cleaning shops C to G. The frequency of the chemical in the identified products is also stated (N = 17 chemical products)
-: No CAS number informed

CAS number	Name of chemical	Name used in safety data sheet	Used in number of products
64742-48-9 90622-57-4	Hydrocarbon compounds	Isoalkanes, Iso-undekanes, Hydrocarbon compound, isopar-affin	15
112-34-5	2-(2-Butoxyethoxy)ethanol	2-(2-Butoxyethoxy)ethanol	6
-	Anion tensid	Anion active tensid	5
577-11-7	Di(2-ethylhexyl)-sulfosuccinat, natrium salt	Diisooctylsulfosuccinat, natrium-salz	4
64742-48-9	Isoparaffin	Isoparafinishes Kohlenwassest-offgemish	4
69011-36-5	Poly(oxy-1,2-ethanediyl)	Fettalkoholethoxylat	3
68425-47-8	Fatty acid diethanolamide	Fettsäurediethanolamid	3
-	Nonion tensid	Non-ionic tensid	3
34590-94-8	Dipropylen glycol mono ethyl ether	(2-Methoxymethylethoxy)propanol	2
-	Cationic tensid	Cationic tensid	2
68411-30-3	C_{10}-C_{13} Alkyl benzene sulfonate (LAS)	Alkylbenzolsulfonate	1
61790-12-3	Fatty acid	Ölsaure	1
-	Hydrocarbon compound (C11)	Iso-undekanes	2
-	Compound of tensides	Compound of tensides	1
-	Flouride alkyl polymers	Flouride alkyl polymers	1
-	Glycol ether acetate	Glycol ether acetate	1
-	Hydrocarbon compound, isopar-affin	Hydrocarbon compound, isopar-affin	1
-		3295 Hydrocarbons, liquid NOS	1
-	Aromatic hydrocarbons	Alkyl benzol	1
-	Glycol/glycolether	Alkyl glycol	1
-	Coconut soap	Coconut soap	1

According to tables 4.2 and 4.3, it is to a high degree the same chemicals that are used and declared in the chemical products.

4.5 Providing information from other interested parties

In 1996, Research Institute Hohenstein, developing and testing materials and products for dry-cleaning, carried out chemical analyses of selected products used by the alternative dry-cleaning shops. Some of the tested products have the same name as the products from the gross list. The results of the analyses appear from table 4.4 below. Please note that the composition of the products may have changed since 1996.

Table 4.4: Content of chlorinated solvents in selected products used in hydrocarbon dry-cleaning shops (Hohenstein, 1996).
No content of 1,1,2-trichlorethan, 1,1,1,2-tetrachlorethan, chloroform, tetrachlormethan, cis and trans-1,2-dichlorethan and dichlormethan in concentrations exceeding 0.001 weight/weight% has been demonstrated (0.001% corresponds to 10 mg/kg).

Product	Use	Tetrachlore-thylen weight/weight %	Trichlore-thylen Weight/weight %	1,1,1-Trichlorethan weight/weight %
Hydrocarbon dry-cleaning shops				
Frankotex KW	Cleaning intensifier	0.020	<0.001	<0.001
Cetox KWI	Waterproofing fluid	0.800	<0.001	<0.001
Solvex 1	Pre-brushing fluid Pre-brushing fluid	0.020	0.003	0.010
Solvex 2	Pre-brushing fluid	0.015	0.003	0.010
Solvex 3	Pre-brushing fluid	0.010	0.003	0.010
Rynex dry-cleaning shops				
Secafix 1	Pre-brushing fluid	0.320	0.005	0.010
Secafix 2	Pre-brushing fluid	0.340	0.005	0.008
Secafix 3	Pre-brushing fluid	0.280	0.005	0.018

As it appears from table 4.4, chlorinated solvents have been demonstrated in all the tested products. The tested cleaning intensifier Frankotex KW (identical to Frankotex HCR) contains 0.020 weight% chlorinated solvents, equivalent to 200 mg/kg. With a typical consumption of cleaning intensifier of 100-500 kg/year, this corresponds to a consumption of approximately 20-100 g chlorinated solvents/year via the cleaning intensifier.

According to information from Kemikalier og Sikkerhed (2002), stabilizers are added to tetrachlorethylen, which is used in cleaning products. It is stated that mainly alkyl amines and morpholin derivatives are used as stabilizers. No such information is available for either hydrocarbons or glycolether.

In connection with the project of the Danish Environmental Protection Agency on alternative dry-cleaning shops, Environmental Project 686/2002, it was demonstrated that the Rynex cleaning fluid did not contain 2-propylenglycol-tert-butylether (CAS number 57018-52-7) and dipropylenglycol butylether (CAS number 29911-28-2) as supposed on the basis of the then existing safety data sheets, but it did contain dipropylenglycol propylether. Furthermore, the measurements showed that hydrocarbon dry-cleaned textile contained a residue of dipropylenglycol monometylether (CAS number 34590-94-8) (the Danish Environmental Protection Agency, 2002a).

5 Phase 2 – Screening analyses of selected products

5.1 Selection of chemical products for screening analysis

13 products and a contact water sample have been selected for screening analysis from the gross list in appendix 3.

The selection criteria were as follows:

- The chemical product is used in relatively large quantities in the dry-cleaning shops
- The product is used in several dry-cleaning shops
- It has been informed or it is expected that the product may contain problem substances

Furthermore, products with identical functions have been selected for comparison.

The chemical products selected for the chemical screening analysis appear from table 5.1 below.

Samples of the chemical products have been provided through contact to the suppliers. The samples were taken by Kampsax A/S in red cap glasses, which were subsequently sent to Eurofins Denmark A/S. Please see section 5 for a description of the sampling conditions.

Table 5.1: Selected chemicals for screening analysis. Please also see the gross list in appendix 3 for further information
[A]: corresponds toTPM 1075 (this trade name has been changed)
[B]: The consumption quantity in dry-cleaning shop D includes both Frankotex KW and Preclin Odosorb
[C]: As informed by the dry-cleaning shops taking part in the investigation
[D]: In accordance with the safety data sheet from the supplier
[E]: Dry-cleaning shop D draws off approximately 100 l distillate from the machine annually
[D]: Quantity not informed

Selected chemical product	**Use**	**Typical quantity used per year [C]**	**Declared chemicals, CAS number [D]**
Products used in hydrocarbon dry-cleaning shops			
Solvex 1	Spot remover	10 l (dry-cleaning shop D) 4 l (dry-cleaning shop E) 10 l (dry-cleaning shop F)	Isoalkanes (CAS number 90622-57-4) Anion active tenside (no CAS number informed) 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5)
Solvex 2	Spot remover	10 l (dry-cleaning shop D) 4 l (dry-cleaning shop E) 10 l (dry-cleaning shop D)	Isoalkanes (CAS number 90622-57-4) Anion active tensid (no CAS number informed) 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5)
Solvex 3	Spot remover	10 l (dry-cleaning shop D) 4 l (dry-cleaning shop E) 10 l (dry-cleaning shop D)	Non-ionic tensid (no CAS number informed) Anionic tensid (no CAS number informed) Cationic tensid (no CAS number informed) 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5) (2-methoxymethylethoxy)propanol (CAS number 34590-94-8)
Toptrel HP	Cleaning fluid	50 l (dry-cleaning shop F)	Isoalkanes C9-C12 (CAS number 90622-57-4)
Actrel 3356-D	Cleaning fluid	-100 l (dry-cleaning shop D)[E]	Iso-undekanes (CAS number 90622-57-4)
Prenett Pur	Pre-brushing fluid	7 l (dry-cleaning shop C) 120 l (dry-cleaning shop D)	Alkyl benzol (no CAS number informed) Coconut soap (no CAS number informed) "Sulfbernstensyre-ester" (no CAS number informed) Alkyl glycol (no CAS number informed)
Frankotex KW	Cleaning intensifier	45 l (dry-cleaning shop G) 425 l (dry-cleaning shop D)[B]	Isoalkanes (CAS number 90622-57-4) Tensides (no CAS number informed) 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5)
Preclin Odosorb	Cleaning intensifier	25 l (dry-cleaning shop G) (dry-cleaning shops E and D)[F, B]	Non-ionic tensid (no CAS number informed) Anionic tensid (no CAS number informed) Isoalkanes (CAS number 90622-57-4) (2-methoxymethylethoxy)propanol (CAS number 34590-94-8)
Clip Comfort	Cleaning intensifier	150 l (dry-cleaning shop C) 150 l (dry-cleaning shop F)	No information available
Cetox KWI	Waterproofing fluid	160 l (dry-cleaning shop D) 60 l (dry-cleaning shop G) (dry-cleaning shop E)[F]	Hydrocarbon compound, isoparaffin (no CAS number informed) Flouride alkyl polymers (no CAS number informed) Glycolether acetate (no CAS number informed) Isoalkanes (CAS number 90622-57-4)
Products used in Rynex dry-cleaning shops			
Rynex 2	Cleaning fluid	60 l (dry-cleaning shop B)	Propane diolether (CAS number is confidential)
TempoRyn [A]	Cleaning intensifier	20 kg (dry-cleaning shop B)	2-(2-butoxyethoxy)ethanol (CAS number 112-34-5) Fatty alcohol ethoxylat (CAS number 69011-36-5)
Products used in both Rynex and hydrocarbon dry-cleaning shops			
Polysol KwV	Pre-brushing fluid	20 l (dry-cleaning shop A) 15 l (dry-cleaning shop D)	Non-ionic tensid (no CAS number informed) Anionic tensid (no CAS number informed) Isoalkanes (CAS number 90622-57-4) 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5)

Furthermore, contact water from dry-cleaning shop D has been analysed. The contact water sample was taken when the dry-cleaning shop had just changed from cleaning intensifier Frankotex KW to Prenet Pur.

During the project work, it became known that addition of pure cleaning fluids is often very limited and that the distillates function as cleaning fluid in practice. As a supplement, a screening was therefore made for volatile organic solvents in the distillates from the dry-cleaning machines used for dry-cleaning the test textiles in the two dry-cleaning shops. Please also see section 6.

5.2 Analysis programme and methods

The selected products have been analysed for the following chemicals and groups of chemicals:

1. Volatile organic compounds

   A screening has been carried out for volatile organic compounds in the products. For all products, a quantitative determination of the content of hydrocarbon compounds, glycolether (Rynex) and chlorinated solvents has been made.

   The analyses were made as gas chromatographical analyses of solutions of the product samples.

2. Alkylphenolethoxylates

   It appears from the safety data sheets for several of the products that the products contain non-ionic tensides. These non-ionic tensides can include octyl and nonylphenolpolyethoxylates. As octyl and nonylphenolpolyethoxylates can be decomposed to nonylphenol, which cannot degrade easily and has shown harmone-like effects, it was decided to include these in the analysis programme.

   It was analysed if the samples contained nonyl and octylphenolethoxylates, using a specific analysis.

3. Alkyl amines

   Chemical cleaning fluids containing tetrachlorethylen may contain stabilizers in the form of alkyl amines (Kemikalier og Sikkerhed, 2002). No corresponding information is available for hydrocarbon or glycolether-based cleaning fluids. To investigate if this kind of stabilizers is also added to the alternative cleaning fluids, a screening for alkyl amines has been carried out.

An analysis of organic solvents and alkyl amines has been made by thinning in dichlormethan and subsequent gas chromatographical analysis with mass selective detection (GC/MS). Internal standards have been included for glycolether, n-octane, n-triacontane and tetrachlorethylen. The quantification was either made in relation to the internal standard or semi-quantitatively in relation to the octane/acontane (hydrocarbons) or diproplyenglycolbutylether

(glycolether). For alkyl amines, the method includes volatile and semi volatile compounds.

Alkylphenolethoxylates have been analysed through fluid chromatographic mass selective detection.

Please see appendix 7 for a detailed description of the methods used. All chemical analyses of this project have been carried out by Eurofins Denmark A/S.

5.3 Analysis results – products

The result of the analyses appears from table 5.2.

Table 5.1: The result of the product analyses. The result is stated as percentage by weight.

[A] : Hydrocarbon compounds, typically C_9-$C_{15,}$
- : Not detected
[B:]: Identification by MS alone. It has not been possible to verify with reference standard
[C] : Identified on the basis of chromatogram "fingerprint"

Product name Chemicals/groups of chemicals	**Toptrel HP**	**Actrel 3356-D**	**Frankotex KW**	**Rynex 2**	**TempoRyn**
Used in dry-cleaning shop	D and F	E	D and E	A and B	A and B
Hydrocarbons[A]	100	95	50	-	
Butoxyethoxyethanol (CAS number 112-34-5)	-	-	5.3	-	5.6
Dipropylenglycol mono methylether (isomer compound)[B]	-	-	-	2	-
Dipropylenglycol-t-butylether (CAS nr. 132739-31-2)	-	-	-	>95	-
Bis(ethylhexyl)maleate	-	-	1.8	-	-
Tetrachlorethylene	-	-	-	0.01	-
Poly(oxy-1,2-ethanediyl)[C],	-	-	-	-	20
Octylphenolpolyethoxylates	-	-	-	-	-
Nonylphenolpolyethoxylates	-	-	2.6	-	-
Bis(2-ethylhexyl) natrium sulfo succinate[B]	-	-	9	-	-
Alkylamines	-	-	-	-	-

Product name **Chemicals/groups of chemicals**	**Cetox KWI**	**Prenett Pur**	**Solvex 1**	**Solvex 2**	**Solvex 3**
Used in dry-cleaning shop	D, E and G	C and D	D, E and F	D and E	D and E
Hydrocarbons[A]	>99	-	23	-	-
Butoxyethoxyethanol (CAS number 112-34-5)	-	-	-	-	-
Dipropylenglycol mono methylether (isomer compound)[B]	-	-	-	-	23
Dipropylenglycol-t-butylether (CAS number 132739-31-2)	-	6.6	-	-	-
Butoxyethanol (CAS number 111-76-2)	0.5	-	2.8	10	3.5
Butyldiglycolacetate (CAS number 124-17-4)	-	-	61	-	-
Bis(ethylhexyl)maleate	-	1.6	-	-	-
Tetrachlorethylene	0.008	-	-	-	-
Poly(oxy-1,2-ethanediyl)[C],	-	-	-	-	-
N,N-dimethylalkylamines (C_{10}-C_{12})	-	-	-	-	6.1
Substituted alkylbenzenes C_{12}-C_{14}	-	50	-	-	-
Octylphenolpolyethoxylate	-	-	-	-	0.1
Nonylphenolpolyethoxylate	-	-	-	0.26	3.3
Bis(2-ethylhexyl) natrium sulfo succinate[B]	-	5.9	-	-	-
Alkylamines	-		-	-	-

Product name **Chemicals/groups of chemicals**	**Clip Comfort**	**Polysol**	**Preclin Odosorb**
Used in dry-cleaning shop	C and F	A and D	D, E and G
Hydrocarbons[A]	-	17	7.3
Butoxyethoxyethanol (CAS number 112-34-5)	-	-	-
Dipropylenglycolmonomethylether (isomer compound)[B]	-	-	16
Dipropylenglycol-t-butylether (CAS number 132739-31-2)	5.9	-	-
2-Propylenglycol-t-butylether (CAS number 57018-52-7)	4.0	-	-
Butoxyethanol (CAS number 111-76-2)	-	14	-
Bis(ethylhexyl)maleate	-	-	-
Tetrachlorethylene	-	-	-
Poly(oxy-1,2-ethanediyl)[C]	-	-	-
N,N.dimethylurea	0.3	-	-
N,N-dimethyl alkylamines (C_{10}-C_{12})	1.3	-	-
Substituted alkylbenzenes C_{12}-C_{14}	18	2.6	3
Octylphenolpolyethoxylate	-	0.86	0.89
Nonylphenolpolyethoxylate	-	47	3.3
Bis(2-ethylhexyl) natrium sulfo succinate[B]	-	6.1	3.9

During the analysis, a multi component mixture of glycolether was demonstrated. MS has identified 1-propanol, 2-(2-hydroxypropoxy) and 1,1-oxybis(2-propanol) respectively. These two components are included in the isomer compound with trival name dipropylenglycolmonomethylether.

Poly(oxy-1,2-ethanediyl) was identified on the basis of the chromatogram (”fingerprint”). The mixture is a multi component mixture with a characteristic composition of several small groups of homogenous mixtures. The product data sheet states the content of poly(oxy-1,2-ethanediyl). It has not been possible to verify this with a reference standard, but it is considered an acceptable identification on the basis of the composition.

5.4 Analysis results – distillate and contact water

The distillate analysis results from the two dry-cleaning shops in relation to the content of volatile organic solvents appear from table 5.3.

Table 5.3: Analysis af distillates. The result is stated as percentage by weight
[A]: Mixture of four glycolethers
-: Not detected

Chemical	**Distillate Dry-cleaning shop D**	**Distillate Rynex dry-cleaning shop B**
Hydrocarbon compound	>99	-
Glycolether[A]	-	>95
Tetrachlorethylene	0.01	0.04
Unknown residue	<1	<5

The contact water analysis results from hydrocarbon dry-cleaning shop D appear from table 5.4.

Table 5.4: Contact water analysis. The result is stated as percentage by weight.
[A] Mixture of three glycolethers
-: Not detected (less than 0,01 percentrage by weight)

Chemical	**Contact water Hydrocarbon dry-cleaning shop D**
Hydrocarbon compound	-
Tetrachlorethylene	-
Glycolether[A]	1.1
Nonylphenolpolyethoxylates	<0.001

6 Phase 3 – Dry-cleaning of textiles and determination of residual content

6.1 Introduction to residual content

Dry-cleaned clothes contain chemical residues that were not removed during the drying process of the dry-cleaning machine. These residues are also called the residual content and can consist of volatile and non-volatile components.

The volatile components can be liberated to the surrounding air and in this way constitute a risk of exposure. The non-volatile components can be absorbed by the organismn via skin contact and by breathing in textile dust.

The composition and size of the residual content in dry-cleaned textile depend on the chemical products and cleaning programme used and if the drying period is long enough. The volume of clothes and the textile type apparently also have an influence on the residual content.

6.1.1 Determination of residual content

In connection with Environmental Project 686/2002, the Danish Environmental Protection Agency has determined the residual content of selected components from hydrocarbon and Rynex cleaning fluid respectively (the Danish Environmental Agency, 2002a). During the tests in the climatic chambers, the emission showed a progress that could be modelled by a curve of exponential decay. This curve is identical to the curve of the emission for tetrachlorethylen dry-cleaned textile (the Danish Environmental Protection Agency, 2001).

The emission as a function of time can be stated as:

(1) $$R = R_0 e^{(-kt)}$$

Where

R	The emission rate for dry-cleaned clothes in time t, mg/m^2h,
R_0	Initial emission rate, mg/m^2h
k	Rate constant, h^{-1}

The emission determinative parameters can be determined by testing dry-cleaned textiles in a climatic chamber.

The residual content at the starting time is obtained by integrating the above function from t=0 to infinite and can be calculated as weight/weight%.

The residual content of non-volatile components can be determined by different types of extraction and analysis of textile samples after dry-cleaning. Using these methods, the residual content is determined as weight/weight%.

6.1.2 Referred residual content

The below residual content is residual content after chemical dry-cleaning and shaping, i.e. pressing.

In a project made by the Danish Environmental Protection Agency, different textiles dry-cleaned in Rynex or hydrocarbon dry-cleaning shops were tested in climatic chambers (the Danish Environmental Protection Agency, 2002a). Emission parameters were determined (equation (1)). The results appear from table 6.1.

The calculated residual content is stated as % of the weight.

Table 6.1: Emission parameters of textiles dry-cleaned in Rynex and hydrocarbon cleaning fluid respectively determined via measurements in climatic chambers. The area is calculated as the area of one side of a coat and suit respectively. From the Danish Environmental Protection Agency (2002a).

R^2: Correlation coefficient

Textile	Area	Weight	R_0	K	R^2	Residual content	
	m^2	kg	$mg/m^2/h$	h^{-1}	-	mg	weight%
Rynex dry-cleaning shop							
Winter coat	2.0	1.4	3.40	0.005	0.93	1,400	0.10
Suit 1	2.5	0.91	14.3	0.011	0.90	3,300	0.36
Suit 2	2.5	0.87	27.2	0.017	0.98	4,000	0.46
Hydrocarbon dry-cleaning shop							
Winter coat	2.0	1.4	60.0	0.020	0.82	6,000	0.43
Suit 1	2.5	0.91	0.13	0.061	>0.99	5,3	0.001

Tests made by Research Institute Hohenstein (1998) and published in Tagge (1998) showed that the residual content of hydrocarbons was generally higher in materials with leather braids or membranes such as Gore-Tex, etc. It is assumed that the fibre types have an influence on the size of the residual content as also known from tetrachlorethylen dry-cleaned textile (Brodmann, 1975 and Hohenstein, 1995).

6.2 Selection of textiles, spots and dry-cleaning shops

The purpose of the tests in this project is that they should reflect the worst case conditions, but still give a realistic and true picture of the residual content of the chemicals that can be expected in textile chemically dry-cleaned.

6.2.1 Selection of dry-cleaning methods and textiles

The dry-cleaning shops were asked to which extent dry-cleaning was carried out without final treatment (cleaning per kilo). Investigations made by Weber (1992) and Brand et al. (1999) show that shaping by pressing results in a much lower residual content of the cleaning fluid tetrachlorethylen. Similar conditions can be expected for the alternative cleaning fluids.

From the responses, it appeared that more of the dry-cleaning shops characterise both wet cleaning (i.e. ordinary washing by using detergent) and chemical dry-cleaning without final treatment as cleaning per kilo. The owners of

the dry-cleaning shops have estimated the part of dry-cleaning per kilo that is carried out as chemical dry-cleaning. Several of the owners of the dry-cleaning shops inform that they generally dissuade the customers from using cleaning per kilo as chemical dry-cleaning as the textiles may smell if they are not shaped (pressed). Furthermore, the Rynex dry-cleaning shops typically advise not to use dry-cleaning per kilo, as the clothes crease. Other dry-cleaning shop owners point out that the need for dry-cleaning per kilo is very limited, as most of the clothes to be dry-cleaned require pressing. This consumer advice from the dry-cleaning shops is reflected in the responses (please also see appendix 2), as dry-cleaning per kilo only amounts to a few per cent of the production of the dry-cleaning shops.

In this investigation, dry-cleaning is therefore carried out as ordinary chemical dry-cleaning with pre-treatment and final treatment, but without waterproofing.

The criteria of the selection of textiles for the tests were as follows:

- The textiles should be textiles that are normally chemically dry-cleaned
- The textiles should be textiles that to the widest possible extent get in contact with the skin of the consumer or where liberation of chemical residues can be breathed in.
- The textiles should make an important part of the textiles that are dry-cleaned.

The owners of the dry-cleaning shops were asked if it is normal to chemically dry-clean eiderowns, mats, etc.

All the owners of the dry-cleaning shops informed that they did not dry-clean eiderdowns and mats, as ordinary wet cleaning gives a better result. It has therefore been decided not to include eiderdowns and mats as test textiles in the investigation.

To the question which textiles are clinging or worn close to the face and which are typically chemically dry-cleaned, several of the owners of the dry-cleaning shops answered trousers, dresses, jackets and coats.

On the basis of the above responses, it was decided to use one dress, one jacket and one pair of trousers as test textiles.

Two identical unused pieces of each textile were purchased from retail shops. The shops are not situated near to any dry-cleaning shops.

Table 6.2 gives an overview of the selected textiles.

Table 6.2: Used textile types

Jacket and trousers	28% wool, 69% polyester, 3% lycra
Dress	60% viscose, 40% acetate

6.2.2 Selection of spots

To make sure that the textiles were spot-cleaned prior to the actual dry-cleaning, they should be provided with spots.

- The spots should be ”stubborn” spots that normally require considerable pre-treatment, i.e. that require a substantial consumption of spot removers.

The owners of the dry-cleaning shops selected food spots such as fruit juice, egg, etc. as being stubborn. Furthermore, they informed that it is more difficult to remove old spots than new spots.

The Nordic Environmental Label (the Swan) includes environmental labelling of textile detergents (Nordic Environmental Labelling, 2001). The criterion document describes standardized spots to be used for washing tests. It was decided to use the same spot types for the present tests. The selected spot types appear from table 6.3 below as spot number 1, 2, 5 and 6. The Danish Environmental Protection Agency wanted to supplement with egg and black currant juice (type 3 and 4).

Table 6.3.: Selected spot types

Spot number	**Spot type**
1	Soot/oil mixture
2	Cocoa
3	Egg
4	Black currant juice
5	Redwine
6	Blood

The spots were added to the textile 2 days before the dry-cleaning on the assumption that the consumers will typically bring in stained clothes for dry-cleaning within this period of time.

The test conditions appear from the test protocol in appendix 4. The main features appear from sections 6.3 and 6.4.

6.2.3 Selection of dry-cleaning shops

As all dry-cleaning shops were basically found qualified for the tests, great importance was attached to the physical location of the dry-cleaning shops and if the owners of the dry-cleaning shops could take samples of the distillate without any technical assistance. Furthermore, dry-cleaning shops that had participated in environmental projects earlier, were selected, using the old data for this present project.

Hydrocarbon dry-cleaning shop D and Rynex dry-cleaning shopo B were selected to dry-clean the textiles.

As for information about the dry-cleaning machines used and the year of production of these machines, the ventilating conditions in the dry-cleaning shops as well as the operation conditions during the dry-cleaning, drying and shaping, please see section 6.4 and 6.4.2.

6.3 Test preparation

Prior to the spotting and dry-cleaning, samples were taken from each piece of textile. These samples are used as reference samples for the content of alkylphenolethoxylates after dry-cleaning.

6.4 Chemical dry-cleaning of textiles

The dry-cleaning of the textiles was carried out in co-operation with the owners of the dry-cleaning shops. According to agreement with the Danish Environmental Protection Agency, the dry-cleaning shops were only informed about the type of spots 1-4, whereas spots 5 and 6 were unknown.

An employee from Kampsax A/S supervised the pre-treatment, the dry-cleaning as well as the final treatment.

6.4.1 Dry-cleaning in hydrocarbon dry-cleaning shop D

The owner of hydrocarbon dry-cleaning shop D informed that prior to a chemical dry-cleaning, all textiles were examined and sprayed with a mixture of water and the spotting fluid Polysol. He also informed that the mixture consists of ½ l Polysol in 15 l water and that the weekly consumption of this mixture is approximately 10 l. In case of special stubborn spots, these will also be treated with Solvex 1, 2 or 3.

The textiles used for the tests were spot cleaned. The spot treatment appears from table 6.4.

Table 6.4.: Spot treatment, hydrocarbon dry-cleaning shop D. Please note that the dry-cleaning shop did not get any information about spot type 5 and 6. Generally, each spot was treated with ½-1 ml of the mentioned spotting fluid.

Number	Spot type	Trousers	Jacket	Dress
1	Soot/oil mixture	Solvex 1	Solvex 1	Solvex 1
2	Cocoa	Solvex 2	Solvex 2	Solvex 2
3	Egg	Solvex 2	Solvex 2	Solvex 2
4	Black currant juice	Solvex 3	Solvex 3	Solvex 3
5	Redwine	Solvex 1	Solvex 2	Solvex 2
6	Blood	Solvex 2	Solvex 2	Solvex 2

Then, an ordinary chemical dry-cleaning of the textiles was carried out. No waterproofing was performed.

During the dry-cleaning and the subsequent shaping, a number of treatment and operation parameters were noted down. Please also see table 6.5 below. For a further description of the function of the dry-cleaning machine, please see figure 3.1.

Table 6.5: Test conditions, hydrocarbon dry-cleaning shop D.
LEL: Lower explosive limit

Parameter	**Parameter value**		
Used cleaning fluid	Toptrel HP		
Weight of textiles in batch	20 kg		
Combination of textiles in batch – estimated	Wool: 30-40% Polyester fibre: 30-40% Acetate: 5-10% Viscose and cotton fibres: 10-20%		
First bath	Add 90-100 l rinsing water from the second bath of the previous charge Add 250 ml Prenet Pur Washing time: 10 minutes Pumping out liquid for distillation Spin-drying, 750-800 rotations/minute (305-320 G) for 2 minutes		
Second bath	Add 90-100 l distillate 6-8 minutes washing with filter Add 100 ml Frankotex KW 3 minutes washing without filter Pumping out liquid to tank Spin-drying, 750-800 rotations/minute (305-320 G) for 5 minutes		
Drying	Drying for 20 minutes whereupon the temperature increases to 75°C. Drying to take place until the temperature reaches 75°C and the concentration of hydrocarbons in the drum air is 8% of LEL. Cooling down to 40°C in 3½ minutes (3% of LEL)		
Distillation	Approximately 143-152 °C, 4-4½ bar		
Shaping	Presssing using	Dummy	Ironing board
	Trousers	30 seconds	25 seconds
	Jacket	30 seconds	20 seconds
	Dress	15 seconds	20 seconds

As to the construction and ventilation technical conditions of the tested hydrocarbon dry-cleaning shops, please also see appendix 9 for a description of dry-cleaning shop 3 in Environmental Project number 686/2002 of the Danish Environmental Protection Agency.

6.4.2 Dry-cleaning in Rynex dry-cleaning shop B

The pre-treatment of the test textiles prior to the dry-cleaning in Rynex dry-cleaning shop B appears from table 6.6 below. The test conditions during the dry-cleaning and the subsequent shaping appear from table 6.7. Please also see figure 3.1 for a further description of the function of the dry-cleaning machine.

Table 6.6.: Spot treatment, Rynex dry-cleaning shop B. Please note that the dry-cleaning shop did not get any information about spot type 5 and 6. Generally, each spot was treated at a spotting table (with water spray and suction). Upon this introductory dry-cleaning, the textiles were brushed with approximately 2-3 ml Devantol Soft.

Number	**Spot type**	**Trousers**	**Jacket**	**Dress**
1	Soot/oil mixture	Devantol soft	Devantol soft	Detafix Color and Devantol soft
2	Cocoa	Devantol soft	Devantol soft	Devantol soft
3	Egg	Devantol soft	Devantol soft	Devantol soft
4	Black currant juice	Devantol soft	Devantol soft	Devantol soft
5	Redwine	Devantol soft	Devantol soft	Detaprofi Tanex and Devantol soft
6	Blood	Devantol soft	Devantol soft	Devantol soft

Table 6.7: Test conditions, Rynex dry-cleaning shop B.

Parameter	**Parameter value**		
Used cleaning fluid	Rynex 2		
Weight of textiles in batch	12 kg		
Combination of textiles in batch – estimated	Wool: 30-40% Polyester fibre: 30-40% Acetate: 5-10% Viscose and cotton fibres: 10-20%		
First bath	Add approximately 50 l rinsing water from the second bath of the previous charge No cleaning intensifier is added Washing time: 8 minutes Pumping out liquid for distillation Spin-drying, 750-800 rotations/minute (305-320 G) for 2 minutes		
Second bath	Add approximately 50 l distillate Add 25 ml TPM 1075/Tempo Ryn Washing time: 8 minutes Pumping out liquid to tank 1 for use in the first bath of the next charge Spin-drying, 750-800 rotations/minute (305-320 G) for 10 minutes		
Drying	Drying for 65 minutes with 75 °C drum air Cooling down to 45°C in 4 minutes Bleeding of drum for 4 minutes		
Distillation	Approximately 159-165 °C, 6-7 bar.		
Shaping	Pressing using	Dummy / pressing bench	Ironing board
	Trousers	20 seconds	60 seconds
	Jacket	10 seconds vapour + 60 seconds air	60 seconds
	Dress	0 seconds	60 seconds

As to the construction and ventilation technical conditions for the tested Rynex dry-cleaning shops, please see appendix 9 for a description of dry-cleaning shop 1 in Environmental Project number 686/2002 of the Danish Environmental Protection Agency.

6.4.3 Transport of dry-cleaned textiles to laboratory

After the dry-cleaning, the textiles did not have any spots – either the textiles dry-cleaned in the Rynex dry-cleaning shop or the textiles dry-cleaned in the hydrocarbon dry-cleaning shop. As soon as the textiles were finished, they were put in ordinary cleaning bags and transported to Kampsax A/S - a trip of approximately 40 minutes. Then, the textiles and cleaning bags were put in Rilsan bags, closed and transported to Eurofins Denmark A/S in Galten where they were placed in a climatic chamber. The transport from Kampsax A/S to Eurofins Denmark A/S took approximately 3 hours. It took approximately 4 hours from the pressing was finished till the textile was in the climatic room.

6.5 Climatic chamber measurements of residues of volatile compounds

When the textiles were received in the laboratory, they were unpacked, shaken in order to be straightened and then placed in the climatic chambers. The time the textiles were placed in the climatic chambers was defined as t=0.

During the emission test, the textiles were kept in the climatic chambers. The conditions were selected so that they correspond to the test conditions determined in the test standard for Danish Indoor Climate Labelling (1998) with the modification that the air speed was not adjusted. The Danish Indoor Climate Labelling prescribes an air speed of 0.15 m/s for building materials, but this air speed is much higher than the air circulation in a wardrobe.

As the purpose of the investigation was to imitate the conditions during normal use, it was decided not to increase the air speed further in relation to the air circulation that the change of air in the climatic chamber creates. The measurement conditions were as follows:

Temperature:	23 ° C ± 1 °C
Air humidity:	50% ± 5%RF
Change of air:	0.5 times per hour

During the 14 days, air samples were taken 6 times from the climatic chambers for analysis of the cleaning fluids. The first air sample was taken 1 day after the start of the test. Sampling was made on adsorption tube with active coal, whereas the analysis was carried out by gas chromatographical analysis (GC/MS). Please see appendix 5 for a detailed description of the method including method references.

6.6 Analysis of residue in dry-cleaned textiles

After the emission tests, the textiles were removed from the climatic chambers. Samples were taken from an area of 10 x 10 cm from each textile on the place where the spots were originally put. The samples were subsequently analysed for the content of alkyl phenol poly ethoxylates.

Another sample was taken from each textile to be analysed for any residue of volatile components.

6.7 Results

6.7.1 Emission of volatile organic compounds

The results of the emission tests were used for determining emission parameters. Also see equation (1). Raw data and curves of decay of all tests are available in appendix 6.

Table 6.8: Emitted chemicals and emission parameters for textiles dry-cleaned using hydrocarbon-based cleaning fluids
-: Evaporation of cleaning fluids not demonstrated
A: Hydrocarbon compound, C10-C15
B: Consists of a mixture of several glycolethers. Please see the text for a detailed description
R^2: Correlation coefficient
R_0: Initial emission rate
k: The emission rate

Textile	**Area**	**Weight**	**R_0**	**K**	**R^2**	**Residual content**	
	m^2	kg	$\mu g/m^2/h$	h^{-1}	-	mg	weight%
Jacket							
Hydrocarbons [A]	1.26	0.704	120	0.011	0.97	11	0.002
Glycolethers[B]			78	0.0076	0.98	10	0.001
Trousers							
Hycrocarbons [A]	1.34	0.502	55	0.014	0.98	3.9	<0,001
Glycolethers[B]			21	0.0058	0.96	3.6	<0,001
Dress							
Hydrocarbons [A]	1.32	0.210	-	-	-	-	-
Glycolethers[B]			-	-	-	-	-

Table 6.9: Emitted chemicals and emission parameters for textiles dry-cleaned using glycolether-based cleaning fluids
A: Consists of a mixture of several glycolethers. Please see text for a detailed description
R^2: Correlation coefficient
R_0: Initial emission rate
k: The emission rate

Textile	**Area**	**Weight**	**R_0**	**K**	**R^2**	**Residual content**	
	m^2	kg	$\mu g/m^2/h$	h^{-1}	-	mg	vægt%
Jacket							
Glycolethers[A]	1.26	0.730	3,500	0.0086	0.98	410	0.056
Trousers							
Glycolethers[A]	1.34	0.485	810	0.0062	0.96	130	0.026
Dress							
Glycolethers[A]			222	0.0061	0.95	36	0.015
Tetrachlorethylen	1.32	0.238	7.4	0.012	>0.99	0.62	<0.001

The glycolethers consist of a multi component mixture with 3-4 single components. The primary component is an isomer compound of dipropylenglycol-t-butylether (CAS number 132739-31-2). In all samples containing glycolethers, the content of butoxyethoxyethanol has been demonstrated. In samples from dry-cleaning using glycolether-based cleaning fluids, the quantity of butoxyethoxyethanol was smaller than 1% of the total quantiy of glycolethers, whereas butoxyethoxyethanol made up between 3 and 20% of the glycolether quantity in textiles where the primary cleaning fluid is hydrocarbon-based.

6.7.2 Residue of alkylphenolpolyethoxylates

The analyses for alkylphenolpolyethoxylates before and after the dry-cleaning of the textiles have given the following results (table 6.10 and 6.11). The results have been corrected for blind values (content before dry-cleaning).

Table 6.10: Residue of alkylphenolpolyethoxylates after dry-cleaning (hydrocarbon-based cleaning fluids). Corrected for blind values, as the blind values varied as follows:
Nonylphenolpolyethoxylate: 17-130 mg/kg
Octylphenolpolyethoxylate: <5 mg/kg.

Tekstiles	Nonylpolyphenolethoxylate	Octylphenolpolyethoxylate
	mg/kg	mg/kg
Jacket	130	<10
Trousers	20	<10
Dress	<10	<10

Table 6.11: Residue of alkylpolyethoxylates after dry-cleaning (glycolether-based cleaning fluids). Corrected for blind values, as the blind values varied as follows:
Nonylphenolpolyethoxylate: 30-140 mg/kg
Octylphenolpolyethoxylate: <5 mg/kg.

Textiles	Nonylphenolpolyethoxylate	Octylphenolpolyethoxylate
	mg/kg	mg/kg
Jacket	<10	<10
Trousers	<10	<10
Dress	<10	<10

6.7.3 Residual content of cleaning fluids

After the emission tests, part-samples were taken from each textile. It was analysed if the part-samples contained hydrocarbons, glycolethers and tetrachlorethylen. The result appears from table 6.12 and 6.13.

Table 6.12: Residual content of cleaning fluids (hydrocarbon-based cleaning fluids) after the emission tests

	Hydrocarbons mg/kg	Glycolethers mg/kg	Tetrachlorethylene mg/kg
Jacket	<2	34	<2
Trousers	<2	150	<2
Dress	<3	1200	<5

The glycolethers consist of 4-5 components with dipropylenglycolbutylether, butyldiglycolacetate, diethylenglycolmonobutylether and dipropylenglycol-monomethylether as the main components.

Table 6.13: Residual content of cleaning fluids (glycolether-based cleaning fluids) after the emission tests

	Hydrocarbons mg/kg	Glycolethers mg/kg	Tetrachlorethylene mg/kg
Jacket	<2	130	<2
Trousers	<2	73	<2
Dress	<4	4400	<6

The glycolethers consist of 3-4 components with dipropylenglycolbutylether as the dominant component.

7 Phase 4 – Modelling of the indoor climate influence from dry-cleaned textile

7.1 Development of a mathematical model

The purpose of phase 4 is to set up a simple method for conversion of the evaporation speeds of the components determined by measurements in climatic chambers in phase 3 into resulting concentrations (contribution) in the indoor air of residences. The data provided in phase 3 will be used together with the model for exemplification of the indoor climate concentrations when introducing dry-cleaned clothes into the residence.

Literature describing the influence of various parameters on the resulting concentration of the cleaning fluids in a given room has been searched for. Please note that the literature covering this field is very sparse.

The Danish Environmental Protection Agency (2001a) has set up a simple mass balance describing the concentration development when introducing dry-cleaned clothes into a given room.

This model is based on the following assumptions. It is assumed that:

- There is no biological decomposition of the substances.
- Zinc effects are eliminated. Zinc effects describe the condition that building parts and interior adsorp and desorp the chemicals. Elimination of adsorption/desorption in the model means that the maximum concentrations from the calculations are probably overestimated. It also means that the estimated concentration of cleaning fluid in the air in the last part of the emission period is most likely too low compared with most real situations. Please also see Environmental Project number 673/2002 (the Danish Environmental Protection Agency, 2002b).
- As far as the substances are concerned, dry-cleaned clothes are the only internal pollutant. Furthermore, it is assumed that the emission of the substances from dry-cleaned clothes as a function of time can be described as

  (1) $R = R_0 e^{-kt}$, where

  R Emission factor of dry-cleaned clothes in time t, mg/m^2h
  R_0 Initial emission factor, mg/m^2h
  k Rate constant, h^{-1}
  t Time, h.

- The air in the room and/or residence is completely mixed. Many investigations have shown that this is not the case. Please also see the experiences with tetrachlorethylen from Amagai et al. (1999), Tichenor et al. (1990) and Thomas et al. (1991). The assumption of completely mixed conditions means that the calculated concentration of substance in the air is lower than the actual maximum concentrations in the indoor air, as a given emitted quantity of substance is mixed in a larger volume of air. Due to the simplicity of the model, it is, however, assumed that the room and/or residence is completely mixed.

- It is also assumed that the effect of the temperature and atmospheric humidity variations in the emission of the components from dry-cleaned clothes is insignificant, as the emission parameters found in this project have been determined under typical indoor climate conditions.

- It is assumed that the dry-cleaned textile is taken out of the bag and is kept freely in the room. It is also assumed that the clothes remain in the room/ residence throughout the whole emission period.

Based on the above assumptions, a "single chamber unsteady state" mass balance can be set up for the situation where dry-cleaned textile is introduced into the residence. The model is modified according to Bouhamra & Elkilani (1999a & 1999b), Kraenzmer (1999) and Tichenor et al. (1988 & 1990).

Initially, a model is developed for the situation where one piece of dry-cleaned textile is introduced into the residence. Then, a model is developed where it is assumed that more types of dry-cleaned textile are introduced into the residence at the same time.

Finally, the size of the starting value (background concentration) is discussed.

7.1.1 Model for introduction of one piece of dry-cleaned textile

The following mass balance forms the basis of the model for calculation of the resulting concentration in the indoor climate upon introduction of one type of dry-cleaned textile:

(2) Change in mass = mass emitted – mass removed

(3, 4)

$$VdC = AR_0 e^{-kt} dt - QCdt$$

$$\Updownarrow$$

$$\frac{dC}{dt} + \frac{Q}{V} C = \frac{AR_0}{V} e^{-kt}$$

as

V Volume of room or residence, m^3
C Concentration of substance in room or residence, mg/m^3
A The area of the dry-cleaned clothes, m^2

Q Air flow through room, m^3/hour
N Air change = Q/V, h^{-1}
R The emission rate for dry-cleaned chothes in time t, mg/m^2h, as $R=R_0e^{-kt}$
R_0 Initial emission rate, mg/m^2h
k Rate constant, h^{-1}
t Time, h

The above equation is a linear, non-homogenous differential equation that can be solved, using the boundary condition C = $C_{indoor, start}$ to t= 0:

(5)

$$C = \frac{AR_o}{V(N-k)}(e^{-kt} - e^{-Nt}) + e^{-Nt}C_{indoor,start}$$

7.1.2 Model for introduction of more types of dry-cleaned textile

If various types of dry-cleaned clothes with different emission controlling parameters (R_o, k) are introduced simultaneously in the residence, the mass balance will look as follows:

(6)

$$VdC = A_1R_{0,1}e^{-k_1t}dt + ...A_iR_{0,i}e^{-k_it}dt + ... + A_nR_{0,n}e^{-k_nt}dt - QCdt$$

A_i stating the area of the i'th piece of dry-cleaned textile, whereas $R_{0,i}$ and k_i are stating the initial emission rate and the rate constant of the i'th piece of dry-cleaned textile.

This equation can be solved by means of the boundary condition t = 0, C = $C_{indoor, start}$

(7)

$$VdC = A_1R_{0,1}e^{-k_1t}dt + ...A_iR_{0,i}e^{-k_it}dt + ... + A_nR_{0,n}e^{-k_nt}dt - QCdt$$

as

$$C = (\sum_1^n \frac{A_iR_{o,i}}{V(N-k_i)}(e^{-k_it} - e^{-Nt})) + e^{-Nt}C_{indoor,start}$$

A_i Area of the i'th piece of dry-cleaned textile
$R_{0,i}$ Initial emission rate of the i'th piece of dry-cleaned textile, mg/m^2h
k_i Rate constant of the i'th piece of dry-cleaned textile, h^{-1}.

7.1.3 The size of $C_{indoor, start}$ in the models

As to the size of the $C_{indoor, start}$ in equation (5) and (7), experience values for normal indoor climate concentrations of the substances in question can be used.

In case of any information about soil pollution or pollution of the nearby secondary groundwater basins, this should be included in the model.

The starting concentrations $C_{indoor, start}$ of hydrocarbons in the indoor climate can be set to 0.042 mg/m^3, as this value is an average of the measurements made in non-affected residences according to Environmental Project number 686/2002 of the Danish Environmental Protection Agency (the Danish Environmental Protection Agency, 2002a). The value is assumed to be representative of a non-affected background level in both single-family houses and apartments.

The background level of glycolether in the indoor climate is set to 0 mg/m^3, as glycolether exceeding the detection limit of 0.0005 mg/m^3 has not been measured in the tested non-affected residences included in the above-mentioned project. The background level is assumed to be representative of both single-family houses and apartments.

The background level of tetrachloroethylene in the indoor climate is set to 0.027 and 0.15 mg/m^3 for non-affected single-family houses and apartments not using dry-cleaning (the Danish Environmental Protection Agency, 2001).

7.2 Model calculations and discussion

On the basis of the model and the results from the measurements in the climatic chamber, the resulting concentrations of cleaning fluid are illustrated in a poorly ventilated apartment and in a large well-ventilated residence for emissions from clothes that have been cleaned by using alternative cleaning fluids. It is assumed that there is no soil pollution and/or pollution of nearby ground water basins.

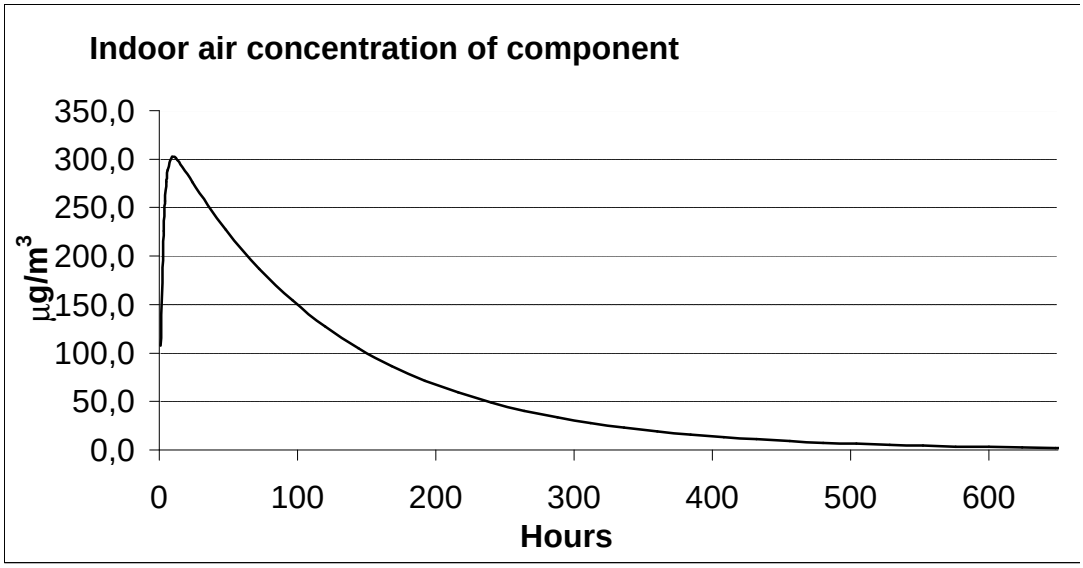
In scenario 1, it is assumed that dry-cleaned textiles are introduced into a small, poorly ventilated apartment. To illustrate any differences between the concentration in the room where the cleaned textiles are kept and the other rooms of the residence, it is assumed that all textiles are kept in the same room, e.g. the bedroom. Calculations are made for this single room and for the complete residence. It is assumed that the total area of the single storey residence is 60 m^2 and that the room height is 2.3 m. The area of the room where the dry-cleaned textiles are kept is assumed to be 18 m^2. The air change is assumed to be 0.4 time per hour.

In scenario 2, it is assumed that the residence is large and well-ventilated, e.g. a single-family house. It is assumed that the area of the single storey residence is 120 m^2, that the room height is 2.3 m and that the air change is 1 time per hour. The area of the room where the dry-cleaned textiles are kept is assumed to be 18 m^2.

Other assumptions are described in section 7.1. As to the sizes of the initial emission rate, $R_{0,}$ and the emission rate constant, k, for the cleaned textiles, the values determined by the measurements in the climatic chamber are used. Please also see section 6.7.

An example of the progress in the indoor climate concentrations is shown in figure 7.1.

Figure 7.1: Example of model results: The concentration of glycolethers in the indoor climate when a Rynex dry-cleaned suit has been introduced into a poorly ventilated apartment.



The main lines of the results are listed in table 7.1-7.3. In the tables, you can find the calculated maximum concentration of the component in the indoor climate, an estimate of the average concentration over a period of 7, 14 and 21 days and when the concentration of the component in the indoor climate is below any air quality criterion. Please note that the air quality criteria cannot be used for estimating what is an acceptable or unacceptable exposure in connection with the indoor climate influences as a result of the consumption patterns of private persons, including bringing home dry-cleaned textile.

As there is no air quality criterion for the primary glycolether dipropylen-tert-butylether (CAS number 132739-31-2), the total exposure of glycolether is made relatively in relation to the air quality criterion for dipropylenglycol-butylether (CAS number 29911-28-2).

7.2.1 Model calculation – textiles dry-cleaned in Rynex dry-cleaning shop

As it appears from section 6.7, glycolethers have been demonstrated in all Rynex dry-cleaned textiles during all measurements made in climatic chambers. Furthermore, the jacket and trousers bore traces of tetrachlorethylen, whereas liberation of tetrachlorethylen from the dress could be measured.

Table 7.1 shows the model results for the emission of glycolether from Rynex dry-cleaned textile.

Table 7.1: Model calculations of the resulting concentration of glycolethers (dipropylengycol-butylether) as a result of the Rynex dry-cleaning process.

[a:] It is assumed that all the dry-cleaned textiles are kept in this room.
[b:] Estimated relatively to the air qualtiy criterion of the Danish Environmental Protection Agency for di-propylenglycol-butylether (CAS number 29911-28-2).

Rynex dry-cleaned textile Emission af glycolethers		**Small poorly ventilated apartment**		**Large well-ventilated single family house**	
Scenario		**1**		**2**	
		Single room[A]	**Whole apartment**	**Single room[A]**	**Whole residence**
Number of suits (jacket and trousers)		1	1	1	1
Average indoor climate concentration $\mu g/m^3$	7 days	178	54	72	11
	14 days	113	34	45	7
	21 days	80	24	32	5
Maximum concentration, $\mu g/m^3$		302	91	126	19
Air quality criterion[B] $\mu g/m^3$		40			
Number of days from introduction of dry-cleaned textile till the size of the concentration is identical to the size of the air quality criterion[B]		11	5	7	<1

It appears from table 7.1 that the introduction of even a small number of Rynex dry-cleaned textiles into a poorly ventilated apartment results in concentrations of glycolethers, the average values of which are larger than 40 $\mu g/m^3$ over a period of one week and more than 21 days in a single room.

It also appears that if the calculations are made for a single well-ventilated room in a single-family house, the average concentrations will be of 40 $\mu g/m^3$ over a period of 14 days.

If the calculation is made for a completely mixed single-family house, the results show that the concentration of cleaning fluid in the indoor climate will be smaller than the air quality criterion for di-propylenglycol-butylether.

The calculations show that the size of the concentration in the indoor climate will be identical to the size of the air quality criterion for di-propylenglycol-butylether after typically 1-2 weeks in case of poorly ventilated conditions and after a few days in case of well-ventilated conditions.

Therefore, indoor climate problems may occur due to emission of glycolether from Rynex dry-cleaned textile for residences.

If the calculations are made for emission of tetrachlorethylen from the Rynex dry-cleaned dress, it can be demonstrated that the concentration contribution of tetrachlorethylen from the dress to the indoor climate in a room of a poorly ventilated apartment will never exceed 0.2 $\mu g/m^3$. It this connection, it can be mentioned that the air quality criterion for tetrachlorethylen is 6 $\mu g/m^3$. Indoor

climate problems are therefore not expected in consequence of a similar residual content of tetrachlorethylen in Rynex dry-cleaned textile.

7.2.2 Model calculations - textiles dry-cleaned by using hydrocarbon cleaning fluid

According to section 6.7, the measurements carried out in the climatic chambers showed emission of hydrocarbons and glycolethers from the hydrocarbon dry-cleaned trousers and jacket. No emission of tetrachlorethylen from the mentioned textiles could be demonstrated. It was not possible to measure any emission of the above substances from the dress.

The results of the model calculations appear from table 7.2 and 7.3 for hydrocarbons and glycolethers emitted from hydrocarbon dry-cleaned textile.

Tablel 7.2: Model calculations of the resulting concentration of hydrocarbons from hydrocarbon dry-cleaned textiles introduced into residences.

[A]: It is assumed that all the dry-cleaned textiles are kept in this room.
[B]: The air quality criterion of the Danish Environmental Protection Agency for hydrocarbons from hydrocarbon cleaning fluid.

Hydrocarbon dry-cleaned textile Emission of hydrocarbons		**Small poorly ventilated apartment**		**Well-ventilated single-family house**	
Scenario		**1**		**2**	
		Single room[A]	**Whole apartment**	**Single room[A]**	**Whole house**
Number of suits (jacket and trousers)		1	1	1	1
Average indoor climate concentration, µg/m^3	7 days	7	3	3	<1
	14 days	4	2	2	<1
	21 days	3	1	1	<1
Maximum concentration, µg/m^3		33	29	19	16
Air quality criterion[B] µg/m^3		600			
Number of days from introduction of dry-cleaned textile till the size of the concentration is identical to the size of the air quality criterion[B]		<1	<1	<1	<1

The calculations show that the found residual content of hydrocarbons in the hydrocarbon dry-cleaned textiles results in average concentration contributions for both scenarios of only a few µg/m^3. The concentrations never reach the size of the air quality criterion of 0.6 mg/m^3.

If you introduce 3 hydrocarbon dry-cleaned suits into a room of a small poorly ventilated apartment, you will get an average concentration contribution of hydrocarbons of 19 µg/m^3 in the room over a period of 1 week with a maximum value of 41 µg/m^3 a few hours after the dry-cleaning. To reach hydrocarbon contributions from hydrocarbon dry-cleaned texiles of the same

size as the air quality criterion of 0,6 mg/m^3, you have to introduce unrealistic quantities of textiles.

Based on this, it is estimated that introduction of textiles with a similar residual content of hydrocarbons as found in this investigation will not cause any indoor climate problems.

Table 7.3: Model calculations of the resulting concentration of glycolethers from hydrocarbon dry-cleaned textiles introduced into residences.

A: It is assumed that all the dry-cleaned textiles are kept in this room.
B: Estimated relatively to the air quality criterion of the Danish Environmental Protection Agency for di-propylenglycol-butylether (CAS number 29911-28-2).

Hydrocarbon dry-cleaned textile Emission af glycolethers		**Small poorly ventilated apartment**		**Well-ventilated single-family house**	
Scenario		**1**		**2**	
		Single room[A]	**Whole apartment**	**Single room**[A]	**Whole house**
Number of suits (jacket and trousers)		1	1	1	1
Average indoor climate concentration, µg/m^3	7 days	4	1	2	<1
	14 days	3	<1	1	<1
	21 days	2	<1	<1	<1
Maximum concentration, µg/m^3		7	2	3	<1
Air quality criterion[B] µg/m^3		40			
Number of days from introduction of dry-cleaned textile till the size of the concentration is identical to the size of the air quality criterion[B]		<1	<1	<1	<1

As it appears from the results of table 7.3, the contribution of glycolethers from the hydrocarbon dry-cleaned textiles is so small that the glycolethers will not pose an indoor climate problem.

8 Discussion

8.1 Chemicals used in hydrocarbon and Rynex dry-cleaning shops

As it appears from section 4, a large number of chemical products are used in the alternative dry-cleaning shops. The chemicals have different functions in the dry-cleaning process, but the safety data sheets of the chemical products used show that some of the chemicals appear frequently in the products. Some of these chemicals are 2-(2-butoxyethoxy)ethanol (CAS number 112-34-5), poly(oxy-1,2-ethanediyl) (CAS number 69011-36-5), isoalkanes and isoparaffins.

The many products used in the dry-cleaning shops makes it difficult, without previous knowledge of the operation of the dry-cleaning shop in question, to predict for instance the residual content in the textiles, the residual compositions or components in connection with any soil and ground water pollutions. Please also see section 8.3

8.2 Product combination and marking

The result of the analysis of volatile organic compounds and the declared content information appear from table 5.2 and 5.1 respectively.

The products typically contain hydrocarbons or glycolethers as the dominant component. A product contains both hydrocarbons and glycolether.

The product analyses showed that 5 of 13 products contained octyl- or nonylphenolpolyethoxylates in a quantity of 0.1 to 47 percentage by weight.

N,N-dimethylalkyl amines have been found during the screenings in 2 out of 13 products.

In two of the products - Rynex 2 and Cetox KWI – tetrachlorethylen has been demonstrated in concentrations of up to 0.01 percentage by weight.

Contrary to the results from Hohenstein (1996) – please see table 4.4 – the present analyses of Frankotex HCR/KW did not demonstrate any chlorinated solvents.

The declared components of the chemicals and the analysis results conform to the rules of the authorities with regard to marking of chemicals of this type of products. Please see the list of dangerous chemicals of the Danish Environmental Protection Agency. Due to the small concentration of tetrachlorethylen in Rynex 2 and Cetox KWI, the data sheets of the products does not have to be marked.

The analyses have shown a considerate number of volatile/semi-volatile substances that do not have to be marked according to law or they appear in such low concentrations that they do not have to be marked.

Futhermore a sample of contact water was analysed. The contact water contained glycolethere in a concentration of 1.1 % (percentage by weight) and nonylphenolethoxylates in a concentration of less than 0.001 % (percentage by weight). Hydrocarbons or tetrachlorethylene was not detected (detection limit was 0,01 percentage by weight).

8.3 Residual content

As it appears from section 6.1.2, this investigation includes a hydrocarbon dry-cleaning shop that has earlier delivered dry-cleaned textile for measurements in climate chambers (the Danish Environmental Protection Agency, 2002a).

The tests show comparable emission rate constants in relation to the results found earlier. It is, however, remarkable that the residual content of hydrocarbons determined in this investigation is considerably lower than the residual content found in similar textiles after dry-cleaning in the same dry-cleaning shop approximately one year earlier. The explanation may be that the variation in residual content is very dependent on fiber types, the distillation process, the chemicals used as well as the drying process. When asked, the dry-cleaning shop owner informed that the drying process has been optimized. The temperature has been increased by 5 °C and thick textiles such as coats (the drying time of which is long) are generally kept separately in a small charge size. It is therefore probable that the low residual content for volatile components to a large extent is due to these optimizations. However, other conditions may also play an important part.

It is outside the scope of this project to investigate which of the optimizations result in the low residual content. As the results show that it is possible to reach a very low residual content via hydrocarbon dry-cleaning, it is recommended to take action so that other dry-cleaning shops can benefit from these experiences.

As it notoriously is easier to dry tetrachlorethylen out of the dry-cleaned textiles than glycolethers and hydrocarbons, it is likely that the experiences from the hydrocarbon dry-cleaning shop can also be used for the other dry-cleaning types.

The content of cleaning fluids after an emission period of 14 days appears from table 6.10 and 6.11. As it can be seen, there are no demonstrable quantities of hydrocarbons left in the textiles. This confirms the above conclusions on the basis of the climate chamber measurements.

Glycolethers are left in all six textiles after dry-cleaning and emission in the climate chambers. Especially the dress textile seems to contain large quantities of glycolether. This indicates that even with optimized drying, it can be complicated to remove the glycolethers from the textiles completely.

The content of nonylphenolpolyethoxylates in one of the cleaning intensifiers could also be found in the jacket and the trousers after dry-cleaning in the hydrocarbon dry-cleaning shop.

8.4 The dry-cleaning process – concentration of volatile components in the distillate

Studing the processes in the hydrocarbon and Rynex dry-cleaning shops taking part in the investigation shows that a thorough knowledge of the dry-cleaning processes is necessary to predict which substances will be residual content in the dry-cleaned textile and which substances will be emitted to the surroundings or removed as waste (please also see section 3).

The distillation process is of special importance, as it determines the components ending up in the textiles: by adding cleaning fluids, cleaning intensifiers, etc. in connection with the dry-cleaning processes, chemicals are conveyed to the system. The volatile substances subsequently end in the distillate that is used as fluid for the second bath of the dry-cleaning process. Due to the continuous addition of chemicals, the distillate may change its composition. The distillate is therefore only "pure cleaning fluid" in the first charge when it has just been added or it has been replaced by new cleaning fluid.

As the distillate can change its composition from charge to charge, the residual content in the dry-cleaned textiles may also change. The residual content in a given textile will, besides being dependent on the ability of the text fibres to keep the chemicals used as well as the drying process, also be dependent on the use of helping agents and additives, the effectivity of the distillation and the number of charges since cleaning fluid was added to the machine. This makes it more complicated to predict the size of the residual content and the combination of the volatile components.

A chemical analysis of distillats from the Rynex and hydrocarbon dry-cleaning shops in this investigation shows that the distillates from both dry-cleaning shops contain tetrachlorethylen. The reason for this may be the small quantities of tetrachlorethylen that can appear in cleaning fluids, helping agents and additives. The contribution from textiles that have earlier been dry-cleaned in tetrachlorethylen dry-cleaning shops may also have an influence.

8.5 Model calculations – indoor climate influence

First of all, it should be noticed that a model has been used in section 7, the assumptions of which have not been demonstrated. This model has only been demonstrated to a limited extent via measurements. Among other things, it is assumed that there are no zinc effects. This is very doubtful, as investigations have shown that zinc effects can be demonstrated in nearly all substances. Please also see Environmental Project 673/2002 (the Environmental Protection Agency, 2002b). In case of any zinc effects, these will on the one hand reduce the maximum concentrations, but on the other hand extend the influence of the indoor climate.

The results from background measurements for tetrachlorethylen by the Environmental Protection Agency (2001a) showed average concentrations of 2.2 $\mu g/m^3$ over a period of 14 days in a residence where one piece of dry-cleaned textile was introduced during the measurement period. Model calculations in a similar residence showed average contributions from an identical piece of dry-cleaned textile of 2-3 $\mu g/m^3$ over a period of 14 days. There is therefore reason to assume that the model gives a thrustworthy estimate of – at least – the size of the influence.

As it appears from table 7.1-7.3, it is estimated that the emission of glycolethers from Rynex dry-cleaned textiles can cause indoor climate problems. Based on the calculations and the given conditions, it is estimated that the contribution of hydrocarbons or glycolethers from hydrocarbon dry-cleaned textile is low. It is therefore estimated that there is no risk involved with the introduction of textiles in the given quantities and with the given residual content into residences.

It has to be emphasized that the present results cannot be used for characterizing the whole trade, as there may be considerable variations in the residue of textiles dry-cleaned by different dry-cleaning shops. More extensive measurements have to be carried out to determine any residue under given conditions.

8.6 Final comments

As it appears from the investigation, some of the components in the chemical products used by the dry-cleaning shops are not listed in the declarations of the safety data sheets. This can involve a number of work, environmental and health risks, as the dry-cleaning shops do not know the characteristics of the products fully.

According to the results in section 4.5 and 8.4, it is likely that chemical products containing tetrachlorethylen are used both in the Rynex as well as the hydrocarbon dry-cleaning shops. As many of the alternative dry-cleaning shops advertise their dry-cleaning as being chlorine-free, these dry-cleaning shop owners ought to make sure that the products do not contain any chlorinated solvents.

As the chemicals in the cleaning fluids can end as residual content in the textile that has been finally treated (and thereby influence the consumers), the dry-cleaning trade ought to demand better declaration of the chemical products from the suppliers and producers.

Until a better declaration of the products is provided, it is recommend that the dry-cleaning trade has the composition of its distillate verified at regular intervals so that unintended components do not end in textiles that have been finally treated.

Furthermore, it is recommended that the dry-cleaning trade have the expected residual content of a given chemical examined under homogenous operation conditions in co-operation with the suppliers of dry-cleaning machines and chemical products. This makes it possible for the dry-cleaning trade to compare the chemical products. Furthermore, the dry-cleaning shops can control the dry-cleaning processes and the residual content, thereby evaluating the operation of the dry-cleaning shop in relation to these homogenous operation conditions.

9 References

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Questionnaire dealing with chemicals in dry-cleaned textile

The questionnaire has been divided into 2 parts.

The first part includes a number of general questions relating to the dry-cleaning shop and its operation.

The second part includes a number of questions relating to the use of chemicals in connection with the dry-cleaning.

In case of any questions to this material, please do not hesitate to contact Dorte Glensvig or Jan Dam Christensen, Kampsax A/S, telephone +45 36 39 07 00.

We thank you very much for your assistance.

PART 1:

Basis data	
The name of the dry-cleaning shop	
Address	
Telephone number	
Owner	

Information about the dry-cleaning machine
The manufacture of the dry-cleaning machines (machine name/brand) and the cleaning fluid being used (Rynex, hydrocarbons)? Machine 1: _____ Cleaning fluid: _____ Machine 2: _____ Cleaning fluid: _____ Please enclose any available information about the machines.
When were the dry-cleaning machines installed? Machine 1: _____ Machine 2: _____ **Have any essential changes been made to the machine since the installation?** Machine 1: Yes No

If ”Yes” – which changes have been made and when? _____

Machine 2: Yes No

If ”Yes” – which changes have been made and when? _____

Does the machine have automatic drying control?

Machine 1: Yes No

If ”Yes” - please briefly describe how the automatic drying control works (according to the residue in the drum air or according to the drying time)

_____

_____

_____

Other control mechanisms: Yes No

If ”Yes” - which? _____

Machine 2: Yes No

Other control mechanisms: Yes No

If ”Yes” - which? _____

If ”Yes” - please briefly describe how the automatic drying control works (according to the residue in the drum air or according to the drying time)

_____

_____

_____

What is the capacity of the machine?

Machine 1: _____kg/charge

Machine 2: _____kg/charge

Quantity of dry-cleaned clothes per year (kg)?

Number of charges per year?

Number of working days per year?

Evaluation of the cleaning fluids, helping agents, etc.

Have you experienced any obnoxious smells due to the cleaning fluid used and/or the helping agents and additives?

Yes No

If "Yes" – please describe the problem:_____

Have you experienced any operation problems due to the cleaning fluid used and/or the helping agents and additives?

Yes No

If "Yes" – please describe the problem:_____

Have you received any complaints from the customers due to the cleaning fluid used and/or the helping agents and additives?

Yes No

If "Yes" – please describe the problem:_____

Do you find the dry-cleaning sufficiently good?

Yes No

If "No" – please describe the problem:

Any other advantages or disadvantages connected to the cleaning fluids, helping agents and additives?

PART 2: Consumption of chemicals during the dry-cleaning process

Consumption of chemicals for pre-treatment, dry-cleaning and final treatment:

[A]: Please enclose any available data sheets

[B:] Cleaning fluid, cleaning intensifiers, bactericides, helping agents, spot removers, deodorizers, etc.

[C]: Name, address, telephone number, contact person

Trade name[A]	**Use**[B]	**Supplier/producer**[C]	**Consumption per year** **Please state the unit (litre or kg)**	**Consumption per kg clothes**

Consumption of chemicals for pre-treatment, dry-cleaning and final treatment:

[A]: Please enclose any available data sheets
[B:] Cleaning fluid, cleaning intensifiers, bactericides, helping agents, spot removers, deodorizers, etc.
[C]: Name, address, telephone number, contact person

Trade name[A]	**Use**[B]	**Supplier/producer**[C]	**Consumption per year Please state the unit (litre or kg)**	**Consumption per kilo clothes**

			Dry-cleaning shop A	Dry-cleaning shop B
The dry-cleaning machine		Machine 1	Satec	Satec
		Cleaning fluid	**Rynex**	**Rynex**
		Installation of machine	06.08.2001	11.04.2001
		Changes made	No	No
		Machine 2	None	None
		Automatic drying control	No	No
		How	Automatic time control, 70 minutes. Can also be set manually.	Automatic time control, 70 minutes. Can also be set manually.
		Other control mechanisms	No	No
		Which		
		Normal drying time in minutes	70	70
		Machine capacity - kg	15	15
		Quantity per year	Approx. 9,500 kg	6,000
		Charges per year	Approx. 900	750
		The quantity dry-cleaned per kilo (without pressing)	< 5%	Only half of the curtains
		Number of working days a year	240	230
Evaluation of cleaning fluids, etc.		Obnoxious smells	No	No
		Operation problems	Long drying time	No
		Complaints from customers	No	No
		Is the dry-cleaning good?	Yes	Yes
		Other advantages or disadvantages	No comments	No comments

			Dry-cleaning shop A	Dry-cleaning shop B
Consumption of chemicals	1 Pre-brushing fluid	Trade name	Secafix 1-2-3	Devantol Soft
		Use	Spot removers	Pre-brushing - masking off
		Supplier/producer	Bendsen A/S	Bendsen A/S
		Consumption per year	Few litres	20 kg
	1 Pre-brushing fluid	Trade name	Polysol	DetaProfi and Detafix series
		Use	Pre-brushing fluid	Spot removal
		Supplier/producer	Aktern A/S	Bendsen A/S
		Consumption per year	20 l	500 ml
	2 Pre-cleaning fluid	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	3 Cleaning fluid	Trade name	Rynex 2	Rynex 2
		Use	Cleaning fluid	Cleaning fluid
		Supplier/producer	HJM Teknik	HJM Teknik
		Consumption per year	No consumption	60 l
	4 Cleaning intensifiers	Trade name	Tempo Ryn	TPM 1075
		Use	Cleaning intensifier	Cleaning intensifier
		Supplier/producer	Bendsen A/S	Bendsen A/S
		Consumption per year	150 l	20 kg
	5 Starching fluid	Trade name	Ingredient of cleaning intensifier	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	6 Anstistatica	Trade name	Ingredient of cleaning intensifier	Ingredient of cleaning intensifier
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	7 Waterproofing fluids	Trade name	Vinoy Plus	Vinoy Plus
		Use	Waterproofing fluid	Waterproofing
		Supplier/ producer	H.H.	H.H.
		Consumption per year	20 l	15 kg
	8 Spotting fluids	Trade name	-	Same products as in 1)
		Use	-	-
		Supplier/producer	-	-

		Consumption per year	-	-
	9 Filter powder	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	10 Dubbin	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-

-: No information available

The supplier informs, that in Dry-celaning shop C, D, E and F the same technical construction of cleaning machines has been used.

			Dry-cleaning shop C	Dry-cleaning shop D
The dry-cleaning machine		Machine 1	Satec B-300	Satec B-700
		Cleaning fluid	**Hydrocarbon**	**Hydrocarbon**
		Installation of machine	23.12.2001	06.2001
		Changes made	No	No
		Machine 2	None	None
		Automatic drying control	Yes	Yes
		How	Infra-red sensor for measuring residue in the drum air	Infra-red sensor for measuring residue in the drum air. Heating stops at 75% of LEL
		Other control mechanisms	Yes	Yes
		Which	Minimum time for drying, typically 25-35 minutes.	Minimum time for drying, typically 25-35 minutes.
		Normal drying time in minutes		30
		Machine capacity – kg	15	35
		Quantity per year	22,000 kg	40,000 kg
		Charges per year	1,600	1,300
		Quantity dry-cleaned per kilo (without pressing)	Max. 1%	< 3%
		Number of working days a year	220	275
Evaluation of cleaning fluids, etc.		Obnoxious smells	No	No
		Operation problems	No	No
		Complaints from customers	No	No
		Is the dry-cleaning good?	Yes	Yes
		Other advantages or disadvantages	Is very satisfied with the non-smelling cleaning fluid	More comfortable smell in the dry-cleaning shop

			Dry-cleaning shop C	Dry-cleaning shop D
Consumption of chemicals	1 Pre-brushing fluid	Trade name	Product from Kreussler	Solvex 1, 2 and 3
		Use	Spot removal	Spot removal
		Supplier/producer	H.H.	Aktern A/S
		Consumption per year	Low	3 x 10 l
	1 Pre-brushing fluid	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	2 Pre-cleaning fluid	Trade name	Prenett Pur	Prenet
		Use	Pre-cleaning fluid	Pre-rinse
		Supplier/producer	H.H.	H.H.
		Consumption per year	7 l	120 l
	3 Cleaning fluid	Trade name	-	Toptrel HP
		Use	-	Cleaning fluid
		Supplier/producer	-	H.H.
		Consumption per year	No consumption	100 l have been drawn off
	4 Cleaning intensifiers e	Trade name	Clip Comfort	Frankotex and Preclin
		Use	Cleaning intensifier	Cleaning intensifier
		Supplier/producer	H.H.	Aktern A/S
		Consumption per year	150 l	425 l in total
	5 Starching fluid	Trade name	Included in 2)	Included in 2)
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	6 Anstistatica	Trade name	Included in 2)	Included in 2)
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	7 Waterproofing fluids	Trade name	Included in 2)	Cetox KWI
		Use	-	Waterproofing
		Supplier/producer	-	Aktern A/S
		Consumption per year	-	160 l
	8 Spotting fluids	Trade name	Included in 2)	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	9 Filter powder	Trade name	-	Kieselguhr
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	15 kg
	10 Dubbin	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-

-: No information available

			Dry-cleaning shop E	Dry-cleaning shop F
The dry-cleaning machine		Machine 1	Satec B-300	Satec B-440
		Cleaning fluid	**Hydrocarbon**	**Hydrocarbon**
		Installation of machine	06.2002	28.03.2002
		Changes made	No	No
		Machine 2	None	
		Automatic drying control	Yes	Yes
		How	Infra-red sensor for measuring residue in the drum air	Infra-red sensor for measuring residue in the drum air
		Other control mechanisms	Yes	Yes-
		Which	Minimum time for drying, typically 25-35 minutes.	Minimum time for drying, typically 25-35 minutes.
		Normal drying time in minutes		
		Machine capacity - kg	15	22
		Quantity per year	Unknown new machine	25,000
		Charges per year	Unknown new machine	1,800
		Quantity dry-cleaned per kilo	-	<10%
		Number of working days a year	300	312
Evaluation of cleaning fluids, etc.		Obnoxious smells	No	No
		Operation problems	No	No
		Complaints from customers	No	No
		Is the dry-cleaning good?	Yes	Yes
		Other advantages or disadvantages	Positive feedback from customers	-

			Dry-cleaning shop E	Dry-cleaning shop F
Consumption of chemicals	1 Pre-brushing fluid	Trade name	Solvex 1, 2 and 3	Solvex 1, 2 and 3
		Use	Spot removal	Spot removal
		Supplier/producer	Aktern A/S	Aktern A/S
		Consumption per year	4 l (new)	3 x 10 l
	1 Pre-brushing fluid	Trade name	Polysol KWV	-
		Use	Pre-brushing	-
		Supplier/producer	Aktern A/S	-
		Consumption per year	-	-
	2 Pre-cleaning fluid	Trade name	Preclin Odosorb	-
		Use	Pre-cleaning fluid	-
		Supplier/producer	Aktern A/S	-
		Consumption per year	-	-
	3 Cleaning fluid	Trade name	Actrel 3356 D	Toptrel HP
		Use	Cleaning fluid	Cleaning fluid
		Supplier/producer	Aktern A/S	H.H.
		Consumption per year	-	50 l
	4 Cleaning intensifiers	Trade name	Frankotex HCR	Prenet Pur and Clip Comfort
		Use	Cleaning intensifier	Cleaning intensifier
		Supplier/producer	Aktern A/S	H.H.
		Consumption per year	-	200 and 150 kg respectively
	5 Starching fluid	Trade name	Included in 2)	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	6 Anstistatica	Trade name	Included in 2)	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	7 Waterproofing fluids	Trade name	Cetox KWI	Vinoy Plus
		Use	Waterproofing	Waterproofing
		Supplier/producer	Aktern A/S	H.H.
		Consumption per year	-	100 kg
	8 Spotting fluids	Trade name	Solvex 1, 2 and 3	-
		Use	Spot removal	-
		Supplier/producer	Aktern A/S	-
		Consumption per year	-	-
	9 Filter powder	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-
	10 Dubbin	Trade name	-	-
		Use	-	-
		Supplier/producer	-	-
		Consumption per year	-	-

-: No information available

			Dry-cleaning shop G
The dry-cleaning machine		Machine 1	Satec DX 101
		Cleaning fluid	**Aroma free hydrocarbon**
		Installation of machine	12.1993
		Changes made	No
		Machine 2	None
		Automatic drying control	Yes
		How	Drying time
		Other control mechanisms	-
		Which	-
		Normal drying time in minutes	-
		Machine capacity - kg	10
		Quantity per year	14,000
		Charges per year	1,800
		Quantity dry-cleaned per kilo (without pressing)	<1%
		Number of working days a year	250
Evaluation of cleaning fluids, etc.		Obnoxious smells	No
		Operation problems	No
		Complaints from customers	No
		Is the dry-cleaning good?	Yes
		Other advantages or disadvantages	No comments

			Dry-cleaning shop G
Consumption of chemicals	1 Pre-brushing fluid	Trade name	Polysol KWV
		Use	Pre-brushing
		Supplier/producer	Aktern A/S
		Consumption per year	45 l
	1 Pre-brushing fluid	Trade name	-
		Use	-
		Supplier/producer	-
		Consumption per year	-
	2 Pre-cleaning fluid	Trade name	Preclin Odosorb
		Use	Pre cleaning intensifier
		Supplier/producer	Aktern A/S
		Consumption per year	25 l
	3 Cleaning fluid	Trade name	-
		Use	-
		Supplier/producer	-
		Consumption per year	80 l
	4 Cleaning intensifiers	Trade name	Frankotex HCR
		Use	Cleaning intensifier
		Supplier/producer	Aktern A/S
		Consumption per year	45 l
	5 Starching fluid	Trade name	Included in 4)
		Use	-
		Supplier/producer	-
		Consumption per year	-
	6 Anstistatica	Trade name	Included in 4)
		Use	-
		Supplier/producer	-
		Consumption per year	-
	7 Waterproofing fluids	Trade name	Cetox KWI
		Use	Waterproofing
		Supplier/producer	Aktern A/S
		Consumption per year	60 l
	8 Spotting fluids	Trade name	Solvex 1, 2 and 3
		Use	-
		Supplier/producer	-
		Consumption per year	-
	9 Filter powder	Trade name	-
		Use	-
		Supplier/producer	-
		Consumption per year	-
	10 Dubbin	Trade name	Leder Öl
		Use	Dubbin
		Supplier/producer	Aktern A/S
		Consumption per year	65 l

-: No information available

Product name	Use[2]	Dealer/ importer	Producer[1]	PR No.[1]	Consumption per year [2]	
Devantol Soft	Pre-treatment	F1	P1	807-0004	B: 20 kg	
Rynex 2	Cleaning fluid	F2	P2	-	A: - B: 60 l	
TPM 1075	Cleaning intensifier	F1	P1	803-0001	B: 20 kg	
Secafix 1	Pre-brushing	F1	P1	848-0101	A: few litres	
Secafix 2	Pre-brushing	F1	P1	848-0102	A: few litres	
Secafix 3	Pre-brushing	F1	P1	848-0103	A: few litres	
Tempo Ryn	Identical to TPM 1075	F1	P1	803-0001	A: 150 l	
Detafix Rostol	Pre-brushing - rust, food and blood	F1	P1	844-0006	B:*	
Detafix Tintol	Pre-brushing – ink and felt pen	F1	P1	844-0005	B:*	
Detafix Color	Pre-brushing – oil, paint, lubricating oil, etc.	F1	P1	844-0004		B: 250-500 ml
Detafix Tanol	Pre-brushing – tannin and tanning agents	F1	P1	844-0003		
Detafix Blotol	Pre-brushing - blood and albumens	F1	P1	844-0002		
Detaprofi Tanex	Pre-brushing – tannin and tanning agent spots	F1	P1	842-0012		
Detaprofi Blodex	Pre-brushing – blood and albumens	F1	P1	842-0011		
Detaprofi Lacex	Pre-brushing – colour, grease and wax spots	F1	P1	842-0013		
Detaprofi Ferex	Pre-brushing - rust and metal stains	F1	P1	842-0015		
Detaprofi Medex	Pre-brushing – medicaments, etc.	F1	P1	842-0014		
Polysol KwV	Pre-brushing	F3	P3	1 304 111	A: 20 l	
Vinoy Plus	Waterproofing	F4	P4	-	A: 20 l B: 15 kg	

NOTES:

Dealer/importer:
F1: Bendsen A/S
F2: HJM Teknik APS
F3: Aktern A/S
F4: H.H. Pels- og skindservice A/S

Producer:
P1: Büsing & Fasch GmbH
P2: Vopak Products Europe
P3: Seitz GmbH
P4: Kreussler & Co GmbH

1: From safety datasheets
2: From response to questionnaire – dry-cleaning shops
Dry-cleaning shop A: 9,500 kg textile dry-cleaned annually
Dry-cleaning shop B: 6,000 kg textile dry-cleaned annually
-: No information available
*: No longer used

Product name	Use[2]	CAS No. [1]	Chemicals [1]	Content in % [1]	Danger symbol [1]
Devantol Soft	Pre-treatment	112-34-5	2-(2-butoxyethoxy)ethanol	2,51-10,00	Xi; 36
		64742-48-9	Isoparafinisches Kohlenwassestoffgemish	10,01-25,00	
		68425-47-8	Fettsäurediethanolamid	10,01-25,00	Xi; 36 38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36 38
		69011-36-5	Fettalkoholethoxylat	2,51-10,00	Xi: 36 38
		68411-30-3	Alkylbenzolsulfonate	0,01-2,50	Xi; 36 38
Rynex 2	Cleaning fluid	-	Propandiolether	-	-
TPM 1075	Cleaning intensifier	112-34-5	2-(2-butoxyethoxy)ethanol	2,5-10,00	Xi; 36
		69011-36-5	Fettalkoholethoxylat	25,01-50,00	Xi; 36/38
Secafix 1	Pre-brushing	112-34-5	2-(2-butoxyethoxy)ethanol	10,01-25,00	Xi; 36
		64742-48-9	Isoparafinisches Kohlenwassestoffgemish	10,01-25,00	
		68425-47-8	Fettsäurediethanolamid	2,51-10,00	Xi; 36 38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36 38
		69011-36-5	Fettalkoholethoxylat	10,01-25,00	Xi: 36 38
Secafix 2	Pre-brushing	112-34-5	2-(2-butoxyethoxy)ethanol	2,5-10,00	Xi; 36
		64742-48-9	Isoparafinisches Kohlenwassestoffgemish	10,01-25,00	
		50-21-5	2-Hydroxypropionsäure (milchsäure)	0,01-2,50	Xi; 36/38
		68425-47-8	Fettsäurediethanolamid	2,51-10,00	Xi; 36 38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	10,00-25,00	Xi; 36 38
		69011-36-5	Fettalkoholethoxylat	10,01-25,00	Xi: 36 38
Secafix 3	Pre-brushing	345590-94-8	Diprpylenglykolmethylether (Isomerengemish)	2,51-10,00	
		112-34-5	2-(2-butoxyethoxy)ethanol	10,01-25,00	Xi; 36
		68425-47-8	Fettsäurediethanolamid	2,51-10,00	Xi; 36 38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36 38
		69011-36-5	Fettalkoholethoxylat	10,01-25,00	Xi: 36 38
Tempo Ryn	Identical to TPM 1075	112-34-5	2-(2-butoxyethoxy)ethanol	2,5-10,00	Xi; 36
		69011-36-5	Fettalkoholethoxylat	25,01-50,00	Xi; 36/38
Detafix Rostol	Pre-brushing - rust, food and blood	7664-38-2	Phosphoric acid	2,51-10,00	C; 34/36/38
		1341-49-7	Ammonium hydrogen fluoride	2,51-10,00	C; 34/36/38
Detafix Tintol	Pre-brushing - ink and felt pen	100-51-6	Benzyl alcohol	2,51-10,00	Xn; 20/22
		112-34-5	2-(2-butoxyethoxy)ethanol	10,01-25,00	Xi; 36
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36/38
		69011-36-5	Fettalkoholethoxylat	10,01-25,00	Xi; 36/38
		22-99-6	2-Phenoxyethanol	10,01-25,00	Xi; 36

Product name	Use	CAS No. [1]	Chemicals [1]	Content in % [1]	Danger symbol [1]
Detafix Color	Pre-brushing	100-51-6	benzylalkohol	2,51-10,00	Xn; 20/22
	- oil, paint,	112-34-5	2-(2-butoxyethoxy)ethanol	10,01-25,00	Xi; 36
	lubricating oil, etc.	64742-48-9	Isoparafinisches Kohlenwassestoffgemish	10,01-25,00	
		68425-47-8	Fettsäurediethanolamid	2,51-10,00	Xi; 36 38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36 38
		22-99-6	2-Phenoxyethanol	2,51-10,00	Xi; 36
		68411-30-3	Alkylbenzolsulfonate	2,51-10,00	Xi; 36/38
Detafix Tanol	Pre-brushing	112-34-5	2-(2-butoxyethoxy)ethanol	10,01-25,00	Xi; 36
	- tannin and	69011-36-5	Fettalkoholethoxylat	10,01-25,00	Xi; 36/38
	tanning agents	68411-30-3	Alkylbenzolsulfonate	2,51-10,00	Xi; 36 38
Detafix Blotol	Pre-brushing	112-34-5	2-(2-butoxyethoxy)ethanol	2,51-10,00	Xi; 36
	- blood and	68425-47-8	Fettsäurediethanolamid	0,01-2,50	Xi; 36 38
	albumens	577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36/38
		69011-36-5	Fettalkoholethoxylat	2,51-10,00	Xi; 36/38
Detaprofi Tanex	Pre-brushing	112-34-5	2-(2-butoxyethoxy)ethanol	2,5-10,00	Xi; 36
	- tannin and tanning agent	69011-36-5	Fettalkoholethoxylat	2,5-10,00	Xi; 36/38
	spots	68411-30-3	Alkylbenzolsulfonate	2,5-10,00	Xi; 36/38
Detaprofi Blodex	Pre-brushing - blood and albumens	61790-12-3	Ölsäure	2,5-10,00	Xi; 36
Detaprofi Lacex	Pre-brushing	123-86-4	n-butylacetat	25,01-50,00	
	- colour, grease	107-41-5	2-methyl-2,4-pentandiol	2,51-10,00	Xi; 36/38
	and wax spots	68425-48-9	Fettsäurediethanolamid	10,01-25,00	Xi; 36/38
		68411-30-3	Alkylbenzolsulfonate	2,5-10,00	Xi; 36/38
Detaprofi Ferex	Pre-brushing	7664-38-2	Phosphoric acid	2,5-10,00	C; 34
	- rust and metal stains	1341-49-7	Ammonium hydrogen diflouride	2,5-10,00	T; 25. C; 34
Detaprofi Medex	Pre-brushing	872-50-4	Nmethyl-2-pyrrolidon	10,01-25,00	Xi; 36/38
	- medicaments,	112-34-5	2-(2-butoxyethoxy)ethanol	10,01-25,00	Xi; 36
	etc.	141-43-5	2-aminoethanol	2,51-10,00	Xi; 36/37/38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	0,01-2,5	Xi; 36/38
Polysol KwV	Pre-brushing	-	Non-ionic tensid	10-30	Xi; 36/38-53
		-	Anion active tensid	10-20	Xi; 36/38
		90622-57-4	Isoalkanes	10-20	Xn; 65
		112-34-5	2-(2-butoxyethoxy)ethanol	10-20	Xi; 36
Vinoy Plus	Waterproofing	-	Fluoride carbon resin dissolved in isoparaffin	-	Xn; 62 65

NOTES:
[1]: From safety datasheets
[2]: From response to questionnaires - dry-cleaning shops
-: No information available

Product name	Use[2]	Dealer/ importer	Producer [1]	PR No. [1]	Consumption per year [2]	
Solvex 1	Pre-brushing fluid	F3	P3	1 321 552	D: 10 l E: 4 l F: 10 l *	
Solvex 2	Pre-brushing fluid	F3	P3	1 321 560	D: 10 l E: 4 l F: 10 l *	
Solvex 3	Pre-brushing fluid	F3	P3	1 321 579	D: 10 l E: 4 l F: 10 l *	
Leder Öl LW	Dubbin	F3	P3	1 321 413	G: 65 l	
Actrel 3356-D	Cleaning fluid	F3	P2	-	G: 80 l E: -	
Polysol KWV	Pre-brushing fluid	F3	P3	1 304 111	G: 45 l E: -	
Frankotex KW	Cleaning intensifier	F3	P3	1 304 058	G: 45 l E: -	D: 425 l
Preclin Odosorb	Cleaning intensifier, first bath	F3	P3	1 435 349	G: 25 l E: -	
Cetox KWI	Waterproofing fluid	F3	P3	-	D: 160 l G: 60 l E: -	
Benzapon Sanofresh	Cleaning intensifier	F1	P1	817-0020	Only informed by the supplier	
Benzapon Summer Wind	Cleaning intensifier	F1	P1	817-0022	Only informed by the supplier	
Benzapon Sanofresh	-	F1	P1	817-0020	Only informed by the supplier	
Benzapon Pre	Pre-brushing fluid	F1	P1	807-0011	Only informed by the supplier	
Toptrel HP	Cleaning fluid	F4	-	-	D:-100 l. F: 50 l.	
Prenett Pur	Pre-brushing fluid	F4	P4	-	C: 7 l D: 120 l	
Clip Comfort	Cleaning intensifier	F4	P4	-	C: 150 l; F: 150 kg	
Vinoy Plus	Waterproofing fluid	F4	P4	-	F: 100 kg	

NOTES:

Dealer/importer:
F1: Bendsen A/S
F2: HJM Teknik APS
F3: Aktern A/S
F4: H.H. Pels- og skindservice A/S

Producer:
P1: Büsing & Fasch GmbH
P2: Chemex Products A/S
P3: Seitz GmbH
P4: Kreussler & Co GmbH

[1]: From safety datasheets
[2]: From response to questionnaire – dry-cleaning shops
Dry-cleaning shop C: 22,000 kg textile dry-cleaned annually
Dry-cleaning shop D: 40,000 kg textile dry-cleaned annually
Dry-cleaning shop E: Unknown new machine
Dry-cleaning shop F: 25,000 kg textile dry-cleaned annually
Dry-cleaning shop G: 14,000 kg textile dry-cleaned annually
-: No information available
*: No longer used

Product name	Use[2]	CAS No. [1]	Chemicals [1]	Content in % [1]	Danger symbol [1]
Solvex 1	Pre-brushing fluid	90622-57-4	Isoalkanes	10-30	Xn; 65
		-	Anion active tensid	10-20	C; 34
		112-34-5	2-(2-Butoxyethoxy)ethanol	<5	Xi; 36
Solvex 2	Pre-brushing fluid	-	Anion active tensid	10-30	C; 34
		112-34-5	2-(2-Butoxyethoxy)ethanol	<20	Xi; 36
		90622-57-4	Isoalkanes	<5	Xn; 65
Solvex 3	Pre-brushing fluid	34590-94-8	(2-Methoxymethylethoxy)propanol	10-30	
		-	Anion active tensid	10-20	C; 34
		-	Cationic tensid	<5	C; N; 22-34-50/53
		-	Non-ionic tensid	<5	Xi; 36/38-53
		112-34-5	2-(2-Butoxyethoxy)ethanol	<5	Xi; 36
Leder Öl LW	Dubbin	-	Cationic tensid	<20	Xi; 36/38
Actrel 3356-D	Cleaning fluid	-	3295 Hydrocarbons floating N.O.S:		
		-	Iso-undekanes		
		-	Isododecanes		
Polysol KWV	Pre-brushing fluid	-	Non-ionic tensid	10-30	xi, 36/38-53
		-	Anion active tensid	10-20	xi,; 36/38
		90622-57-4	Isoalkanes	10-20	Xn; 65
		112-34-5	2-(2-Butoxyethoxy)ethanol	10-20	Xi; 36
Frankotex KW	Cleaning intensifier	90622-57-4	Isoalkanes	30-50	Xn; 65
		-	Mixture of tensids	20-50	Xi; 36/38
		112-34-5	2-(2-Butoxyethoxy)ethanol	<5	Xi; 36
Preclin Odosorb	Cleaning intensifier, first bath	-	Non-ionic tensid	<20	Xi; R36/38-53
		34590-94-8	(2-methoxymethylethoxy)propanol	<20	-
		-	Anion active tensid	<10	Xn; R22-36/38
		90622-57-4	Isoalkanes	<10	Xn; R65
Cetox KWI	Waterproofing fluid	-	Hydrocarbon mixture, isoparaffin	15-39	
		-	Flouride alkyl polymers		Xi; R36/38
		90622-57-4	Isoalkanes	50-100	Xn; R65
		-	Glycol ether acetate	<5	Xn; R20/21

Product name	Use[2]	CAS No. [1]	Chemicals [1]	Content in % [1]	Danger symbol [1]
Benzapon Sanofresh	Cleaning intensifier	64742-48-9	Isoparafinisches Kohlenwassestoffgemish	25,01-50,00	Xn; 65
		68425-47-8	Fettsäurediethanolamid	2,51-10,00	Xi; 36/38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	10,01-25,00	Xi; 36/38
		69011-36-5	Fettalkoholethoxylat	2,51-10,00	Xi; 36/38
Benzapon Summer Wind	Cleaning intensifier	112-34-5	2-(2-butoxyethoxy)ethanol	2,5-10,00	Xi; 36
		64742-48-9	Isoparafinisches Kohlenwassestoffgemish	25,01-50,00	Xn; 65
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	2,51-10,00	Xi; 36/38
		68411-30-3	Alkylbenzolsulfonate	2,5-10,00	Xi; 36/38
		61790-12-3	Ölsäure	2,5-10,00	Xi; 36
Benzapon Sanofresh	-	64742-48-9	Isoparafinisches Kohlenwassestoffgemish	25,01-50,00	Xn; 65
		68425-47-8	Fettsäurediethanolamid	2,51-10,00	Xi; 36/38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	10,01-25,00	Xi; 36/38
		69011-36-5	Fettalkoholethoxylat	2,51-10,00	Xi; 36/38
Benzapon Pre	Pre-brushing fluid	64742-48-9	Isoparafinisches Kohlenwassestoffgemish	25,01-50,00	Xn; 65
		68425-47-8	Fettsäurediethanolamid	0,01-2,50	Xi; 36/38
		577-11-7	Diisooctylsulfosuccinat, Natriumsalz	10,01-25,00	Xi; 36/38
		69011-36-5	Fettalkoholethoxylat	2,51-10,00	Xi; 36/38
Toptrel HP	Cleaning fluid	90622-57-4	Isoalkanes, C9-C12	-	Xn, R65, R66
Prenett Pur	Pre-brushing fluid	-	Alkyl benzene	-	-
		-	Coconut soap	-	-
		-	Sulfbernstensyraester	-	-
		-	Alkyl glycol	-	-
Clip Comfort	Cleaning intensifier	-	-	-	Xi; 36/38
Vinoy Plus	Waterproofing fluid	-	-	-	Xn; 62 65

NOTES:
[1]: From safety datasheets
[2]: From response to questionnaires – dry-cleaning shops
-: No information available

The Danish Environmental Protection Agency
Consumer project – mapping of chemical substances in dry cleaner shops
Prepared by: Peter Mortensen, Eurofins Danmark A/S & Dorte Glensvig, Kampsax A/S

Revised 01, 9 September 2002

Test protocol

The purpose is to perform an analysis for residual content in textiles cleaned with hydrocarbon based cleaning fluid and Rynex cleaning fluid respectively.

The tests include volatile compounds as well as non-volatile compounds. Prior to the tests a selection of analytical parameters has been carried out based on the obtained product information from the supplier.

Analysis for volatile compounds

Principle: Selected textiles are added standardised stains. Accordingly the textiles are cleaned in a hydrocarbon dry cleaner and a Rynex dry cleaner respectively. The liberation of volatile compounds is measured over a period of fourteen days with selective measurement methods that allows qualitative and quantitative analyses.

Textiles: The tests are carried out with a dress, a pair of trousers, and a jacket. Each textile is purchased in duplicate.

Pletter: The textiles are each added a stain of approximately 2x2 cm of the following dirt types:

- Soot/oil mixture (carbon black suspended in olive oil)
- Blood (from cattle or pig)
- Cocoa (purchased ready-made cocoa)
- Red wine
- Blackcurrant juice
- Egg

The stains are dried for 48 hours before delivery to dry cleaning.

Dry cleaning: Carried out in commercial dry cleaner shops. The dry cleaner applies methods considered necessary to remove the stains.

The stain treatment and cleaning are monitored because a number of significant parameters are recorded for later assessment of the results:

- Pre-treatment: Name and amount of the applied products
- Cleaning fluid and subsidiary materials: product name, and supplier

- Cleaning machine: type and age
- Progress: cleaning time, drying time, other textiles in same batch, stop criteria for drying (e.g. % LEL in the spin air's or the likes).
- Finishing treatment: Type, scope, and duration
- Emission reducing measures: filters and coolers
- Ventilation: type and age
- Discard: age, placing of ventilator

Plans for registration of information have been prepared.

Transport: When ready from the dry cleaners the textiles are transported to the laboratory immediately. In the laboratory they are placed in climate chambers with a view to measuring the emission of volatile compounds. The textiles are wrapped in ordinary wrapping from the dry cleaner during transport (typically plastic bag).

Climate chamber: Thermostatic climate chambers of polished stainless steel are used. The chambers are cleaned thoroughly with aqueous cleaning materials prior to the test. A blind sample is taken immediately before the testing with the climate chamber connected to the air supply.

The following test conditions are used:

- Temperature: 23° C ± 1°C
- Air humidity: 50% ± 5%RF
- Air change: 0.5 times per hour

Sampling: Samples are taken of the chamber air 1, 3, 5, 7, 9, 11, and 13 days and nights after test start. The samples are taken on combi-adsorption tubes typed Tenax TA/Chromosorb 106 and carbon tubes by drawing known air amounts through the tubes. The flow is controlled with a calibrated mass flow controller.

Analyses: The analysis is carried out for volatile organic compounds at thermal desorption/solvent desorption/gas chromatography with mass selective detector (ATD/GC/MS).

Identification and quantification are carried out of the volatile organic compounds.
The following are quantified as a minimum:

- Hydrocarbons
- Glycol ether (Rynex)
- Chlorinated solvents

When the screening analyses test results of the five products are available additional analytical types may be included if necessary.

The analyses of the initial sample set (day 1) are analysed by emergency procedure immediately after collection. Based in the analytical results and the product information on the applied chemicals, the final compounds are selected for identification and quantification in the samples.

Report: The emission is stated as source strength of the single components (µg/kg/hour subsidiary µg/m^2/hour). However, for hydrocarbons as a sum of components for relevant boiling point intervals.

Analysis for non-volatile compounds

Principle: A sample is taken of the textile following the climate chamber test. The samples are analysed for selected chemical compounds. The result is compared with the result of the analysis for the identical compounds on samples taken from the textiles before dry cleaning.

Sampling: Before hand on to dry cleaning three pieces of 10x20 cm are taken from each textile. The samples are identified and stored in annealed glass packaging until analysis.

Following the climate chamber test conclusion a similar piece is cut of the textiles.

Analysis The samples are extracted with a suited extraction agent and analysed accordingly.

The analytical programme is arranged based on collected information in product composition, including possibly applied stabilisations in the cleaning fluids.

Analysis for alkylphenolpolyethoxylates is performed on each textile.

Results The result is stated as residual amount per kg textile. Possible content before dry cleaning is compensated.

Product	Sampling data
Toptrel HP	Sample taken on 02.09.2002 at HJM Teknik, Ringsted. Sample taken from 200 l metal drum with a residue of approximately 50 l
Rynex 2	Sample taken on 27.08.2002 at HJM Teknik, Ringsted. Sample taken from 200 l metal drum with a residue of approximately 5 l.
Tempo Ryn	Sample taken on 28.08.2002 at Aktern A/S, Allerød. Sample taken from unopened 20 l plastic bottle.
Actrel 3356 D	Sample taken on 28.08.2002 at Aktern A/S, Allerød. Sample taken from unopened 200 l metal drum.
Frankotex HCR	Sample taken on 29.08.2002 at Sober Rens, Allerød. Sample taken from 25 l bottle with a residue of approximately 15 l.
Prenett Pur	Sample taken on 29.08.2002 at Sober Rens, Allerød. Sample taken from unopened 20 l bottle.
Cetox KWI	Sample taken on 29.08.2002 at Sober Rens, Allerød. Sample taken from unopened 20 l bottle.
Preclin Odosorp	Sample taken on 08.11.2002 at Aktern A/S, Allerød. Sample taken from unopened 25 l dunk
Polysot Kwv	Sample taken on 05.11.2002 at Sober Rens, Allerød 25 l bottle, approximately 10 l left
Solvex 1	Sample taken on 05.11.2002 at Sober Rens, Allerød 5 l bottle, approximately 2.5 l left
Solvex 2	Sample taken on 05.11.2002 at Sober Rens, Allerød 5 l bottle, approximately 1.5 l left
Solvex 3	Sample taken on 05.11.2002 at Sober Rens, Allerød 5 l bottle, approximately 2.5 l left
Clip Comfort	Sample taken on 05.11.2002 at Sober Rens, Allerød 25 l bottle, approximately 10 l left
Contact water	Sample taken on 06.11.2002 at Sober Rens, Allerød

Sampling procedures:
The chemical samples have been taken with either 20 ml plastic syringes or bailers or they have been poured directly into 100 ml Red-Cap glasses that were sent to the analysis laboratory the same day.

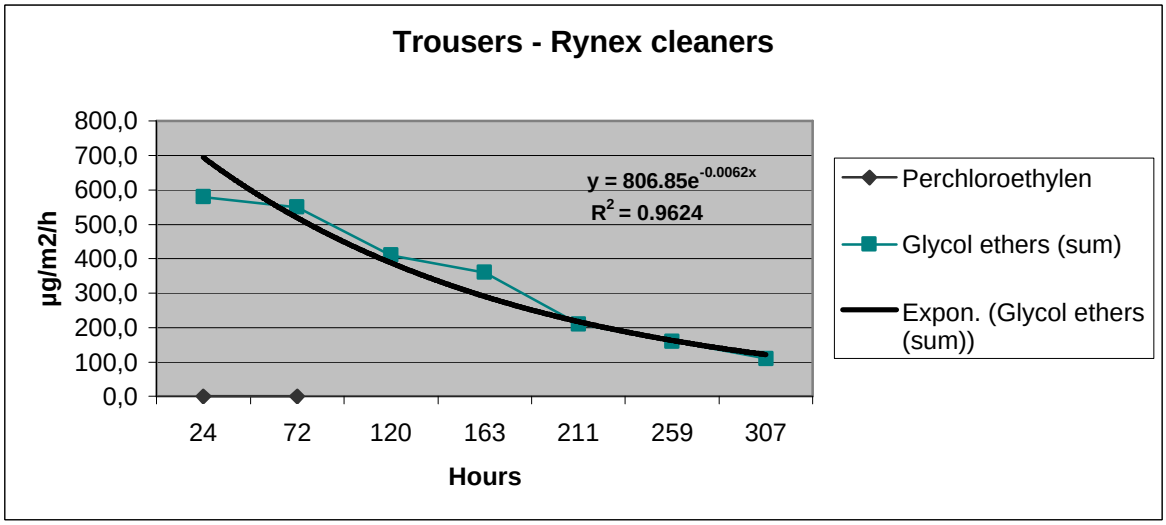
Sample identification	**Trousers no 6, Rynex**	Chamber conditions		
		temperature:	23	°C
		Air change	0,5	per hour
Chamber no:	13	Rel. Humidity	50	%
		Chamber volume	0.119	m³
		weight of sample:	0.485	kg
		Area of sample	1.34	m²

Weight specific emission rate µg/kg/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Perchloroethylen	**2,0**	**<2**					
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**<2**						
Dipropylene glycol butyl ether (DPMB)	**<2**						
2-Ethylhexanol	**<2**						
Glycol ethers (sum)	**1600**	**1500**	**1100**	**990**	**590**	**430**	**310**

Area specific emission rate µg/m²/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Hours	**24**	**72**	**120**	**163**	**211**	**259**	**307**
Perchloroethylen	**0.7**	**<1**					
Propylene glycol butyl ether	**<1**						
Hydrocarbons (as Decan)	**<1**						
Dipropylene glycol butyl ether (DPMB)	**<1**						
2-Ethylhexanol	**<1**						
Glycol ethers (sum)	**580**	**550**	**410**	**360**	**210**	**160**	**110**



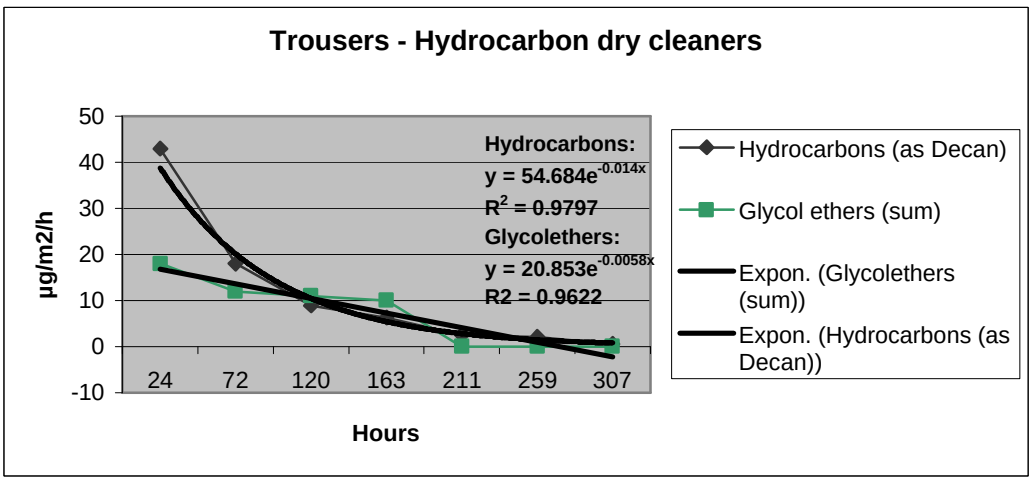
		Chamber conditions		
Sample identification	**Trousers no 4, Hydrocarbon**	temperature:	23	°C
		Air change	0.5	per hour
Chamber no:	15	Rel. Humidity	50	%
		Chamber volume	0.119	m³
		weight of sample:	0.502	kg
		Area of sample	1.34	m²

Weight specific emission rate µg/kg/h

Component	1	3	5	7	9	11	13
Perchloroethylen	**<2**						
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**110**	**47**	**24**	**17**	**6.8**	**5.6**	**1.7**
Dipropylene glycol butyl ether (DPMB)	**30**	**26**	**25**	**22**	**12**	**11**	**7,0**
2-Ethylhexanol	**8.7**	**7.5**	**3.6**	**3.2**	**1.2**	**0.6**	**0.45**
Glycol ethers (sum)	**49**	**33**	**29**	**28**	**15**	**13**	**8.7**

Area specific emission rate µg/m²/h

Component Hours	1 24	3 72	5 120	7 163	9 211	11 259	13 307
Perchloroethylen	**<2**						
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**43**	**18**	**8,9**	**6,3**	**2,5**	**2,1**	**0,6**
Dipropylene glycol butyl ether (DPMB)	**11**	**9,7**	**9,3**	**8,2**	**4,5**	**4,1**	**2,6**
2-Ethylhexanol	**3.3**	**2.8**	**1.3**	**1.2**	**0.4**	**0.2**	**0.2**
Glycol ethers (sum)	**18**	**12**	**11**	**10**	**5.6**	**4.9**	**3.3**



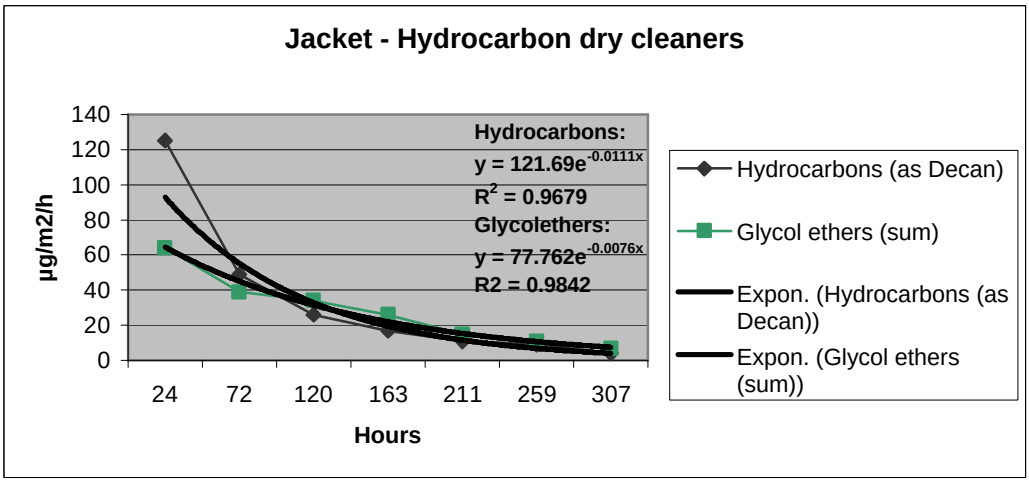
Sample identification	**Jacket no 5, Hydrocarbon**	Chamber conditions			
		temperature:	23	°C	
		Air change	0,5	per hour	
Chamber no:	11	Rel. Humidity	50	%	
		Chamber volume	0,238	m³	
		weight of sample:	0,704	kg	
		Area of sample	1,26	m²	

Weight specific emission rate µg/kg/h

Component	1	3	5	7	9	11	13
Perchloroethylene	**<2**						
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**220**	**88**	**46**	**30**	**19**	**16**	**7,2**
Dipropylene glycol butyl ether (DPMB)	**91**	**65**	**58**	**44**	**26**	**19**	**12**
2-Ethylhexanol	**12**	**6,2**	**3,5**	**2,3**	**1,1**	**1,0**	
Glycol ethers (sum)	**110**	**70**	**61**	**47**	**27**	**20**	**12**

Area specific emission rate µg/m²/h

Component	1	3	5	7	9	11	13
Hours	24	72	120	163	211	259	307
Perchloroethylene	**<1**						
Propylene glycol butyl ether	**<1**						
Hydrocarbons (as Decan)	**125**	**49**	**26**	**17**	**11**	**9,1**	**4,0**
Dipropylene glycol butyl ether (DPMB)	**51**	**36**	**32**	**24**	**15**	**11**	**6,7**
2-Ethylhexanol	**6,9**	**3,5**	**2,0**	**1,3**	**0,6**	**0,6**	
Glycol ethers (sum)	**64**	**39**	**34**	**26**	**15**	**11**	**6,9**



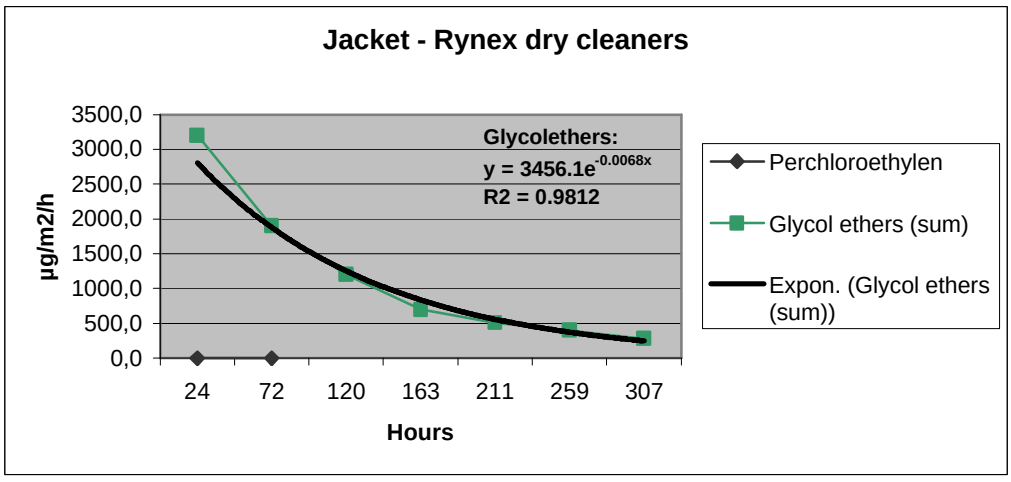
Sample identification	**Jacket no 3, Rynex**		Chamber conditions		
			temperature:	23	°C
			Air change	0,5	per hour
Chamber no:	8		Rel. Humidity	50	%
			Chamber volume	0,238	m³
			weight of sample:	0,73	kg
			Area of sample	1,26	m²

Weight specific emission rate µg/kg/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Perchloroethylen	**2,5**	**<2**					
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**<2**						
Dipropylene glycol butyl ether (DPMB)	**<2**						
2-Ethylhexanol	**<2**						
Glycol ethers (sum)	**5500**	**3300**	**2000**	**1200**	**890**	**690**	**480**

Area specific emission rate µg/m²/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Hours	**24**	**72**	**120**	**163**	**211**	**259**	**307**
Perchloroethylen	**1.4**	**<1**					
Propylene glycol butyl ether	**<1**						
Hydrocarbons (as Decan)	**<1**						
Dipropylene glycol butyl ether (DPMB)	**<1**						
2-Ethylhexanol	**<1**						
Glycol ethers (sum)	**3200**	**1900**	**1200**	**700**	**510**	**400**	**280**



Sample identification	**Dress no 1, Hydrocarbon**	Chamber conditions		
		temperature:	23	°C
		Air change	0.5	per hour
Chamber no:	2	Rel. Humidity	50	%
		Chamber volume	0.238	m^3
		weight of sample:	0.21	kg
		Area of sample	1.32	m^2

Weight specific emission rate µg/kg/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Perchloroethylene	**<2**						
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**<2**						
Dipropylene glycol butyl ether (DPMB)	**<2**						
2-Ethylhexanol	**<2**						
Glycol ethers (sum)	**<2**						

Area specific emission rate µg/m²/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Hours	**24**	**72**	**120**	**163**	**211**	**259**	**307**
Perchloroethylene	**<1**						
Propylene glycol butyl ether	**<1**						
Hydrocarbons (as Decan)	**<1**						
Dipropylene glycol butyl ether (DPMB)	**<1**						
2-Ethylhexanol	**<1**						
Glycol ethers (sum)	**<1**						

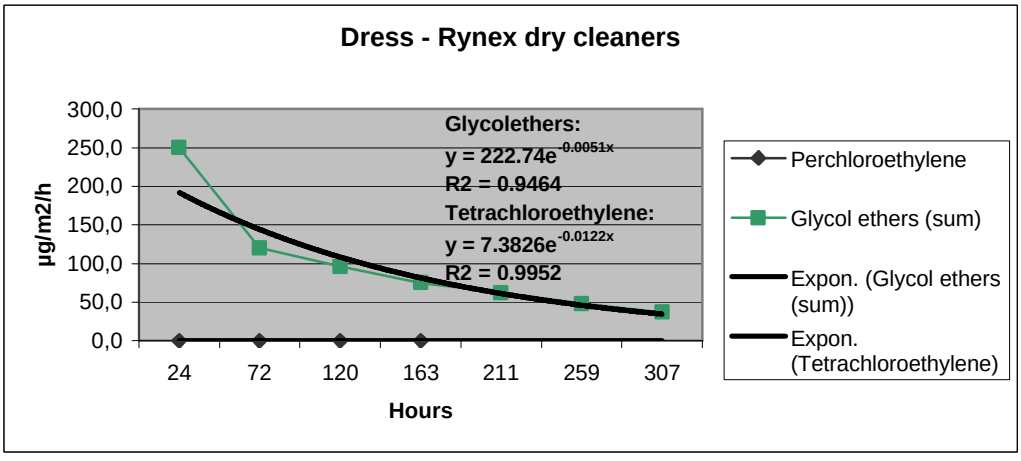
Sample identification	**Dress no 2, Rynex**		Chamber conditions		
			temperature:	23	°C
			Air change	0.5	per hour
Chamber no:	5		Rel. Humidity	50	%
			Chamber volume	0.238	m³
			weight of sample:	0.238	kg
			Area of sample	1.32	m²

Weight specific emissionrate µg/kg/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Perchloroethylene	**32,0**	**16,0**	**9,2**	**5,8**			
Propylene glycol butyl ether	**<2**						
Hydrocarbons (as Decan)	**<2**						
Dipropylene glycol butyl ether (DPMB)	**<2**						
2-Ethylhexanol	**<2**						
Glycol ethers (sum)	**1400**	**690**	**530**	**420**	**340**	**270**	**210**

Area specific emssion rate µg/m²/h

Component	**1**	**3**	**5**	**7**	**9**	**11**	**13**
Hours	**24**	**72**	**120**	**163**	**211**	**259**	**307**
Perchloroethylene	**5.8**	**2.9**	**1.7**	**1.0**			
Propylene glycol butyl ether							
Hydrocarbons (as Decan)	**<1**						
Dipropylene glycol butyl ether (DPMB)	**<1**						
2-Ethylhexanol	**<1**						
Glycol ethers (sum)	**250**	**120**	**96**	**75**	**62**	**48**	**37**



Climate chamber test

Climate chamber test (MK-method 9810G)

Principle: The tests are performed in a 120 liters climate chamber of polished stainless steel. The chambers are equipped with purified atmospheric air from a central supply system. Temperature, air humidity, and added air amount are monitored and registered continuously by EDP.

Temperature:	21 ± 1°C
Air humidity:	50 ± 5%RF
Air exchange rate:	0.5 times per hour

References: ISO 13419-1
Prøvningsstandard for Dansk Indeklimamærkning

Volatile organic solvents (VOC) in air (MK-2404)

Principle: Volatile organic components are collected on carbon tubes, desorbed with dimethylformamide, and analysed by gas chromatography with flame ionisation detector (GC/FID).

References: AMI L1 (mod.)
ISO/FDIS 16200-1
MDHS 1-54
NIOSH 1403
VDI 3482

Product samples

Cleaning fluids, alkylamines etc.

Principle: Part samples are shaken in dichloromethane. Analysis is carried out at GC/MS without further dilution. References of the following compounds: n-octane, n-triacontane, 2-propylenglycone-t-butylether, dipropylenglycolbutylether, dipropylenglycolmonomethylether, and tetrachloroethylene have been taken.

Alkylphenolethoxylates

Principle: The textiles are extracted with methanol/ammonium chloride solution. The extracts are analysed for content of nonyl- and octylphenolpolyethoxylates at LC/MS. Double determination and standard addition are carried out on a number of samples in each sample series.

Cleaning fluids and subsidiary chemicals are analysed after dilution according to the same method.