DANISH MINISTRY
OF THE ENVIRONMENT
Environmental
Protection Agency

Survey and Health Assessment of Products for Interior Car Care

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Survey of Chemical Substances in Consumer Products, No. 105 2010

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Contents

Preface

The project ”Survey and Health Assessment of Products for Interior Car Care” was carried out from April 2007 till November 2007.

This report describes the project results, comprising a survey of products as well as chemical analyses and a health assessment on a number of selected products.

Initially, it was examined which products exist on the Danish market within the category products for interior car care.

A screening phase followed and in a number of products quantitative analyses of a number of selected, problematic substances were carried out.

Finally, a health assessment was performed on a number of problematic substances.

The project was carried out by Danish Technological Institute with Master of arch. (cand.arc.) Kathe Tønning as project manager and head of laboratory Eva Jacobsen, laboratory technician Eva Pedersen and head of section Paul Lyck Hansen as project co-workers. The health related evaluation was carried out by BEng. (cand. polyt.) Pia Brunn Poulsen from FORCE Technology.

The project was followed by a reference group consisting of:

Sidsel Dyekjær	The Danish Environmental Protection Agency (Chairman of the reference group)
Frank Jensen	The Danish Environmental Protection Agency
Shima Dobel	The Danish Environmental Protection Agency
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Kathe Tønning	Danish Technological Institute

The project was financed by the Danish Environmental Protection Agency.

Summary and conclusions

The number of cars on the roads in Denmark is increasing steadily and more and more Danes daily spend some or more time in their cars commuting between home and work. Therefore, exposure to chemical substances through the indoor car climate has become an important issue.

According to Statistics Denmark, app. 2 million passenger cars were registered as at 1 January 2007 in Denmark. Of that amount, app. 1.970.000 cars were used for private driving. In addition, 459.000 vans and 35.000 trucks were registered. It must be expected that interior car care products - to some extent – are used for these vehicles.

This project solely deals with products for interior maintenance and car care. Products for exterior car care were treated in a previous project.

Products for interior car care can be organized in the following categories:

- Cleaning agents, including fabric cleaner, vinyl cleaner and glass cleaners.
- Protectants including vinyl dressing, vinyl make-up (for dashboards, door upholstery, ceiling upholstery etc.), leather care and fabric waterproofing.
- Odour removers and air fresheners.
- Anti-mist products for windows.

The project consisted of the following sub-elements: a survey and then an initial screening of which volatile and semi-volatile organic substances the products contain. With a starting point in the screening results products were subsequently selected for quantitative analyses. Likewise, 4 products were selected for emission tests on the basis of the screening investigation.

Survey

The survey comprised the following activities:

- Contact to the retail trade – a total of 21 shops were visited, including 2 car dealers, 4 car accessories dealers, 5 service stations, 5 DIY markets and 5 supermarkets.
- Internet searching – a large number of homepages (100-200 pages) with internet shops were visited and to a high degree it turned out that the products sold in internet shops are also sold in physical shops.
- Contacts to professional car care centres – a total of 4 professional car care centres were contacted. The car care centres informed that mainly soapy water is used to clean seats, door upholstery, dashboards etc.
- Contact to manufacturers/importers. Contacting importers of the products forming part of the survey resulted in information about substances in the products, whereas information about the amount of products sold in Denmark only was received from 9 out of the 6 importers who were contacted.

Consumption of products for interior car care

It has not been possible to obtain information from all contacted importers about the extent of sales in the Danish market and therefore it has not been possible to outline the amount of products sold for interior car care.

Selection of products for further investigation

The survey resulted in the registration (purchase) of 41 products and 29 products were selected for chemical screening analyses, see Table 0.1.

Table 0.1 Registered (purchased) and selected products

Product type	Number of registered products	Number of selected products for screening analyses
Vinyl make-up products	9	5
Glass cleaner	5	3
Products for fabric waterproofing	3	3
Fabric cleaners	9	4
Odour removers	2	2
Vinyl cleaners	3	2
Leather cleaners	2	2
Cleaning tissues	4	2
Anti-mist products	2	1
Detergents	1	1
Synthetic materials sealant	1	1

Chemical analyses

The declared information on the packaging and safety data sheets of the purchased products was analysed and it turned out that most likely the most critical substances were volatile organic compounds. Therefore, focus was on that group of substances, when the chemical screening and the following quantitative measurements were carried out. For that purpose, gas chromatography combined with mass spectrometry (GC/MS) as analysis principle was applied.

Two different screening investigations were carried out by means of GC/MS. One method investigated the semi-volatile compounds in the products and a semi-quantitative determination of the content was carried out. According to the survey, several of the products contained propellants and very volatile solvents. Therefore, a qualitative analysis of these compounds was carried out by analyzing headspace by means of SPME-GC/MS.

In connection with the initial screening, many of the declared substances of the products were found as well as a number of others, e.g. solvents, propellants, perfume and preservatives. In the following, the most substantial results of the initial screening of each product type are listed (number of investigated products stated in parenthesis):

- Vinyl make-up (5): In several of the products a high content of different hydrocarbons was found and one product contains terpenes.
- Glass cleaner (3): They are dominated by different types of alcohols and glycol. One product contained alkyl benzenes and aliphatic hydrocarbons.
- Fabric waterproofing (3): One product had a rather high content of different aliphatic hydrocarbons and limonene.
- Fabric cleaner (4): The products are dominated by glycols and several products contain limonene.
- Odour remover (2): The products consist of alcohols, glycols and terpenes.

- Vinyl cleaner (2): In one product a content of glycol ethers was demonstrated. The other product contained isopropyl alcohol and terpenes.
- Leather cleaner (2): In one product a number of aliphatic hydrocarbons and BHT were determined. The other product contained limonene and phthalate.
- Cleaning tissues (2): One product contained parabens and the other benzyl chloride.
- Anti-mist products (1): The product contains glycols and limonene.
- Detergent (1): Terpenes were demonstrated.
- Synthetic materials sealant (1): The product has a high content of different aliphatic hydrocarbons.

The results of the initial screening investigations were used to carry out a screening of possible health hazardous substances. In consultation with the Danish Environmental Protection Agency (the Danish EPA), 15 products were selected for quantitative determination of selected compounds. The tables below show selected results of the quantitative analyses.

Table 0.2 Selected results of quantitative analyses

Substance	CAS no.	Product no. and product type, content in mg/g							
		Vinyl make-up		Glass cleaners		Fabric waterproofing		Fabric cleanser	
		1	2	25	23	24	37	5	7
Aliphatic hydrocarbons		250	219				130	350	
Xylenes	95-47-6, 108-38-3, 106-42-3						24		
Bis-(2-ethylhexyl)-phthalate	117-81-7			0.25					
1-methoxy-2-propanol	107-98-2				50	10			
2-butoxy-ethanol	111-76-2					47			
1-butoxy-2-propanol	5131-66-8					21			
Butyl acetate	123-86-4							55	
Ethyl acetate	141-78-6							3.8	
Limonene	5989-27-5							2.7	0.1

Table 0.3 Selected results of quantitative analyses, continued

Substance	CAS no.	Product no. and product type, content in mg/g						
		Odour removers	Vinyl cleaners	Leather cleaners	Cleaning tissues	Anti-mist products	Detergents	Synthetic materials sealant
		8	10	13	40	33	34	38
Aliphatic hydrocarbons				33				120
Xylenes	95-47-6, 108-38-3, 106-42-3						0.012	
Limonene	5989-27-5		0.2			0.08		
Benzyl chloride	100-44-7	0.37			0.077			
Butylhydroxy-toluene (BHT)	128-37-0			1.0				

With a starting point in the results of the initial screenings and the danger classification of the compounds, 4 products were selected for evaporation

tests. The 4 products for evaporation tests were selected to represent different product types (vinyl make-up, fabric waterproofing, vinyl cleaner and glass cleaner). The following list shows the most substantial substances that were demonstrated:

- Vinyl make-up (product no. 1): Aliphatic hydrocarbons and terpenes
- Fabric waterproofing (product no. 5): Aliphatic hydrocarbons, acetates (i.a. ethyl and butyl acetate) and terpenes (i.a. limonene)
- Vinyl cleaner (product no. 10): Butane, 2-propanol and terpenes (i.a. limonene)
- Glass cleaner (product no. 24): Glycol ethers (i.a. 2-butoxyethanol and 1-butoxy-2-propanol).

Nano products

Four of the selected spray products are marketed as being based on nano technology. The concentration and particle size distribution of airborne particles (aerosols), created when the product is used, were measured in the four products. In connection with three of the products (no. 23, 24 and 41) the measured aerosol concentrations were low compared to other propellant based spray products for fabric waterproofing, and therefore special risks connected with aerosols from these products are not expected. In one product (no. 22), nano aerosols were measured (medium size 36 nm) at a level that exceeded the level of normal indoor air 100 times. It is well-known that inhaling ultra fine aerosols can have negative health effects[1], but it is not possible to comment on the health effects of the product in question as it had not been selected for closer health assessment as other products contained compounds that caused greater anxiety (according to the safety data sheet the product contains min. 60% water). In addition, it would not be possible to carry out a health assessment of the consequence of the product compounds appearing in nano form as currently very little knowledge is available about the effect of specific substances when they appear in nano form (see chapter 7).

Health and risk assessment of products for interior car care

In the light of the results of the quantitative analyses (15 products selected for quantitative analysis and 4 products selected for evaporation tests), a health assessment was carried out on a number of substances and a risk assessment was carried out of the health-related most problematic compounds in relation to inhalation and skin contact.

The analyses of the 4 products in the evaporation tests showed that a number of chemical substances evaporate from the 4 analysed products. Chemical substances with a relevant classification concerning health (i.e. classification that deals with health risks or irritation in connection with inhalation and skin contact) and that simultaneously evaporate with the highest concentrations have been investigated closer in the exposure calculations. The substances were:

- Hydrocarbons/petroleum distillates
- Xylenes
- 1-methoxy-2-propanol
- 2-butoxy ethanol
- 1-butoxy-2-propanol
- Butyl acetate
- Benzyl chloride.

[1] Refer to e.g. ISO/TC 146/SC 2 N 399

Benzyl chloride only appears in very small concentrations in two products (0.037% and 0.0077%), but was also selected as the substance is classified as carcinogenic.

A number of the above substances were previously assessed in relation to their health properties in analysis projects carried out by the Danish Environmental Protection Agency (DEPA). Therefore, the substances will not be assessed again in this report, but the NOEL values (No Observed Effect Level) or TDI values (tolerable daily intake) from the previous projects will be used in the risk assessment of the products for interior car care.

Therefore, this project has carried out a health assessment on five substances (substance groups): hydrocarbons, butane, ethyl acetate, 1-methoxy-2-propanol and benzyl chloride. In addition, a risk assessment was carried out of all the above-mentioned substances in relation to health effects in connection with inhalation and skin contact.

Conclusion

The investigation shows that the potentially most health hazardous compounds in the investigated products for interior car care are hydrocarbons/petroleum distillates, limonene, ethyl acetate and butyl acetate. That assessment is based on the effects of the compounds compared with the typical concentration in the investigated products. Table 0.4 shows in which product types the mentioned compounds appear.

Table 0.4 Outline of which products the selected compounds appear in.

Compound	Product type the compound appears in (number is stated in parenthesis)
Hydrocarbons/petroleum distillates	Vinyl make-up (4) Fabric waterproofing (1) Leather cleaner (1) Synthetic materials sealant (1) Glass cleaner (1)
Limonene	Fabric cleaners (3) Fabric waterproofing (1) Vinyl cleaner (1) Anti-mist product (1) Leather cleaner (1) Odour remover (1) Vinyl make-up (1) Glass cleaner (1)
Ethyl acetate	Fabric waterproofing (1)
Butyl acetate	Fabric waterproofing (2)
Benzyl chloride	Cleaning tissue (1) Odour remover (1)

Benzyl chloride is classified as carcinogenic and was identified in two products, but the concentration was so small that it does not form a health risk if hands are washed after application or if the car care products are used max. once a week. The risk assessment was carried out in the light of the critical effect of benzyl chloride which is not cancer but acute and chronic infection in the gastritis.

The exposure calculations for inhalation of the chemical substances that evaporate from the four analysed products show that irrespective of the car being used immediately after application of the car care products for a short drive (15 minutes) or a long drive (5 hours), then there is no health risk when using the analysed products for interior car care unless the products are used every day for a longer period of time. In that case, exposure may result in liver

and blood changes (e.g. cell enlargement). However, the changes seen in the liver of experimental animals are reversible, meaning that the changes can return to normal. As long as the product only is used once a week – or a couple of times a year, which probably is the most realistic – then there is no health risk related to using the products that have been closer investigated in this project. The products must be used in double amounts and more frequent than every second week before a long term risk is possible.

The exposure calculations for skin contact show that even though the products for interior car care are applied without using gloves (but with an application cloth), then there will be no health risk connected with using the analysed product as long as the user washes hands after use or only uses interior car care products every fortnight. That also goes for cleaning tissues when there is direct contact with the compounds.

The inhaled amount and the amount absorbed via skin contact have to be added up for each compound in order to obtain total exposure. However, exposure during skin contact is much less than during inhalation of the same substances and therefore the conclusion remains the same: As long as the analysed products for interior car care during normal use only are used max. twice a week or less, then there is no health risk when using the products investigated in this project.

No substances evaporate in concentrations that exceed the individual threshold limiting values (TLV) of the compounds. Calculations show that in worst-case situations more than one full can has to be used (in this case vinyl make-up) at once in order to exceed the limit value of the compounds. Even though no limit values are exceeded, some of the compounds may be liberated in concentrations where irritating effects can appear and therefore it is recommended to apply car care products with the car door open and to ensure proper ventilation in the car if going for a drive in the car immediately after application. It is also recommended to use gloves as the compounds may degrease the skin and result in dry skin.

In general, the following is recommended when using interior car care products:

- Ensure proper ventilation during application of products (open the car doors).
- Use as small an amount as possible.
- When using spray products – spray away from the inhalation area and avoid inhalation of spray mist.
- Wash hands after using the products or use gloves.

1 Introduction

1.1 Background

The Danish Environmental Protection Agency has previously focused on products for exterior car care. This project focuses on products for interior car care.

Car detailing is not only carried out to prolong the durability of the individual material components of the car, but also to make the car look clean and ”new”. A wide range of car care products are available for that purpose and they can clean and maintain the surfaces in the cabin or create a pleasant smell.

Interior car care will usually be carried out by the car owner but can also be performed by e.g. car care centres, typically before resale.

More and more Danes daily spend shorter or longer periods of time in their cars commuting between home and work. Therefore, exposure to chemical substances through the indoor car climate is expected to be of substantial importance.

Car care products are products that either have purifying properties, protecting properties, cosmetic properties or a combination of all these properties.

Many car care products contain organic solvents, preservatives and fragrances that from other types of products are known as potential health hazardous substances.

Many cleaning agents are based on different mixtures of alcohol-based solvents and tensides, perhaps with ammonia, preservatives and fragrances. Solvents can be hazardous to health and as the solvent concentrations in the products are rather high they can be inhaled during application of the car care product or during subsequent use of the vehicle as the substances are easily evaporative. When emitted to the environment, tensides can be poisonous for aquatic organisms but they are not very problematic in relation to health.

Preservatives in cleaning products can be based on isothiazolinon compounds that are potential allergy-causing agents. In addition, allergy-causing fragrances might have been added to the products.

Protectants are supposed to give the material in the cabin a well-kept surface, e.g. shiny, ductile or dirt repellent. The product range i.a. comprises agents to care for plastics (so-called vinyl make-up), leather care and waterproofing spray for fabric surfaces.

To remove bad smell in the cabin, e.g. from cigarettes, agents can be used to freshen the air. Contrary to the traditional air fresheners the unpleasant smell is not drowned in perfume but it is removed by means of constituents that fixate bad odour.

Recently, new products have entered the market and they are based on nano technology. The products can e.g. be aimed at fabric waterproofing or windows. The agents are applied in a thin layer so a dirt-repellent surface or a surface that counteracts the creation of mist is created.

1.2 Objective

The objective of this project has been to outline and assess selected compounds in products for interior car care and to assess possible health related effects for consumers.

1.3 Structure of the report

The project consisted of the following sub-elements: a survey and then an initial screening of which volatile and semi-volatile organic substances the products contain. With a starting point in the screening results, products were subsequently selected for quantitative analyses. Likewise, 4 products were selected for emission tests on the basis of the screening investigation. Then a health assessment of selected compounds was carried out.

Chapter 2 shows the results of the survey, including an outline of the 41 purchased products and information about compounds from the packaging and safety data sheet of the products, respectively. In addition, the criteria for the selection of 26 products for the screening analysis are shown.

In chapter 3, relevant legislation for the product group in question is discussed.

Chapter 4 shows relevant exposure scenarios for the purchased car care products. The exposure scenarios have formed the basis of the preparation of the emission analyses.

Chapter 5 demonstrates the results of a screening investigation for content of volatile and semi-volatile organic substances in the 26 selected products.

In the light of the results of the screening analysis in chapter 5, the quantitative analyses carried out on 15 selected products are described in chapter 6. In addition, the results of the emission tests on four selected products are shown.

Chapter 7 shows the results of the investigation for nano particles in four products that are marketed as being based on nano technology.

A health assessment of the selected compounds in the products analysed in chapter 6 appears in chapter 8.

Chapter 9 shows the exposure calculations of the four products, on which emission measurements were carried out (as described in chapter 6).

2 Survey

2.1 Objective

The objective of the survey was to:

- Identify the most frequently used products for interior car care
- Procure products for chemical analyses
- Try to procure information about the materials (including compounds) to the extent information was available.

2.2 Description of the product group

Products for interior car care can roughly be divided into the following categories:

- Cleaners, including fabric cleaner, vinyl cleaner and glass cleaner (inside of windows).
- Protectants including vinyl dressing, vinyl make-up (for dashboards, door upholstery, ceiling upholstery etc.) leather care and fabric waterproofing.
- Odour removers and air fresheners.
- Anti-mist products for windows.

Protectants for rubber door seals etc. do not form part of the project.

2.3 Survey of supply of products for interior car care

2.3.1 Procedure

This project focuses on products for interior car care and the following activities form part of the survey of the supply of products in Denmark within this product category:

- Contact to the retail trade
- Internet searching
- Contact to the Federation of Danish Motorists (FDM)
- Contact to professional car care centres
- Contact to manufacturers/importers.

Contacting the retail trade (physical shops and internet shops) had the purpose of finding information about which products (within the field of interior car care products) are sold in Denmark. The contact also had the objective of trying to uncover which products Danish car owners mainly purchase.

In addition to ”visiting” the internet shops when searching for available products on the market and purchasing products, the search on the internet had the purpose of obtaining information about the individual products in the form of compound knowledge and instructions for use.

The purpose of contacting the Danish consumer organisation FDM was to try to procure information about which products car owners use for interior car care.

The purpose of communicating with the professional car care centres was to find out which products they use.

Manufacturers/importers were contacted to procure information about product compounds and to obtain information about the amounts sold in the Danish market.

2.3.2 Shop visits

A total of 21 shops were visited, including:

- 2 car dealers
- 4 car accessories dealers
- 5 service stations
- 5 DIY shops
- 5 supermarkets.

In connection with shop visits, the staff was asked which products groups are best selling and which products within the different product groups are best selling, if the customers ask for instructions on how to use the products and which answers the staff, if possible, gives.

2.3.3 Internet searching

Searching took place on Google.dk with different words and word combinations (e.g. interior car care, vinyl cleaner, fabric cleaner, fabric waterproofing and odour removers).

In addition, searching took place by using named car care products.

When going through the homepages of the internet shops it often became apparent that the products also can be purchased in physical shops. When the products could be purchased in physical shops that procedure was preferred because then it was possible to speak with the staff.

2.4 Survey results

2.4.1 Quantification of products

Through Statistics Denmark it has not been possible to establish the quantity of the products used for interior car care. "Skat" (the Danish Revenue Office) has informed that there is no KN code[2] that solely deals with these products.

According to Statistics Denmark, a total of app. 2 million (2.020.013) passenger cars were registered as at 1 January 2007 in Denmark. Of that amount, app. 1.970.000 (1.969.827) cars were used for private driving. In addition, 459.000 vans and 35.000 trucks were registered. It must be expected that products for interior car care - to some extent – are used for these vehicles.

[2] A KN code is an 8 digit product code number (KN ~ combined nomenclature).

According to the staff in the visited shops, all products registered in table 3.1”sell well”.

It has not been possible to obtain information from all of the contacted importers about how much they sell on the Danish market, and therefore it has not been possible to outline the amount of products sold. However, as mentioned above, app. 2 million cars are used for private driving. It is unknown to which extent interior car care products are purchased for these cars.

Two importers have estimated their share of sold products out of the total sold amount of interior car care products in the Danish market. By using that information a total amount of 100.000-150.000 litres/year appears. It should be pointed out that the estimate is encumbered with a presumably very large – but otherwise unknown uncertainty.

2.4.2 Car care centres

Four professional car care centres were approached.

The car care centres informed that mainly soapy wash water is used to clean seats, door upholstery, dashboards etc. In addition, "cleaning foam" is if necessary used for tough stains and Rodalon is used if there is mould in the car. However, one of the contacted car care centres uses a certain product series for vinyl cleaner, seat cleaner etc.

As something relatively new, one of the contacted car care centres offers nano product treatment. That is mainly the case in connection with exterior car care (wax, car windows and rims) but also in connection with fabric waterproofing.

2.4.3 Consumer organisations

The Danish consumer organization FDM was contacted and they informed that they receive many enquiries about car care products (for interior as well as exterior car care). Almost all enquiries are about which products have the intended effect and which do not, and if ”you get value for your money”. FDM has carried out a number of tests on car care products – all with regard to investigating the effect of the products. The most recent test (of wax protecting agents) was carried out 4-5 years ago.

2.4.4 Shop visits

As mentioned earlier, the staff was in connection with shop visits asked which product groups are best selling and which products within the different product groups are best selling, if the customers ask for instructions on how to use the products and which answers the staff gives.

The questions have mainly been answered by the staff in the car accessory shops.

The supply of products for interior car care varied a lot in the shops that were visited. Some car accessory shops had a very large selection with many different products within each product group while the selection at other shops was more limited. The supply of products for exterior car care is generally larger than the supply of products for interior car care. The

products described as best selling by the staff in the visited shops are for exterior car care. Car shampoo and rim cleaner are involved.

The answers to the question of which product groups for interior car care are sold the most in the visited shops were not unambiguous but vinyl cleaner, vinyl make-up and fabric cleaner have been mentioned. In addition, window cleaner has been mentioned, but it was the impression of the staff that the product group is purchased for exterior use (to remove insects etc.). In general, the answer to the question of which products within each product group for interior car care sell the best was that quite an amount is sold of everything on the shelves. However, detailed questions have revealed that some products are sold to a greater extent than others and mainly those products were purchased for this project.

In some shops, the staff said that they believe that most products are sold during spring.

In addition, the staff has informed that they very rarely are asked questions about choice and use of the products, but when small talking during purchase it is regularly mentioned that now spring has arrived it is “the car’s turn next”. In a few of the visited shops the staff has also mentioned that it is their impression that possible directions for use on the packaging only receives a quick glance, e.g. information on how much fabric waterproofing should be used, but the entire content is simply used at once.

The staff (in addition to the staff at the car accessory shops) at a few service stations answered the question of how frequently it is assumed that car care products for interior maintenance are used. The replies were that the frequency varies a lot. Some wash the car, vacuum clean and e.g. use vinyl make-up once a week while others hardly ever used these protectants – perhaps only once a year, typically during spring. Furthermore, the staff informed that mainly men purchase the products.

2.4.5 Internet shops

The main criterion for selection of products for this project was in general that products sold to a certain extent should be in question. When visiting physical shops, the staff was, as mentioned above, asked which products sell the best.

That criterion has been a bit more difficult to use in connection with internet trade; however, several homepages for car care products have a ”top 10 list” or the like of the best selling products.

As mentioned previously, going through the homepages of the internet shops revealed that products that also are sold in physical shops often are in question. The products were purchased in physical shops when possible, because then it was possible to talk with the staff.

2.4.6 Products

All products were purchased in nationwide chain shops or on the internet.

The survey resulted in the purchase of 41 products for closer assessment of which 6 were purchased on the internet.

As mentioned earlier, the 41 products were selected on the basis of information from the staff in the visited shops about which products are sold the most within the individual product groups. In connection with purchase on the internet, the products were selected according to e.g. "top 10 lists" (to the extent products for interior care were on those lists) or by approaching the internet shops with inquiries about "popular products".

2.4.6.1 Product outline

In the below product outline, the purchased products are organized in groups (number of purchased products within the product category is stated in brackets):

- Vinyl make-up (9)
- Glass cleaners (5)
- Fabric waterproofing (3)
- Fabric cleaners (9)
- Odour removers (2)
- Vinyl cleaners (3)
- Leather cleaners (2)
- Cleaning tissues (4)
- Anti-mist products (2)
- Detergents (1)
- Synthetic materials sealant (1).

Table 2.1 shows the declared substances in the purchased products. The information was partly obtained from the declarations on each product and partly from the safety data sheets (SDS). Direct copying from the product labels and the safety data sheet, respectively, is in question. In addition, the application method and the danger symbols and risk phrases appearing on the products and/or safety data sheet are stated. It has been stated, for which products a SDS has not been received. The column to the far right of the table shows which products have been selected for qualitative screening of volatile organic compounds.

Table 2.1 Outline of purchased car care products. The information originates from packaging and safety data sheets, respectively.

No.	Application method	Substance name	CAS no.	Substance category	Danger symbols and risk phrases	Selected for analysis
Vinyl make-up						
1	Spray w. propellant	Distillates (crude oil), hydrogen treated light	64742-47-8	Solvent	Dangerous for the environment Irritant Extremely flammable R12, R51/53, R66	Yes
		Naphtha (crude oil), desulphurized light, dearomatized (benzene content: < 0.1%)	92045-53-9	Solvent		
		Crude oil gases, condensed, sweetened (does not contain 1.3 butadien)	68476-86-8	Solvent		
2	Spray w. propellant	Aliphatic hydrocarbon > 30%		Solvent	Irritant Extremely flammable R12, R38, R52/53, R67	Yes
		Anion tenside < 5%		Soap/ tensides/ detergent		
		Perfume		Perfume		
		Butane	106-97-8	Propellant		
		Naphtha (crude oil), hydrogen treated light	64742-49-0	Solvent		
		Isodo decane	13475-82-6	Solvent		
		Propane	74-98-6	Propellant		
		Naphtha (crude oil),	64742-49-0	Solvent		

No.	Application method	Substance name	CAS no.	Substance category	Danger symbols and risk phrases	Selected for analysis
		hydrogen treated light				
		Naphtha (crude oil), hydrogen treated heavy	64742-48-9	Solvent		
3	Spray w. propellant	Pentane	109-66-0	Solvent	Extremely flammable Dangerous for the environment R12, R51/53, R66, R67	
		Propane	74-98-6	Propellant		
		Butane	106-97-8	Propellant		
		Propan-2-ol	67-63-0	Solvent		
		Isobutane	75-28-5	Propellant		
		Naphtha (crude oil), hydrogen treated heavy	64742-48-9	Solvent		
15	Cream	No substances informed on the safety data sheet. Described as: "Aqueous emulsion of silicone – solvent free"		Fabric waterproofing/ surface treatment	None	Yes
16	Spray w. pump	Non-ionic tenside	Not stated	Soap/ tensides/ detergent	None	
20	Spray w. pump	Fat alcohol polyglycol ether (6-15 mol EO)	Not stated	Soap/ tensides/ detergent	None	
25	Spray w. propellant	Silicone	63148-62-9	Fabric waterproofing/ surface treatment	Extremely flammable R12	Yes
		Propane/ Butane	74-98-6/ 106-97-8	Propellant		
		Heptane	142-82-5	Solvent		
		Perfume – Limonene	138-86-3	Perfume		
26	Spray w. pump	Fat alcohol polyglyolether (6-15 mol EO)			Xn, Xi R22, 36/38	
29	Spray w. propellant	Aliphatic hydrocarbon > 30%		Solvent	Irritant Extremely flammable R12, R38, R52/53, R67	Yes
		Anion tenside < 5%		Soap/ tensides/ detergent		
		Perfume		Perfume		
		Butane	106-97-8	Propellant		
		Naphtha (crude oil), hydrogen treated light	64742-49-0	Solvent		
		Isodo decane	13475-82-6	Solvent		
		Propan-2-ol	67-63-0	Solvent		
		Propane	74-98-6	Propellant		
		Naphtha (crude oil), hydrogen treated heavy	64742-48-9	Solvent		
Glass cleaners						
4	Spray w. propellant	Propane-2-ol	67-63-0	Solvent	Extremely flammable R12	
		Propane	74-98-6	Propellant		
		Butane	106-97-8	Propellant		
		Isobutane	75-28-5	Propellant		
		1-methoxy-2-propanol	107-98-2	Solvent		
		Ammonia 25%	Not stated	Acid/basic regulation		
		Aliphatic hydrocarbons (5-15%)		Solvent		
		Limonene (< 5%)	138-86-3	Perfume		

No.	Application method	Substance name	CAS no.	Substance category	Danger symbols and risk phrases	Selected for analysis
23	Spray w. pump	< 5% anionic tensides		Soap/ tensides/ detergent	R10	Yes
		Odorant		Perfume		
		1-Methoxy-2-propanol	107-98-2	Solvent		
		Ethanol	64-17-5	Solvent		
24	Spray w. pump	< 5% anionic tensides		Soap/ tensides/ detergent	None	Yes
		Preservative: Benzisothiazolinone		Preservation/ antiseptic/ biocide		
		Water	7732-18-5	Solvent		
		2-Propanol	67-63-0	Solvent		
		1-Metoxy-2-propanol	107-98-2	Solvent		
		3-Butoxy-2-propanol	5131-66-8	Solvent		
31	Spray w. propellant	Isopropyl alcohol	67-63-0	Solvent	Extremely flammable R12, R34, R37	
		Ammonia	1336-21-6	Acid/basic regulation		
		Tensides	Not stated	Soap/ tensides/ detergent		
		Propane/butane	74-98-6/ 106-97-8	Propellant		
37	Cream	Tallow amine ethoxylate < 1%	61791-26-2	Soap/ tensides/ detergent	R66	Yes
		Ammonia Solution < 1%	1336-21-6	Acid/basic regulation		
		Naphtha (petroleum) hydro treated heavy 30-50% Petroleum distillate	64742-48-9	Solvent		
No.	Application method	Compound name	CAS no.	Compound category	Danger symbols and risk phrases	Selected for analysis
Fabric waterproofing						
5	Spray w. propellant	Propane/Butane: 20-40%	Not stated	Propellant	Extremely flammable Harmful by inhalation and if swallowed	Yes
		Heptane: 30-40%	142-82-5	Solvent		
		n-Butyl acetate	123-86-4	Solvent		
		Etyl acetate	141-78-6	Solvent		
12	Spray w. propellant	Low boiling hydrogenised naphtha	64742-49-0	Solvent	Extremely flammable Irritant Dangerous for the environment R11, R51/53, R67	Yes
		Butyl acetate	123-86-4	Solvent		
		Fluorcarbon resin		Fabric waterproofing/ surface treatment		

No.	Application method	Substance name	CAS no.	Substance category	Danger symbols and risk phrases	Selected for analysis
41	Spray w. pump	Aqueous fluorine polymer suspension: < 10%		Fabric waterproofing/ surface treatment		Yes
		Methanol < 5%		Solvent		
		Polysiloxane		Fabric waterproofing/ surface treatment		
Fabric cleaner						
6	Spray w. propellant	Butane, content of Butadien < 0.1%	106-97-8	Propellant	Extremely flammable R12, R53, R66	
		Isoparaffins	90622-57-4	Fabric waterproofing/ surface treatment		
		Propane	74-98-6	Propellant		
		Petroleum (redest. C9-C14 < 5% arom.)		Solvent		
7	Foam spray w. propellant	Anionic and non-ionic tensides		Soap/ tensides/ detergent	Extremely flammable R12	Yes
		Fragrance		Perfume		
		Methylthiazolinone		Preservation/ antiseptic/ biocide		
		Benzisothiazolinone		Preservation/ antiseptic/ biocide		
		Ethanol	64-17-5	Solvent		
		Propane	74-98-6	Propellant		
		Butane Content of 1.3 Butadien in applied Butane is < 0.1%	109-97-8	Propellant		
9	Spray w. propellant	> 5%-< 15% aliphatic hydrocarbons		Solvent	Extremely flammable R12	Yes
		< 5% anionic surface active substances		Soap/ tensides/ detergent		
		Methylparaben		Preservation/ antiseptic/ biocide		
		Perfume		Perfume		
		Limonene		Perfume		
		Water	7732-18-5	Solvent		
		2-(2-ethoxyethoxy)-ethanol	111-90-0	Solvent		
		Propane/butane	68475-59-2	Propellant		
11	Foam spray w. propellant	Butane	106-97-8	Propellant	Extremely flammable R12	
		Propane	74-98-6	Propellant		
		Isobutane	75-28-5	Propellant		
		Alcohol ethoxylate	68131-40-8	Solvent		
		EDTA Tetrasodium solution	64-02-8	Soap/ tensides/ detergent		
21	Foam spray w. propellant	Isopropanol	67-63-0	Solvent	Extremely flammable R12	
		Ammonia	1336-21-6	Acid/basic regulation		
		Butane	106-97-8	Propellant		
22	Foam spray w. propellant	Water	7732-18-5	Solvent	None	Yes
		2-(2-ethoxyethoxy)-ethanol	111-90-0	Solvent		

No.	Application method	Substance name	CAS no.	Substance category	Danger symbols and risk phrases	Selected for analysis
		Propane/butane	68475-59-2	Propellant		
		Aliphatic hydrocarbons		Solvent		
		Anionic surface active substances		Soap/ tensides/ detergent		
		Methyl paraben		Preservation/ antiseptic/ biocide		
		Perfume		Perfume		
		Limonene		Perfume		
28	Foam spray w. propellant	Phosphate < 5%		Soap/ tensides/ detergent	Extremely flammable R12	
		Butane/Propane < 15%	106-97-8	Propellant		
		1-methoxy-2-propanol	107-98-2	Solvent		
		Butane/Propane < 15%	74-98-6	Propellant		
30	Spray w. pump	Ethercarboxyl acid, Na-salt	33939-64-9	Soap/ tensides/ detergent	None	Yes
		Ammoniumpoly acrylate	9003-03-6	Preservation/ antiseptic/ biocide		
36	Spray w. pump	Sodium alkyl ether sulphate < 1%	13150-00-0	Soap/ tensides/ detergent	None	
Odour remover						
8	Spray w. pump	2-Propanol	Not stated	Solvent	None	Yes
		Quarternary ammonium compound	Not stated	Soap/ tensides/ detergent		
14	Spray w. pump	Amphotere tensides	Not stated	Soap/ tensides/ detergent	None	Yes
		Glycols		Solvent		
		Odorants		Perfume		
Vinyl cleaner						
10	Spray w. propellant	Propane-2-ol	67-63-0	Solvent	Extremely flammable R12, R67	Yes
		Butane	106-97-8	Propellant		
		Isobutane	75-28-5	Propellant		
		Sodium nitrite	7632-00-0			
		Lemon smell		Perfume		
19	Spray w. pump	Below 5% phosphates		Soap/ tensides/ detergent	None	
		Non-ionic tensides		Soap/ tensides/ detergent		
		Preservative		Preservation/ antiseptic/ biocide		
		Natriumlaurylether sulphate	68585-34-2	Soap/ tensides/ detergent		
		Dipropylene glycolmethyl ether		Solvent		
27	Spray w. pump	Natriumlaurylether sulphate Dipropylene glycolmethyl Ether	68585-34-2		Xi R36/38	Yes
		5-15% anionic tensides		Soap/ tensides/ detergent		
		< 5% phosphates		Soap/ tensides/ detergent		
		Edta		Soap/ tensides/		

No.	Application method	Substance name	CAS no.	Substance category	Danger symbols and risk phrases	Selected for analysis
				detergent		
Leather cleaner						
13	Foam spray w. propellant	Low boiling hydrogenated naphtha. Content of benzene under 0.1%	64742-48-9	Solvent	Extremely flammable R12	Yes
		Propane	74-98-6	Propellant		
		Butane Content of 1,3 Butadien in used Butane is < 0.1%	109-97-8	Propellant		
35	Spray w. pump	Alkyl Amido betaine 1-10%	61789-40-0	Soap/ tensides/ detergent	None	Yes
		Alkyl Polyglycoside 1-10%	110615-47-9	Soap/ tensides/ detergent		
Cleaning tissues						
17	Tissue	No safety data sheet			None	
32	Tissue	No safety data sheet			None	Yes
39	Tissue	No safety data sheet			None	
		Alcohol		Solvent		
		Isopropyl alcohol		Solvent		
		Vinegar		Acid/basic		
		Coconut Alkyl Bis (hydroxyethyl) Methyl Ethoxylated		Soap/ tensides/ detergent		
		Methylisothiazolon		Preservation/ antiseptic/ biocide		
40	Tissue	No safety data sheet			None	Yes
		Isopropyl alcohol		Solvent		
		Butoxyethanol		Solvent		
		Propylene glycol butyl ether		Solvent		
		Alkyldiphenyloxid disulfonat		Soap/ tensides/ detergent		
		Ammonium hydroxide		Soap/ tensides/ detergent		
		Methylchloroisothiazolen		Preservation/ antiseptic/ biocide		
		Methylisothiazolon		Preservation/ antiseptic/ biocide		
Anti-mist products						
18	Tissue	No safety data sheet			None	
33	Spray w. pump	Propane-2-ol	67-63-0	Solvent	Highly flammable Irritant R11, R36, R67	Yes
		Alcohol ether sulphate, sodium salt	68585-34-2	Soap/ tensides/ detergent		
		Isopropanol		Solvent		
		< 5% anionic tensides		Soap/ tensides/ detergent		
		Perfume		Perfume		
		Hexyl cinnamal		Perfume		

No.	Application method	Compound name	CAS no.	Compound category	Danger symbols and risk phrases	Selected for analysis
Detergent						
34	Foam spray w. propellant	Under 5% anionic Surface active substances and non-ionic surface active substances		Soap/ tensides/ detergent	Extremely flammable R12	Yes
		Under 5% NTA (sodium saltoaf nitrilotri acetic acid) and salt hereof		Soap/ tensides/ detergent		
		Perfume		Perfume		
		Butane (containing < 0.1% butadien (203-450-8))	106-97-8	Propellant		
		Glycol	107-21-1	Solvent		
		Trinatriumnitrilotri acetate	5064-31-3	Soap/ tensides/ detergent		
		Ethanol	64-17-5	Solvent		
		Propane	74-98-6	Propellant		
		Sodium nitrite	7632-00-0			
Synthetic materials sealant						
38	Cream	Paraffin wax dissolved in Isoparaffin	Not stated	Waterproofing / surface treatment	None	Yes
		Hydrocarbon	64742-47-8	Solvent		

It appears from Table 2.1 that the products in general contain the following substances:

- Solvents.
- Propellants (contributes to getting the product in spray form/aerosol form).
- Surface active agents (cleans).
- Perfumes (gives the product a fragrance and emits a fragrance to the car).
- Preservatives (preserving effect).
- Waterproofing agents (e.g. fluorine compounds that give the fabric a protective layer to protect against water, grease and dirt).

A number of car protectants have a cleaning effect and therefore they are comprised by the EU Detergent Regulation (see chapter 3). The survey revealed that may of the products have not been correctly declared according to the Regulation.

On the packaging, five of the purchased products are considered to be nano products. Product 22, 23, 24, 38 and 41 are in question. Four of the five products are applied by spraying and for those four products additional investigations were carried out in the form of particle size distribution measurements and particle concentration measurements (see chapter 7).

2.5 Selection criteria

As mentioned earlier, the survey of products for interior car care resulted in the purchase of 41 products.

In consultation with the Danish EPA, 26 out of the 41 products were selected for further investigation in the project.

The selection was carried out in the light of information about product contents, i.e. the substances that were declared by the manufacturer.

In the selection process, great importance was attached to the following criteria:

- Products were selected from all product categories (as far as possible two products from each category).
- The products contain solvents and/or propellants.
- The products contain perfume and/or preservatives.
- Fabric waterproofing and glass cleaners have high priority and these product types might contain polyfluorinated compounds.
- As far as possible, the products were selected to cover the different application methods (i.e. sprays, creams and tissue products were chosen).
- Products with use of nano technology.
- Safety data sheets could not be procured.
- Products from different distributors/manufacturers.

2.5.1 Selected products

In consultation with the Danish EPA, 26 products were selected for qualitative screening of compounds by GC/MS.

The following products were selected for further analysis in the form of a qualitative screening of volatile, organic compounds (the number in brackets refers to the number in Table 2.1):

- 5 vinyl make-up (1, 2, 15, 25 and 29)
- 3 glass cleaners (23, 24 and 37)
- 3 fabric waterproofing agents (5, 12 and 41)
- 4 fabric cleaners (7, 9, 22 and 30)
- 2 odour removers (8 and 14)
- 2 vinyl cleaners (10 and 27)
- 2 leather cleaners (13 and 35)
- 2 cleaning tissues (32 and 40)
- 1 anti-mist product (33)
- 1 detergent (34)
- 1 synthetic materials sealant (38).

3 Legislation

The definition of the Danish Chemical Act of chemical substances and products i.a. includes car care products. Therefore, the Chemical Act and regulations issued under the provision of the Chemical Act applies to this product group.

Danish legislation on chemicals contains a number of restrictions concerning the content of chemical substances in consumer products. The relevant Acts and Regulations concerning consumer health are mentioned in the table below.[3]

In addition, a number of car care products with a cleaning effect are marketed. Therefore, these products are also comprised by the Detergent Regulation on washing powder and detergents.

Table 3.1 List of relevant legislation

Title	Number/Date	Popular title	Relevance to car care products
Act on Chemical Substances and Products	Consolidation Act no. 1755 of 22.12.2006	Chemical Act	Outline provision for regulation of chemical substances and products in Denmark.
Executive Order on Classification, Packaging, Labelling, Sale and Storage of Chemical Substances and Products	Executive Order no. 329 of 16.5.2002	Executive order on classification	Rules concerning classification, packaging, labelling, sale and storage.
Executive Order on the use of Propellants and Solvents in Aerosol Cans	Consolidation Act no. 571 of 29.11.1984	Executive order on aerosols	Lists the substances permitted as propellants and solvents in spray products.
Executive Order on the List of Dangerous Substances	Executive Order no. 923 of 28.9.2005	List of Dangerous Substances	Used in connection with the classification of a product.
The Regulation of the European Parliament and the European Council on Washing Powder and Detergents	Regulation no. 648/2004 of 31 March 2004	Detergent Regulation	I.a. describes rules for compounds and labelling rules for washing powder and detergents.
The Directive of the European Parliament and the European Council on the Limitation of Marketing and use of PFOS	Directive 2006/122/EF of 12 December 2006		Limitation in the use of PFOS.
The Regulation of the European Parliament and the European Council on Registration, Evaluation and Approval as well as Limitations of Chemicals (REACH)	Regulation (EU) No. 1907/2006 of 18 December 2006	REACH	Registration, evaluation and approval as well as limitations on chemicals

[3] Please note that the regulations in table 3.1 were in force in 2007. The existing regulation may be found at www.retsinfo.dk or www.mst.dk

3.1 Danger labelling

The Classification Regulation (Executive Order no. 329, 2002) makes demands for classification and danger labelling of dangerous chemical substances and products. The label text on a car care product is therefore a substantial and simple way for the consumer to obtain information about the possible health risk of the product.

Before sale, all car care products have to be evaluated by the manufacturer/ importer in accordance with the rules concerning classification of chemical products in the executive order on classification. If the product has been assessed to be dangerous, then it has to be labelled in accordance with the rules of the executive order.

If the product is not classified as sensitising, but nevertheless contains such a substance in a concentration of more than 0.1%, then the label shall be labelled with the text: “Contains (name of sensitising substance). May produce an allergic reaction”.

3.2 Very toxic and toxic products

According to the Danish Chemical Act (Consolidation Act no. 1755, 2006) and the Danish Executive Order on Classification (Executive Order no. 329, 2002) no chemical substances or products that have to be labelled with the danger label "very toxic" or "toxic" may be sold in the retail trade. Please note that a product can contain rather large amounts of toxic substances without having to be labelled with the danger description “toxic”. Special rules are connected to aerosol cans concerning the content of toxic substances – please refer to the below section on substances in aerosol cans.

It is forbidden to sell chemical substances and products to private persons classified for carcinogenicity, or mutagenicity, or to sell chemical substances and products that produce or increase the incidence of non-heritable effects in progeny and/or impairment in reproductive functions or capacity and therefore have to be danger labelled as toxic. However, the products may contain compounds with the above effects if the content of the substance is below the classification limit of the danger class.

3.3 Ban on certain compounds in aerosol cans (spray cans)

There are certain rules for compounds in connection with chemical products in spray cans. In general, all very toxic or toxic compounds are forbidden in spray cans (Executive Order 1042, 1997). In addition, all compounds marked with "Ae" in the "List of Dangerous Substances" are forbidden (Executive Order 1042, 1997), (Executive Order 923, 2005).

Only 36 different substances are allowed as propellants and solvents in spray products, cf. the enclosure in (Executive Order 571, 1984). However, several chemical spray products in the market contain other propellants and solvents than the ones determined in the executive order as the Danish EPA in special cases can grant an exemption.

3.4 Detergent regulation

Car care products marketed as detergents, i.e. it is stated on the product that it has a cleaning effect, will as a starting point be comprised by Regulation no. 648, 2004 of the European Parliament and the European Council on washing powder and detergents (Detergent Regulation) with appurtenant changes in the Commission Regulation no. 907, 2006.

According to the Detergent Regulation the surface active substances forming part of the products i.a. have to fulfil a number of criteria for aerobic biodegradability.

In addition, the packaging (label) on the washing powder and detergents has to contain information about the compounds stated in the following percentage intervals < 5%, 5-15%, 15-30%, >30%. The compounds have to be stated in certain groups such as e.g. phosphates, anionic surface-active agents, cationic surface-active agents, chlorine-based bleaching agents etc.

In the same way as preservatives, perfumes have to be stated on the label of consumer products regardless of their concentration in the product (perfume substances have to be stated as "perfume"). In addition, the Detergent Regulation determines that 26 known allergenic perfume substances (cf. Cosmetics Directive, 76/768/EEC and 2003/15/EU) have to be declared by name if their concentration exceeds 0.01% in detergents sold to consumers.

3.5 Limitation in use of PFOS (perfluorooctanesulfonic acid)

In December 2006, it was decided in the EU to limit the use of perfluorooctanesulfonic acid (PFOS) as PFOS is considered to be very persistent, very bio accumulative and toxic. PFOS also has the potential of being transported in the environment across large distances and to have damaging effects. PFOS meets the criteria to be considered as a persistent organic environmental poison (POP) in accordance with the Stockholm Convention. A risk and health assessment of PFOS has demonstrated that it is necessary to reduce the health and environmental risks.

According to the PFOS Limitation Directive, it is not allowed to market PFOS or to use it as a substance or in chemical preparations in concentrations of 0.005% (w/w) or more from 27 June 2008. PFOS must not be marketed in semi-processed products or articles or parts of such if the PFOS concentration amounts to 0.1% (w/w) or more, and must not be marketed in fabrics or other coated materials if the PFOS amount is 1 $\mu g/m^2$ or more of the coated material. However, there are exceptions where PFOS may still be used (Directive 2006/122/EU).

3.6 REACH, the new EU Chemical Regulation

The new EU chemical reform, REACH ((EU) No. 1907/2006) came into force on 1 June 2007. REACH is a comprehensive regulation for chemical substances and products containing chemical substances. The Regulation will be implemented gradually in the course of 15 years. REACH i.a. imposes manufacturers and importers to register the chemical substances that form part of their production and/or their products and to pass on information to their customers about which compounds form part of the products and how the compounds can be dealt with in a safe and secure way.

4 Description of the exposure scenarios

In the light of the survey results, relevant exposure scenarios were set up for the purchased car care products. The exposure scenarios have formed the basis of the preparation of the emission analyses and are used in connection with the exposure assessment in the health assessment.

The purchased car care products cover the following types of car care products:

- Vinyl make-up – 9 spray products with propellant or pump and one single cream product
- Glass cleaner – 5 spray products with propellant or pump and one single cream product
- Fabric coating – 3 spray products with propellant or pump
- Fabric cleaner – 9 spray products with propellant or pump
- Odour remover – 2 spray products with propellant or pump
- Vinyl cleaner – 3 spray products with propellant or pump
- Leather cleaner – 2 spray products with propellant or pump
- Cleaning tissue – 4 tissues
- Anti-mist product – 1 spray product with pump and 1 tissue
- Detergent - 1 foam spray with pump
- Synthetic materials sealant – 1 cream product.

As it appears from the above list, most of the car care products for interior car care are spray products. The survey shows that three car care products are relevant in relation to an exposure assessment:

- Spray products
- Cream products
- Tissues.

Table 4.1 gives an outline of the different application methods that are stated on the products. The table is organized according to the four different application methods found on the purchased products:

- Sprayed on the surface to be treated. Wiped off with a cloth.
- Sprayed directly on the cloth and spread on the surface.
- Cream applied with a cloth.
- Tissue is used.

In general, it applies to all car care products that separate directions for use are not supplied with the product. Only brief directions are written on the product itself. The directions for use on the different products mention the application possibilities that are listed in table 4.1. The four columns in the table represent four different application methods. For each of the four different application methods examples are given from the labels of the different products that were purchased.

Table 4.1 Examples of application methods. Each of the four columns represents the four different application methods described on the labels of the purchased products. The examples in the rows are examples of the application details written on the labels.

	The different application methods of products for interior car care			
Examples from products	Spray on the surface to be treated. Wipe off with a cloth.	Spray directly on the cloth and spread on the surface.	Cream applied with cloth.	Use a tissue.
Example 1	A small amount is sprayed on the surface.	Apply a thin layer with a cloth.	Apply the product with a large cloth.	Clean. The tissue is turned and folded as required.
Example 2	Spray in an even layer on the entire surface.	Spray on the cloth and spread.	Apply a very thin and even layer on the entire surface.	If necessary, wipe off with a dry tissue.
Example 3	Only spray one thin layer on the surface.	Apply with a cloth or sponge.		
Example 4	Spray at a distance of 5-10 cm.			
Example 5	Spray sparingly on the surface.			
Example 6	Spray a thin and even layer from a distance of app. 20-30 cm with circular movements.			
Example 7	Spray at a distance of app. 30 cm. If possible several times after intermediate drying.			
Example 8	Spray directly at a distance of 10-15 cm.			
Period of waiting	Let it penetrate. Let it work. Let it work and dry. Let it work for a short period. Let it work 5-10 min. Let it work 1-2 min. Let it penetrate 30 seconds. Let it work 2-3 min. Let the item dry for some hours (fabric cleaner). Let it work the night over with closed doors/windows (odour remover).		Let it cure 45 min. (synthetic materials sealant)	

On the basis of the directions for use on the products there is in general no great difference between the application method in spite of the product differences (glass cleaner, vinyl cleaner and fabric guard). For instance, it is recommended to wipe off the fabric guard with a cloth after spraying in order to spread the product evenly. Still, it is expected that fabric guards and fabric cleaners are used rarely compared to the other types of car care products.

Information on how often the products are used is sparse. Some shops inform that car care often is a spring activity that especially is carried out by men. Therefore, some shops sell most products during spring. Other information indicates that some car owners drive to the local service station every week to wash, burnish and polish the car inside and outside.

4.1 Exposure scenarios

The situation that is analysed closer in this project is the following:

A car owner drives to the nearest service station for car detailing, i.e. to refuel, wash the car and polish it outside and inside. This project solely concentrates on polishing the inside of the car with products for interior car care.

It is anticipated that it takes app. 15 minutes per product to apply the product inside. During that time exposure can take place via inhalation as the products contain volatile compounds, but exposure can also take place via skin contact when the products are applied.

In connection with the calculations it is anticipated that it takes 15 minutes to apply each product. In the calculations, the exposure to several products is added up if for instance vinyl make-up as well as glass cleaner is used. Therefore, the worst-case situation is anticipated to be when both products are applied simultaneously, i.e. full exposure to both products at the same time. In practice that is not possible, but it is a necessary assumption in relation to the calculations.

Exposure to the substances is calculated per day, but it is anticipated that even the most energetic car care enthusiasts at a maximum polish and care for their cars once a week.

4.1.1 Skin contact

As mentioned, the survey shows that there are three types of car care products:

- Spray products
- Cream products
- Tissues.

As previously mentioned, spray products can be products that are sprayed on the surface and afterwards have to be wiped off with a cloth. Cream products are applied with a cloth and tissues are used as they are.

In connection with spray products and cream products exposure via the skin is possible when the products are applied. Even if the person does not use gloves, the direct skin contact will be low as most of the car care product will be on the cloth. However, when using tissues, direct skin contact will occur.

It is anticipated that persons applying the product wash their hands immediately after application. All products are rather greasy and have a strong oily smell and therefore it is anticipated that there is a need to wash hands if the product gets on the fingers.

Of course, exposure will be higher if the person does not wash hands after application. However, exposure will still be minor as most of the products are applied with a cloth so the main part of the product does not come into contact with the skin.

4.1.2 Inhalation

Exposure via inhalation takes place during and after application, e.g. if the person stays in the car or goes for a drive in the car immediately after application.

This project deals with two inhalation scenarios:

1. The product is applied (15 minutes) and then the person drives the car home from the local service station where application has taken place (15 minutes to drive home). That gives a total exposure of 30 minutes. Then there is no exposure (all substances are aired away before the car is used the next time).

2. The product is applied (15 minutes) and then the person goes for a 5-hour drive in the car. 5 hours have been chosen because the emission tests showed that after that period of time most of the substances had been aired away and the concentrations declined substantially.

4.2 Selection of products for emission tests

A total of 4 emission test were carried out with the selected, purchased products for interior car care. The below types of products were chosen for the emission tests. These product types were selected because there is a wide range of them and they are believed to be the product types that are used most often.

- Vinyl make-up (spray product)
- Glass cleaner (spray product)
- Fabric cleaner/fabric guard (spray product)
- Vinyl cleaner (spray product).

In the light of the screening of compounds in the products, the products were selected that seemed to have the highest content of (health hazardous) volatile organic compounds.

4.3 Preparation of emission tests

The emission tests were prepared to represent a realistic worst-case situation. The relevant parameters chosen for the tests are described below and added up in Table 4.2.

The chemical structure and surface structure of a material are of importance to the evaporation of substances as some substances can be absorbed and in that way lower the evaporation speed. Therefore, realistic test samples were used for the emission tests. Examples are glass, fabric or plastic surfaces.

The size of the car cabin (as well as the temperature and air change) is of importance to the extent of exposure. Centre for Renewable Energy and Transport, Danish Technological Institute, gave the following information about the construction of a car: the volume of an average passenger car is app. 3.5 m^3 while a van is somewhat bigger. The air temperature will often be between 20 and 23 ºC if there is air-conditioning, otherwise the temperature can become considerably higher locally. There is a construction requirement to the plastic parts around the windows, namely that they have to be able to be proof against temperatures over 60 ºC. In particular, there are often problems with the horizontal part of the dashboard and fabric at the rear windows. In several cars, reflecting material is used. Therefore, these plastic parts may have a somewhat higher temperature when protectants are applied.

The ventilation capacity varies a lot according to the type of car. It is estimated that the defroster fan in the most simple systems typically has a capacity of 3–5 m^3 per minute. When driving with reduced fan speed the air change will by and large be the same due to the wind speed. When the fan is switched off, the air change will be speed dependent and can vary from almost 0 when the car is stopped and to almost the same level the fan can supply (i.e. once a minute) when the car is at full speed.

As initial scenario it is anticipated that a car owner drives to a service station to wash and polish his car and clean the car inside. It takes app. 15 minutes to polish/clean the car inside (per product). That is anticipated to be the concluding work and the car owner drives home from the service station immediately after (transport app. 15 min.), i.e. a 30 minute exposure during and after application. Another (worst-case) scenario is that the owner goes for a 5-hour drive in the car immediately after product application and therefore exposure time will be longer.

When using the product, the system will be partly open corresponding to the car door being open but without active air change (therefore air change is set to 0). Then the door is closed. It is anticipated that when driving in the car there is no active air change (the car doors/windows are closed and the ventilation is switched off). When driving in the car there will be a minor air change that will depend on the wind speed and the car speed, but to simulate the worst-case situation it is in these exposure scenarios anticipated that the car is almost completely closed (i.e. air change is set to 0).

Table 4.2 Emission tests

Description of the emission tests	
Volume	0.42 m^3 (cabin size: 420 L, Width 100 cm, Depth 60 cm, Height 70 cm).
Temperature	Room temperature, app. 22 ºC.
Air change	Almost 0 during application (it is anticipated that the car doors are open, but no fan is used). Air change is set to 0 at all measurements to simulate a worst-case situation.
Amount of applied car care agent	An amount is applied as estimated for simulated use.
Applied on	The car care agent is applied on realistic test samples such as glass, fabric or plastic surfaces.
Sampling	See result tables in section 5.2.2.
Stay in car in connection with application	*Time = 0-0.5 hours* 15 minutes to apply the product. Then the cloth is removed from the car as it is anticipated that the person will throw the cloth away or remove it to be washed. It is anticipated that it takes place at a service station and that the car is driven home immediately after (transport time app. 15 minutes), meaning that the total initial exposure is app. 30 minutes. It is anticipated that the air change is zero (car almost tight and no ventilation).
Stay in car after application	*Time = 0.5 - 5 hours* As worst-case a 5-hour car drive after application is anticipated during which time exposure takes place. Therefore, exposure level measurements were carried out continuously for up to 5 hours after test start.

5 Screening of compounds

In connection with the 26 products selected for screening (section 2.5.1), it was initially investigated which compounds they contain in order to estimate if there is a possible content of health hazardous substances that should be investigated closer in exposure scenarios and a more precise quantitative analysis.

The results of the initial screening cannot be used directly as it only is a semi-quantitative analysis, but they can be used to give an impression of the magnitude of the content of the identified compounds and to compare the individual products.

5.1 Applied analysis methods for screening

The chemical screening that was carried out was based on GC/MS analyses. An extraction/dilution with dichloromethane for semi-quantitative GC/MS screening of the products was carried out to identify the product content of semi-volatile organic compounds. In order to identify very volatile compounds, e.g. propellants, a SPME-GC/MS screening was carried out of the headspace of all of the products.

The specific parameters of the applied methods are described in the following.

5.1.1 Semi-quantitative GC/MS screening

A sample amount (app. 2 g) was weighed and a known amount of dichloromethane (50 ml) was added containing internal standards. The extracts were subsequently analysed gas chromatographically (GC/MS). In connection with product 32 and 40, 1 complete tissue was used.

The results of this analysis cover the semi-volatile compounds but not propellants nor volatile solvents. In connection with the screening that was carried out the detected compounds were merely identified by comparing the mass spectra of each compound with a library (NIST MS library, NIST02 Version 2.0) containing more than 150.000 mass spectra of organic substances.

The detection limit of the analysis method is estimated to be 0.01 mg/g and the measuring uncertainty is estimated to be ± 20%, however, higher for some compounds as only semi-quantification was carried out against an internal standard, bromobenzene.

Table 5.1 GC/MS analysis parameters

GC/MS instrument	Agilent HP 5973 ALS
GC parameters	Column: Zebron ZB-1, 20 m x 0.18 mm id., 0.18 µm film thickness Carrier gas: Helium, constant flow at 0.8 ml/min. Oven program: 40 ºC. for 2 min., 15 ºC. /min. at 300 ºC. Injection: 275 ºC. , split 1:10.
MS parameters	Scan mode: 35-550 m/z Solvent delay: 2 min.

5.1.2 Qualitative SPME-GC/MS screening

A sample amount, app. 0.2 g, was weighed directly in a headspace glass. The gas phase was subsequently analysed gas chromatographically by SPME-GC/MS.

The results of this analysis mainly cover the content of propellants, solvents and the most volatile compounds. In connection with the screening that was carried out, detected compounds were merely identified by comparing with a NIST MS library (NIST02 Version 2.0). AMDIS was applied as deconvulation software by means of which compounds with identical retention times could be identified.

The detection limit of the analysis method is estimated to be 0.001 mg/g but will depend on the vapour pressure and affinity of the individual compound for the applied SPME fibre. The results are qualitative and therefore no analysis uncertainty is stated.

Table 5.2 SPME-GC/MS analysis parameters

GC/MS instrument	Finnigan Focus GC-DSQ
GC parameters	Column: Zebron ZB-1, 30 m x 0.25 mm id., 1,0 µm film thickness Carrier gas: Helium, constant flow at 0.8 ml/min. Oven program: 40 ºC.for 1 min., 10 ºC/min. at 275 ºC, 275 ºC for 10 min. Injection: 275 ºC, split 20 ml/min.
SPME parameters	Fibre: 85 µm Carboxen/PDMS Absorption: 35 ºC, 15 min. Desorption: 3 min.
MS parameters	Scan mode: 35-450 m/z Ion source 225 ºC

5.2 Results of screening

The substances identified in connection with the performed screenings are summarized in the following tables. The results have been organized according to product type and analysis method. All identified substances have a CAS no. In connection with some compounds, reasonable identification was not obtained with NIST MS library and it can be a similar compound – therefore, the stated CAS no. is only advisory (marked at the specific compound in the table with a note).

5.2.1 Results of the semi-quantitative screening

For each identified compound an estimated content has been stated and it was calculated against an internal standard, bromobenzene. The detection limit is estimated to be 0.01 mg/g sample.

Table 5.3 Results of vinyl make-up, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.				
		1	2	15	25	29
Hydrocarbons *		400	540	25	-	480
1,3-dimethyl benzene	108-38-3	0.08	-	-	-	-
1-Acetonaphthon	941-98-0	-	0.05	-	-	-
Alkyl-benzenes eg xylenes**		1.1	-	-	-	-
1-methyldodecyl-benzene	4534-53-6	3.4	-	-	-	-
1-ethyldecyl-benzene	2400-00-2	0.74	-	-	-	-
1-methyltridecyl-benzene	4534-59-2	1.4	-	-	-	-
2-(2-ethoxyethoxy)-ethanol	111-90-0	5.2	-	-	-	-
-pinen	80-56-8	1.1	-	-	-	-
-pinen	127-91-3	4.0	-	-	-	-
N,N-dimethyl-1-dodecanamin	112-18-5	-	-	-	-	0.36
Diethyl phthalate	84-66-2	-	0.06	-	-	0.07
Bis(2-ethylhexyl)phthalate	117-81-7	-	-	-	0.25	-
Phthalates		0.27	-	-	-	-
Diisooctyl 1,2-benzene dicarboxylacid	27554-26-3	2.7	-	-	-	-
Siloxanes – silicone oil***		-	57	-	2.4	56
Silicium or fluorine containing oil****		30	-	-	-	-

' - ' Means that the compound was not detected in the product in question.

* This group covers several different aliphatic and cyclic hydrocarbons corresponding to the boiling point from heptane to dodecane.

** This group covers several different compounds where it has not been possible to obtain acceptable identification by means of the NIST library.

*** Product no. 2 and 29 are similar, while other types of siloxanes are present in product no. 25.

**** Requires other techniques to be identified.

Table 5.4 Results of glass cleaner, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.		
		23	24	37
Hydrocarbons *		-	-	280
Alkyl-benzenes**		-	-	X
1-methoxy-2-propanol***	107-98-2	X	-	-
2-butoxy-ethanol	111-76-2	-	21	-
1-butoxy-2-propanol	5131-66-8	-	14	-
5-methyl-3-heptanone	541-85-5	0.02	-	-

' - ' Means that the compound was not detected in the product in question.

* This group covers several different aliphatic and cyclic hydrocarbons corresponding to the boiling point from heptane to undecane.

** This group covers several different compounds where it has not been possible to obtain acceptable identification by means of the NIST library. The compounds are on top of the hydrocarbons and therefore it is not possible to state a possible result.

*** It has not been possible to state a possible result as the top is just at the beginning of the MS programme and therefore it is not included in its full size.

Table 5.5 Results of fabric waterproofing, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.		
		5	12	41*
Hydrocarbons **		400	-	-
Alkyl-benzenes***		0,10	17	-
Butyl acetic acid ester	123-86-4	45	-	-
α-pinen	80-56-8	0.16	-	-
β-pinen	127-91-3	0.89	-	-
Limonene	5989-27-5	5.6	-	-
Terpene		0.38	-	-
(Pentadecafluoroctanal)****		-	0.01	-
Fluorine compound****		-	0.01	-
Hexafluor propene****	116-15-4	0.16	-	-

' - ' Means that the compound was not detected in the product in question.

* Organic compounds were not detected in product no. 41.

** This group covers several different aliphatic and cyclic hydrocarbons corresponding to the boiling point from heptane to octane.

*** This group covers several different compounds where it has not been possible to obtain acceptable identification by means of the NIST library.

**** The identification of these compounds by means of the applied GC/MS technique is very poor. Another analysis method is required to determine whether a content of fluorinated compounds exists and to determine the quantitative content.

Table 5.6 Results of fabric cleaner, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.			
		7	9	22	30
2-(2-ethoxyethoxy)-ethanol	111-90-0	-	42	55	-
1-(2-methoxy-1-methylethoxy)-2-propanol, 2-(2-hydroxyproxy)-1-propanol or similar compounds**	20324-32-7, 106-62-7, 13429-07-7 etc.	4.6	-	-	-
β-pinen	127-91-3	-	0.02	0.01	-
Limonene	5989-27-5	0.16	0.60	0.16	-
Methyl paraben	99-76-3	-	X*	26	-

' - ' Means that the compound was not detected in the product in question.

* Methylparaben was detected in sample no. 9 but is below the estimated detection limit.

** This group covers several different compounds where it has not been possible to obtain acceptable identification by means of the NIST library.

Table 5.7 Results of odour remover, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.	
		8	14
Hydrocarbons*		-	0.61
Benzyl chloride	100-44-7	0.79	-
Propylene glycol	57-55-6	-	3.5
Triethylen glycol	112-27-6	0.20	-
Eucalyptol	470-82-6	-	0.03
Fluorine compounds**		0.01	-
4-amino heptane	16751-59-0	0.02	-
N,N-dimethyl-1-dodecanamin	112-18-5	0.85	-
N,N-dimethyl-1-tetradecanamin	129-24-3	0.21	-

' - ' Means that the compound was not detected in the product in question.

* This covers one or several unidentified hydrocarbons (cyclic, alcohols) with a boiling point corresponding to decane.

** The identification of these compounds by means of the applied GC/MS technique is very poor. Another analysis method is required to determine whether a content of fluorinated compounds exists and to determine the quantitative content.

Table 5.8 Results of vinyl cleaner, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.	
		10	27
1-(2-methoxy-1-methylethoxy)-2-propanol, 2-(2-hydroxyproxy)-1-propanol or similar compounds	20324-32-7, 106-62-7, 13429-07-7 etc.	-	14
α-pinen	80-56-8	0.01	-
β-pinen	127-91-3	X*	-
D-Limonene	5989-27-5	0.24	-
3-caren	13466-78-9	0.04	-
Diethyl phthalates	84-66-2	0.05	-

' - ' Means that the compound was not detected in the product in question.
* The content is below the estimated detection limit.

Table 5.9 Results of leather cleaner, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.	
		13	35
Hydrocarbons *		40	-
Eicosane, heacosane, noncosane **		0.25	-
Butylhydroxy toluene (BHT)	128-37-0	0.32	-
Dodecane acid	143-07-7	-	0.28
D-Limonene	5989-27-5	-	0.02
Diethyl phthalate	84-66-2	-	0.06

' - ' Means that the compound was not detected in the product in question.
* This group covers several different aliphatic and cyclic hydrocarbons corresponding to the boiling point from heptane to undecane.
** It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.10 Results of cleaning tissues, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.	
		32	40
Benzaldehyde *	100-52-7	-	0.02
Benzyl chloride	100-44-7	-	0.01
Ethyl paraben	120-47-8	0.07	-
Butyl paraben *	94-26-8	0.03	-
N,N-dimethyl-1-dodecanamin	112-18-5	-	0.18
N-methyl-N-benzyltetradecan-amin*	83690-72-6	-	0.02

' - ' Means that the compound was not detected in the product in question.
* It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.11 Results of anti-mist products, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		33
1,1'-oxybis-2-propanol *	110-98-5	0.25
1-(2-methoxy-1-methylethoxy)-2-propanol, 2-(2-hydroxyproxy)-1-propanol *	20324-32-7, 106-62-7, 13429-07-7	0.39
2-(phenylmethylene)-octanal	101-86-0	0.14
Sum of esters *		0.17
D-Limonene	5989-27-5	0.18

* It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.12 Results of detergent, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		34
No substances detected		-

Table 5.13 Results of synthetic materials sealant, semi-quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		38
Hydrocarbons *		408
Ethyl butanacid ester	105-54-4	0.08

* This group covers several different aliphatic and cyclic hydrocarbons and alcohols, corresponding to the boiling point from decane to hexadecane.

5.2.2 Results of qualitative screening of volatile organic compounds

In connection with the performed SPME GC/MS screening, no assessment of the amount of the identified substances in the product was carried out. The identified substances were marked with ”X”.

The substances are shown according to a rough volatility scale as they are shown according to retention time. Therefore, substances found at the beginning of the table must to a higher degree be expected to be emitted to the air with the risk of being absorbed via the respiratory passages.

Table 5.14 Results of vinyl make-up, SPME-GC/MS

Identification	CAS no.	Sample no.				
		1	2	15	25	29
Propane	74-98-6	X				
Isobutane	75-28-5	X	X		X	
Butane	106-97-8	X	X			X
Ethyl alcohol	64-17-5	X				
Isopropyl alcohol	67-63-0	X			X	X
Pentane	109-66-0	X			X	
Dimethoxy methane	109-87-5	X				
2,2-dimethyl butane	75-83-2	X			X	
Cyclo pentane	287-92-3				X	
2-methyl pentane, 3-methyl pentane	107-83-5, 96-14-0	X			X	X
Hexane	110-54-3	X	X		X	
1-butanol	71-36-3					X
Cyclo hexane	110-82-7	X	X			X
2-methyl hexane, 3-methyl hexane	591-76-4, 589-34-4	X	X			X
2,3-dimethyl hexane	584-94-1	X	X			
Heptane	142-82-5	X	X			X
Methyl-cyclo hexane	108-87-2	X	X			X
Xylenes	95-47-6, 108-38-3, 106-42-3	X				
2-(2-ethoxyethoxy)-ethanol	111-90-0	X				
α-pinen	80-56-8	X				
2,2,4,6,6-Pentamethyl heptanes	13475-82-6		X			X

Table 5.15 Results of glass cleaner, SPME-GC/MS

Identification	CAS no.	Sample no.		
		23	24	37
Ethyl alcohol	64-17-5	X		
Isopropyl alcohol	67-63-0	X	X	
Acetic formic anhydride	2258-42-6		X	
2-butanone	78-93-3	X		
2,3-butandiol	513-85-9		X	
1-methoxy-2-propanol	107-98-2	X		
Ethyl benzene	100-41-4			X
Xylene	95-47-6, 108-38-3, 106-42-3			X
2-methyl octane, 3-methyl octane	3321-61-2, 2216-33-3			X
Nonane	111-84-2			X
1-butoxy-2-propanol	5131-66-8		X	
1-(1-methylpropoxy)-butane	999-65-5		X	
Alkyl benzenes eg (1-methylethyl)-benzene, 1-ethyl-2-methyl-benzene *	98-82-8, 611-14-3			X
3-methylnonane, 2-methylnonane	5911-04-6, 871-83-0			X
2-ethyl-1-hexanol	104-76-7		X	
5-ethyl-2-methyl-heptane	13475-78-0			X

* It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.16 Results of fabric waterproofing, SPME-GC/MS

Identification	CAS no.	Sample no.		
		5	12	41*
Butane	106-97-8	X		
2-methyl pentane, 3-methyl pentane	107-83-5, 96-14-0	X		
Ethyl acetate	141-78-6	X		
2,4-dimethyl pentane	108-08-7	X	X	
1-butanol	71-36-3	X		
3,3-dimethyl pentane	562-49-2	X	X	
Cyclo hexane	110-82-7	X		
2-methyl hexane, 3-methyl hexane	591-76-4, 589-34-4	X	X	
2,3-dimethyl hexane	584-94-1		X	
Dimethylcyclo pentane	2452-99-5, 1759-58-6	X	X	
Heptane	142-82-5	X	X	
Methyl-cyclo hexane	108-87-2	X	X	
Ethylcyclo pentane	1678-91-7		X	
Butyl acetate	123-86-4	X	X	
D-limonene	5989-27-5	X		

* No volatile organic compounds were detected in product no. 41.

Table 5.17 Results of fabric cleaner, SPME-GC/MS

Identification	CAS no.	Sample no.			
		7	9	22	30
Ethyl alcohol	64-17-5	X			
1-(2-methoxypropoxy)- 2-Propanol	13429-07-7	X			
Benzyl alcohol	100-51-6				X
2-ethyl-1-hexanol	104-76-7	X			
D-limonene	5989-27-5	X	X	X	
Linalool	78-70-6	X			
Acetic acid linalool ester	115-95-7	X			
Nerol acetate or geraniol acetate*	141-12-8, 16409-44-2	X			
1-hexadecanol or similar	36653-82-4				X

* It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.18 Results of odour remover, SPME-GC/MS

Identification	CAS no.	Sample no.	
		8	14
Isopropyl alcohol	67-63-0	X	
1,2-propandiol	57-55-6		X
D-limonene	5989-27-5	X	
Linalool	78-70-6	X	
3,7-dimethyl-3-octanol (linalool tetrahydrid)	78-69-3		X
Acetic acid benzyl ester	140-11-4	X	
p-menth-1-en-8-ol or other terpene*	98-55-5	X	
2-phenylethyl acetic acid ester	103-45-7		X
2-tert-butyl cyclo hexanol	13491-79-7		X
a-Ionon	14901-07-6		X

* It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.19 Results of vinyl cleaner, SPME-GC/MS

Identification	CAS no.	Sample no.	
		10	27
Isopropyl alcohol	67-63-0	X	
1-methoxy-2-propanol	107-98-2		X
α-pinen	80-56-8	X	
dipropylene glycol monomethyl ether*	20324-32-7		X
dipropylene glycol*	110-98-5		X
α-pinen	80-56-8	X	
p-menthane, 1,4-epoxy	470-67-7	X	
Cymen	99-87-6	X	
D-limonene	5989-27-5	X	
Linalool	78-70-6	X	
p-menth-1-en-8-ol or other terpene*	98-55-5	X	
Citral	5392-40-5	X	
1R-α-pinen	7785-70-8	X	
α-citral	106-26-3	X	
Isobornyl acetate	125-12-2	X	
Diethyl phthalate	84-66-2	X	

Identification	CAS no.	Sample no.	
		10	27
α-hexyl cinnemaldehyd	101-86-0	X	

* It has not been possible to identify these compounds with reasonable probability by means of the NIST library. The compound could be a similar compound.

Table 5.20 Results of leather cleaner, SPME-GC/MS

Identification	CAS no.	Sample no.	
		13	35
Octane	111-65-9	X	
2,6-dimethyl heptanes	1072-05-5	X	
C10-C12 alkane	-	X	
2-methyloctan, 3-methyl octane	3321-61-2, 2216-33-3	X	
1-ethyl-3-methyl cyclo hexane	198489-10-2	X	
Nonane	111-84-2	X	
Decane	124-18-5	X	
D-limonene	5989-27-5		X
butylated hydro toluene	128-37-0	X	
Diethyl	84-66-2		X

Table 5.21 Results of cleaning tissue, SPME-GC/MS

Identification	CAS no.	Sample no.	
		32	40
Ethyl alcohol	64-17-5		X

Table 5.22 Results of anti-mist product, SPME-GC/MS

Identification	CAS no.	Sample no.
		33
Isopropyl alcohol	67-63-0	X
2-tert-butyl cyclohexanol	13491-79-7	X

Table 5.23 Results of detergent, SPME-GC/MS

Identification	CAS no.	Sample no.
		34
Xylene	95-47-6, 108-38-3, 106-42-3	X
Allyl heptanoat	142-19-8	X
Tetralin	119-64-2	X
2-tert-butyl cyclo hexanol	13491-79-7	X
4-tert-butyl cyclohexyl acetate	32210-23-4	X

Table 5.24 Results of synthetic materials sealant, SPME-GC/MS

Identification	CAS no.	Sample no..
		38
Isopropyl alcohol	67-63-0	X
2,2,6-trimethyl octane	62016-28-8	X
2,2,7,7-tetramethyl octane	1071-31-4	X
2,2,4,6,6-Pentamethyl heptanes	13475-82-6	X
2,3,6,7-tetramethyl octane	52670-34-5	X

Identification	CAS no.	Sample no..
		38
5-ethyl-2,2,3-trimethyl-heptane	62199-06-8	X
3-methylun decane	1002-43-3	X
2,6-dimethyl decane	13150-81-7	X
2,3-dimethyl decane	1312-44-6	X
Tetra decane	629-59-4	X

5.2.3 Conclusion of screening results

The content of many of the product compounds stated on labels or safety data sheets (see Table 2.1) were detected and so were other organic compounds. In the following, the substantial results of the initial screening of each product type are listed:

- Vinyl make-up (5): A high content of different hydrocarbons was found in several of the products and one product contains terpenes (fragrances).
- Glass cleaner (3): They are dominated by different types of alcohols and glycol ethers. One single product contained alkyl benzenes and hydrocarbons.
- Fabric waterproofing (3): A high content of different hydrocarbons and limonene (perfume) was found in one product.
- Fabric cleaner (4): The products are dominated by glycol ethers and several of the products contain limonene (perfume).
- Odour remover (2): The products consist of alcohols, glycols and perfume.
- Vinyl cleaner (2): In the one product there was a content of glycol ether while the other contained isopropyl alcohol and perfume.
- Leather cleaner (2): In the one product a number of hydrocarbons and BHT were detected and in the other limonene (perfume) and a phthalate were detected.
- Cleaning tissue (2): One product contained parabens and the other benzyl chloride – both are preservatives.
- Anti-mist product (1): The product contains glycol ether and limonene (perfume).
- Detergent (1): Fragrances were detected.
- Synthetic materials sealant (1): The product has a high content of different hydrocarbons.

By comparing the results, the following similarities between some of the products appear:

- Product no. 2 and 29 (vinyl make-up) contain many of the same substances. Almost identical products might be in question.
- Product no. 5 and 12 (fabric waterproofing) are very much alike. However, there is perfume and several volatile compounds in sample no. 5.
- Product no. 9 and 22 (fabric cleaner) are very much alike. It is possible that almost identical products are in question.
- Product no. 7 and 27 (fabric cleaner and vinyl cleaner, respectively) are very much alike. However, product no. 7 has a content of perfume.
- Product 5, 12 and 8 (fabric cleaner and odour remover, respectively) might contain some fluorinated compounds. The identification of

these compounds by means of the applied GC/MS technique is very poor.

5.3 Screening for the effects of compounds – related to health

Based on the identified compounds during the different screening analyses, screening for possible health hazardous substances was carried out. The screening took its starting point in the classification of the List of Dangerous Substances supplemented with the Danish Environmental Protection Agency's advisory list for self classification (both available on www.mst.dk), and the list of limit values of the Danish Working Environment Authority, DWEA, (available on www.at.dk), (the Danish Working Environment Authority, 2007). A dash indicates that the substance has no classification or limit value. The table lists the classification of the substances according to the List of Dangerous Substances.

The identified compounds are summarised in Table 5. In the light of the screening results, 15 products were selected for closer quantification of compounds and 4 products were selected for emission tests to measure the actual concentration under realistic application conditions.

Compounds marked with grey were only identified via the qualitative GC/MS screening and therefore there are no content levels but only an ascertainment of the presence of the compounds. The remaining products were identified via semi-quantitative GC/MS and for a few compounds the highest measured concentration has been stated.

Table 5.25 Complete list of the compounds in investigated car care products (identified by screening) and their classification.

Substance name	CAS no.	Classification according to the List of Dangerous Substances	Advisory classification according to DEPA self classification	Possible limit value (DWEA)	Highest measured value
Dimethoxy methane	109-87-5	-	-	1000 ppm 3100 mg/m^3	-
Ethyl alcohol	64-17-5	F;R11	-	1000 ppm 1900 mg/m^3	-
Propane	74-98-6	Fx;R12	-	1000 ppm 1800 mg/m^3	-
Pentane	109-66-0	Fx;R12 XN;R65 R66 R67 N;R51/53	-	500 ppm 1500 mg/m^3	-
Nonane	111-84-2	-	N;R50	200 ppm 1050 mg/m^3	-
Heptane	142-82-5	-	-	200 ppm 820 mg/m^3	-
Methyl-cyclohexane	108-87-2	F;R11 XI;R38 XN;R65 R67 N;R51/53	-	200 ppm 805 mg/m^3	-
Isopropyl alcohol	67-63-0	F;R11 XI;R36 R67	-	200 ppm 490 mg/m^3	-
Cyclo pentane	287-92-3	F;R11 N;R52/53	-	300 ppm 850 mg/m^3	-
Cyclo hexane	110-82-7	F;R11 Xi;R38 Xn;R65 R67 N;R50/53	-	50 ppm 172 mg/m^3	-
1-butanol	71-36-3	R10 XN;R22 XI;R37/38-41 R67	-	50 ppm (LH) 150 mg/m^3	-
Octane	111-65-9	-	-	200 ppm 935 mg/m^3	-
Butyl acetic acid ester	123-86-4	R10 R66 R67	-	150 ppm 710 mg/m^3	45 mg/g
Butyl acetate	123-86-4	R10 R66 R67	-	150 ppm 710 mg/m^3	-

Substance name	CAS no.	Classification according to the List of Dangerous Substances	Advisory classification according to DEPA self classification	Possible limit value (DWEA)	Highest measured value
Ethyl acetate	141-78-6	F;R11 XI;R36 R66 R67	-	150 ppm 540 mg/^{3}	-
Xylene	95-47-6, 108-38-3, 106-42-3	R10 XN;R20/21 XI;R38	-	25 ppm (H) 109 mg/m^3	-
Alkyl-benzenes	95-47-6, 108-38-3, 106-42-3	R10 XN;R20/21 XI;R38	-	25 ppm (H) 109 mg/m^3	1.1 mg/g
1-butoxy-2-propanol	5131-66-8	XI;R36/38	-	Tentative GV on 100 ppm	14 mg/g
1-methoxy-2-propanol	107-98-2	R10	-	50 ppm 185 mg/m^3	-
Decane	124-18-5	-	N;R50/53	45 ppm 250 mg/m^3	-
Tetraline	119-64-2	R19 XI;R36/38 N;R51/53	-	Tentative GV: 25 ppm	-
1,3-dimethyl benzene	108-38-3	R10 XN;R20/21 XI;R38	-	25 ppm (H) 109 mg/m^3	0.08 mg/g
Hexane	110-54-3	F;R11 XI;R38 XN;R48/20-65 REP3;R62 R67 N;R51/53	-	25 ppm 90 mg/m^3	-
Cymene	99-87-6	-	N;R51/53	25 ppm 135 mg/m^3	-
2-butoxy-ethanol	111-76-2	XN;R20/21/22 XI;R36/38	-	20 ppm (H) 98 mg/m^3	21 mg/g
5-methyl-3-heptanon	541-85-5	R10 XI;R36/37	-	10 ppm 53 mg/m^3	0.02 mg/g
Acetic acid benzyl ester	140-11-4	-	-	10 ppm 61 mg/m^3	-
Butylhydroxy toluene (BHT)	128-37-0	-	Xn;R22 N;R50/53	10 mg/m^3	0.32 mg/g
Bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	REP2;R60-61	-	3 mg/m^3	0.25 mg/g
Diisooctyl 1,2-benzene dicarboxyl acid	27554-26-3	-	-	3 mg/m^3	2.7 mg/g
Diethyl phthalate	84-66-2	-	-	3 mg/m^3	-
Benzyl chloride	100-44-7	CARC2;R45 XN;R22-48/22 T;R23 XI;R37/38-41	-	1 ppm (LK) 5 mg/m^3	0.79 mg/g
Alkyl benzenes eg (1-methylethyl)-benzene, 1-ethyl-2-methyl-benzene	98-82-8, 611-14-3	R10 XI;R37 XN;R65 N;R51/53 or no classification	-	20 ppm (H) 100 mg/m^3 or -	-
Benzaldehyd	100-52-7	XN;R22	-	-	0.02 mg/g
Benzyl alcohol	100-51-6	XN;R20/22	-	-	-
Hexafluor propene	116-15-4	XN;R20 XI;R37	-	-	0.16 mg/g
Citral	5392-40-5	XI;R38 R43	-	-	-
D-Limonene	5989-27-5	R10 XI;R38 R43 N;R50/53	-	-	5.6 mg/g
Isobutane	75-28-5	Fx;R12	-	-	-
Butane	106-97-8	Fx;R12	-	-	-
Ethyl benzene	100-41-4	F;R11 XN;R20	-	-	-
2-butanon	78-93-3	F;R11 XI;R36 R66 R67		-	-
Allyl heptanoat	142-19-8	-	Xn;R22 N;R50/53	-	-
Dimethylcyclo pentane	2452-99-5, 1759-58-6	-	Xn;R22 N;R51/53	-	-
N,N-dimethyl-1-dodecanamin	112-18-5	-	R43 N;R50/53	-	0.85 mg/g
3-caren	13466-78-9	-	N;R51/53	-	0.04 mg/g
a-Ionon	14901-07-6	-	N;R51/53	-	-
4-tert-butyl	32210-23-4	-	N;R51/53	-	-

Substance name	CAS no.	Classification according to the List of Dangerous Substances	Advisory classification according to DEPA self classification	Possible limit value (DWEA)	Highest measured value
cyclohexyl acetate					
1-hexadecanol or similar	36653-82-4	-	N;R51/53	-	-
Tetra decane	629-59-4	-	N;R51/53	-	-
Butyl paraben	94-26-8	-	N;R51/53	-	0.03 mg/g
β-pinene	127-91-3	-	N;R50/53	-	4.0 mg/g
Nerol acetate or geraniol acetate	141-12-8, 16409-44-2	-	N;R50/53	-	-
α-pinen	80-56-8	-	N;R50/53	-	1.1 mg/g
α-citral	106-26-3	-	R43	-	-
3-methylnonan, 2-methylnonan	5911-04-6, 871-83-0	-	N;R50/53	-	-
2-methyl octane, 3-methyl octane	3321-61-2, 2216-33-3	-	- N;R50/53	-	-
2-(phenylmethylene)-octanal	101-86-0	-	-	-	-
cinnemaldehyd, α-hexyl	101-86-0	-	-	-	-
Ethyl butan acid ester	105-54-4	-	-	-	
2,6-dimethyl heptane	1072-05-5	-	-	-	-
2-methyl pentane, 3-methyl pentane	107-83-5, 96-14-0	-	-	-	-
2,4-dimethyl pentane	108-08-7	-	-	-	-
1,1'-oxybis-2-propanol	110-98-5	-	-	-	-
dipropylene glycol or similar	110-98-5	-	-	-	-
2-(2-ethoxyethoxy)-ethanol	111-90-0	-	-	-	-
Triethylenglycol	112-27-6	-	-	-	-
Acetic acid linalool ester	115-95-7	-	-	-	-
Ethyl paraben	120-47-8	-	-	-	-
Isobornyl acetate	125-12-2	-	-	-	-
N,N-dimethyl-1-tetradecanamin	129-24-3	-	-	-	-
2,3-dimethyl decane	1312-44-6	-	-	-	-
2,6-dimethyl decane	13150-81-7	-	-	-	-
2-Propanol, 1-(2-methoxypropoxy)-	13429-07-7	-	-	-	-
5-ethyl-2-methyl-heptane	13475-78-0	-	-	-	-
2,2,4,6,6-Pentamethyl heptane	13475-82-6	-	-	-	-
2-tert-butyl cyclohexanol	13491-79-7	-	-	-	-
Dodecane acid	143-07-7	-	-	-	-
4-amino heptane	16751-59-0	-	-	-	-
Ethylcyclo pentane	1678-91-7	-	-	-	-
1-ethyl-3-methyl cyclo hexane	198489-10-2	-	-	-	-
dipropylene glycol monomethyl ether or similar	20324-32-7	-	-	-	-
1-(2-methoxy-1-methylethoxy)-2-propanol, 2-(2-	20324-32-7, 106-62-7, 13429-07-7	-	-	-	-

Substance name	CAS no.	Classification according to the List of Dangerous Substances	Advisory classification according to DEPA self classification	Possible limit value (DWEA)	Highest measured value
hydroxyproxy)-1-propanol and similar compounds	etc.				
acetic formic anhydride	2258-42-6	-	-	-	-
1-ethyldecyl-benzene	2400-00-2	-	-	-	-
Diethyl phthalate	84-66-2	-	-	-	-
1-methyltridecyl-benzene	4534-59-2	-	-	-	-
1-methyldodecyl-benzene	4534-53-6	-	-	-	-
p-menthan, 1,4-epoxy	470-67-7	-	-	-	-
Eucalyptol	470-82-6	-	-	-	-
2,3-butandiol	513-85-9	-	-	-	-
2,3,6,7-tetramethyloctan	52670-34-5	-	-	-	-
3,3-dimethylpentan	562-49-2	-	-	-	-
Propylene glycol	57-55-6	-	-	-	-
1,2-propandiol	57-55-6	-	-	-	-
2,3-dimethyl hexane	584-94-1	-	-	-	-
2-methyl hexane, 3-methyl hexane	591-76-4, 589-34-4	-	-	-	-
2,2,6-trimethyl octane	62016-28-8	-	-	-	-
5-ethyl-2,2,3-trimethyl-heptane	62199-06-8	-	-	-	-
2,2-dimethyl butane	75-83-2	-	-	-	-
3,7-dimethyl-3-octanol linalool tetrahydrid	78-69-3	-	-	-	-
Linalool	78-70-6	-	-	-	-
N-methyl-N-benzyltetra-decanamin	83690-72-6	-	-	-	
p-menth-1-en-8-ol	98-55-5	-	-	-	-
1-(1-methylpropoxy)-butane	999-65-5	-	-	-	-
3-methylun decane	1002-43-3	-	-	-	-
Acetic acid, 2-phenylethyl ester	103-45-7	-	-	-	-
2-ethyl-1-hexanol	104-76-7	-	-	-	-
2,2,7,7-tetramethyl octane	1071-31-4	-	-	-	-
1-Acetonaphthon	941-98-0	-	-	-	-
Methyl paraben	99-76-3	-	-	-	-

H Means that the compound is skin permeable.
L Means that the limit value is a threshold value that never must be exceeded.
Fx Extremely flammable.
F Highly flammable.
Xi Irritant.
Xn Harmful.
N Dangerous for the environment.
T Toxic.
CARC Carcinogenic (classified as carcinogenic group 1 (substances that are carcinogenic to humans), group 2 (substances that probably are carcinogenic to humans) or group 3 (substances that possibly are carcinogenic to humans).
REP Can cause heritable genetic damage (classified as reproductive toxin group 1, 2 or 3).
R10 Flammable.
R11 Highly flammable.

R12	Extremely flammable.
R19	May form explosive peroxides.
R20	Harmful by inhalation.
R20/21	Harmful by inhalation and in contact with skin.
R20/22	Harmful by inhalation and if swallowed...
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed.
R22	Harmful if swallowed.
R23	Toxic by inhalation.
R36	Irritating to eyes .
R36/37	Irritating to eyes and respiratory system .
R36/38	Irritating to eyes and skin .
R37	Irritating to respiratory system .
R37/38	Irritating to respiratory system and skin .
R38	Irritating to skin .
R41	Risk of serious damage to eyes .
R43	May cause sensitisation by skin contact .
R45	May cause cancer .
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation .
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed .
R50	Very toxic to aquatic organisms .
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment .
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment .
R60	May impair fertility .
R61	May cause harm to the unborn child .
R62	Possible risk of impaired fertility .
R65	Harmful: may cause lung damage if swallowed .
R66	Repeated exposure may cause skin dryness or cracking .
R67	Vapours may cause drowsiness and dizziness .

As a starting point, products with danger classified compounds are relevant in relation to quantitative analysis of compounds in the products and in relation to the emission tests and the final health assessment. However, not all classifications are equally relevant. When selecting products for closer analysis, regard was only given to danger classifications of relevance in relation to inhalation and skin contact. Danger classifications in relation to e.g. danger of fire and environmental danger are irrelevant in relation to the investigations carried out in this project and such classifications have not been considered when selecting products for quantitative analysis.

5.4 Products and compounds selected for quantification and emission tests

As described in chapter 4 (Description of the exposure scenarios) the main ways of exposure to interior car care products are inhalation and skin contact. Product intake has not been considered. It is anticipated that consumers use gloves or wash hands immediately after application of the products, so the products are not consumed e.g. by sucking the fingers.

Even though gloves are not used when applying the products for interior car care, skin contact will presumably be minimal as the main part of the product will be on the cloth used for application. Therefore, it is expected that the most substantial way of exposure is via inhalation.

When selecting compounds for quantitative analysis, great importance was attached to products with a content of volatile substances, and compounds with a relevant health classification and/or a limit value[4].

[4] The occupational threshold limit values have been determined either in the light of the irritative effects of the substances or in the light of the special harmful effects of the substances. The limit values have been determined to protect people who work with the substances everyday. A technical/economic assessment of the limit value level

15 products were selected for further quantitative analysis of compounds and 4 products were selected for analysis of the emission of volatile substances in the climate chamber.

The products selected for quantitative analysis are stated below. It has been taken into account that some of the products, as stated in the chapter ”Screening of compounds”, are very much alike and in some cases they might be identical.

If products are very much alike, the product was selected that contains perfume – if the product exists with as well as without perfume.

Products containing compounds with a relevant health classification and/or limit value are:

- Product 1 - Vinyl make-up
- Product 2 - Vinyl make-up
- Product 25 - Vinyl make-up
- Product 23 – Glass cleaner
- Product 24 – Glass cleaner
- Product 37 – Glass cleaner
- Product 5 – Fabric waterproofing
- Product 7 – Fabric cleaner
- Product 8 – Odour remover
- Product 10 – Vinyl cleaner
- Product 13 – Leather cleaner
- Product 40 – Cleaning tissue
- Product 33 – Anti-mist product
- Product 38 – Synthetic materials sealant
- Product 34 – Detergent.

The 4 below products were selected for the emission tests. The products were selected as there is a wide range of these products and they are believed to be the product types that are used most often. In addition, the products were selected to represent different product types and finally the below products are interesting in relation to the emission tests as they (according to screening and safety data sheets) contain large amounts of compounds with a health classification and/or a limit value.

- Product no. 1 - Vinyl make-up (many volatile substances)
- Product no. 5 – Fabric waterproofing (many volatile substances)
- Product no. 10 – Vinyl cleaner – (many volatile substances)
- Product no. 24 – Glass cleaner (several different solvents).

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can also form part of the determination of the level (Danish Working Environment Authority, 2008) (DWEA, 2007).

6 Quantitative analyses and exposure

In consultation with the Danish Environmental Protection Agency, 15 products were selected for quantitative analyses. In addition, four of the products were selected for emission tests, please refer to section 5.4. The selection for quantitative analyses and emission tests was carried out on the basis of results from screening of volatile and semi-volatile organic compounds, please refer to section 5.2, and related to a screening of the classification and/or determined limit values of possible health hazardous substances, please refer to table 5.25 in section 5.3. The results in this chapter are used in chapter 8 and 9 for health assessments and exposure calculations, respectively.

6.1 Applied analysis methods

The specific parameters of the applied methods are described in the following.

6.1.1 Quantitative analyses for organic compounds

A sample amount (app. 2 g) was weighed and a known amount of dichlormethane (20 ml) was added containing internal standards. The extracts were subsequently analysed by GC/MS, please refer to Table 6.1. Analysis in duplicate was carried out.

The listed compounds were identified by comparing the actual mass spectra with mass spectra in the NIST library (NIST02 Version 2.0) and quantified against the selected external standards. The detection limit is estimated to be 10-50 µg/g and the analysis uncertainty is assessed to be 10%, however, some compounds much higher due to uncertainty during test preparation, please refer to the result tables.

Table 6.1 GC/MS analysis parameters

GC/MS instrument	Agilent GC 5890 MS 5972
GC parameters	Column: CP Sil 8CB low bleed MS, Varian, 30 m x 0.25 mm id., 0.5 µm film thickness Carrier gas: Helium, constant flow at 1.08 ml/min. Oven program: 35 ºC i ½ min., 10 ºC/min. at 70 ºC, 30 ºC/min. at 250 ºC, 20 ºC/min. at 320 ºC Injection: 280 ºC
MS parameters	Scan mode: m/z 29-550 Solvent delay: 2.4 min.

6.1.2 Description of exposure via inhalation

Many factors influence on the concentrations measured and calculated in the exposure scenario. Some examples are cabin volume, degree of ventilation, temperature, type of product, applied product amount, item surface (to which the product is applied) and the material composition of the item. Within the terms of reference, it was not possible to carry out actual tests in cars or to illustrate different combinations of these factors. Therefore, a worst-case

consideration was carried out where a complete evaporation and diffusion profile was measured.

Exposure via inhalation was carried out in a ”box” of app. 420 l (width 100 cm, depth 60 cm, height 70 cm) with the possibility of switching the ventilation on and off (see Enclosure A). An item was placed in the box on which the products were applied, see detailed description below. During the measurements there was only access to the surroundings via two holes in the front of the box so the product could be applied to the item and so the adsorption pipes could be changed. Active air change was not supplied during the investigation in order to simulate a car with closed doors and windows and thus a very limited air change corresponding to leaks in the ventilation system and similar. It is anticipated that the car is almost tight and the air change is set to 0 to describe a worst-case situation.

The four selected products were applied to a surface of 2132 cm^2. A plate size of 52x41 cm^2 was used as that size can be placed in the box and it is possible to apply the car care product on the plate inside the box. The applied product amount corresponds to the product amount that typically is used. That means that the car care product was applied in an amount covering the area and it was applied in a sufficient amount, meaning that the car care product started running down the surface.

The materials to which the products were applied and the product amounts that were used are stated in Table 6.2. After application of the products the surface was wiped off with a tissue and the tissue remained in the box 15 minutes after application and then it was removed.

In the light of the plate size and the applied amount per area unit, it is possible to increase the product amount used in a typical car when the area of the different surfaces in a car (vinyl, glass and fabric) is known. Measuring a random car of medium size (Renault Megane) demonstrated that vinyl amounted to app. 1.73 m^2, windows amounted to app. 2.6 m^2 and fabric on seats to app. 3.63 m^2. From that information a factor was calculated between the plate used and the car surfaces (8.1 for vinyl, 12.2 for glass, 17.0 for fabric (seats)), and finally the expected applied amount for an entire car was calculated, see Table 6.2.

The box used for the measurements has a volume of 0.42 m^3 while an average car has a volume of 3.5 m^3. Therefore, all measurements have to be corrected with the relation between these volumes corresponding to the car cabin being app. one factor 8.3 larger.

Table 6.2 Outline of parameters for exposure scenarios

Product no.	Product type	Applied material (2132 cm^2)	Applied amount on material	Expected amount used for a car	Percentage use of can per application
1	Vinyl make-up	PVC mounted on a glass plate	2.5 g	20 g	8%
5	Fabric waterproofing	Fabric (polyester) mounted on a glass plate	4.6 g	78 g	29%
10	Vinyl cleaner	PVC mounted on a glass plate	6.4 g	51 g	10%
24	Glass cleaner	Glass plate	3.1 g	37 g	7%

Emission measurements were carried out by means of adsorption pipes, Tenax TA. Known air was sucked from the box through a Tenax pipe by

means of which the volatile organic compounds were collected on the pipe. During each measurement the actual air amount was noted in order to calculate the concentration in the air in the box during the specific measuring period (air amount and measuring period appear from the result tables). App. 10% of the air amount in the box was actively removed in order to carry out the measurements corresponding to a minimum air change. The results form a collected expression of the evaporation over time of the most volatile organic compounds and diffusion to the surroundings.

The pipes were subsequently thermally desorbed and analysed by GC/MS, see Table 6.3. The listed compounds were identified by comparing the actual mass spectra with mass spectra in the NIST library (NIST02 Version 2.0) and quantified against toluene. The detection limit of the method is estimated to be 5 ng and the analysis uncertainty of the method is estimated to be 10%. The analysis uncertainty of the analyses in duplicate appears from the result tables.

Table 6.3 GC/MS analysis parameters for exposure via inhalation

GC/MS instrument	Perkin Elmer ATD 400/Auto system XL/Turbomass
GC parameters	Column: CP Sil 8CB low bleed MS, Varian, 30 m x 0.25 mm id., 0.5 µm film thickness Carrier gas: Helium, constant flow at 1.08 ml/min. Oven program: 40 ºC for 2 min., 6 ºC/min. at 100 ºC, 20 ºC/min. at 290 ºC, 2½ min. at 290 ºC Desorption of Tenax TA: 15 min., 280 ºC
MS parameters	Scan mode: m/z 29-450

6.2 Results of quantitative analyses and exposure

In the following, the results are presented from the quantitative GC/MS analyses and measurements of exposure via inhalation for the selected products.

6.2.1 Results of content of organic compounds

The tables below show the results of the quantitative analyses of selected organic compounds in 15 products. The results are an average of analyses in duplicate and the standard deviation of the results is stated. The results have been organised according to product type.

Table 6.4 Results of vinyl make-up, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.		
		1	2	25
Hydrocarbons, C_6-C_8*		110 ± 20	160 ± 10	-
Hydrocarbons, C_{10}-C_{14}**		140 ± 10	59 ± 1	
1-Acetonaphthon***	941-98-0	-	0.04 ± 0.03	-
Toluene	108-88-3	0.016 ± 0.001	-	-
Ethyl benzene and xylenes	100-41-4, 95-47-6, 108-38-3, 106-42-3	0.053 ± 0.008	-	-
α-pinen	80-56-8	1.5 ± 0.1	-	-
β-pinen	127-91-3	0.34 ± 0.03	-	-
Diethyl phthalate	84-66-2	-	0.32 ± 0.02	-
Bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	0.032 ± 0.002	-	0.25 ± 0.03

- Means the compound was not detected.
* This group covers e.g. heptane, methyl cyclohexane, cyclohexane, hexane. Calculated against the external standard for octane.

** This group covers hydrocarbons with boiling points corresponding to decane and dodecane as well as isomerics of tridecane and tetradecane. Calculated against the external standard of dodecane.

*** The result of 1-Acetonaphthone is an estimate as it cannot be distinguished from a siloxane compound and has been calculated against an internal standard.

Table 6.5 Results of glass cleaners, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.		
		23	24	37
Hydrocarbons, C_8-C_{10}*		-	-	130 ± 20
Xylenes	95-47-6, 108-38-3, 106-42-3	-	-	24 ± 3
Ethyl benzene	100-41-4	-	-	5.3 ± 0.3
1,2,4-trimethyl benzene	95-63-6	-	-	6.0 ± 0.6
Toluene	108-88-3	-	-	0.29 ± 0.03
1-methoxy-2-propanol	107-98-2	50 ± 5	10 ± 1	-
2-butoxy-ethanol	111-76-2	-	47 ± 1	-
1-butoxy-2-propanol**	5131-66-8	-	21 ± 1	-
5-methyl-3-heptanon**	541-85-5	0.030 ± 0.001	-	-
2-butanon**	78-93-3	1.0 ± 0.1	-	-
Bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	-	-	0.0026 ± 0.0005

- Means the compound was not detected.

* This group covers e.g. 2- and 3-methylnonane, nonane, 2- and 3-methyloctane. Calculated against an external standard of octane.

** Compound calculated against an external standard with corresponding chemical character.

Table 6.6 Results of fabric waterproofing, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		5
Hydrocarbons, C_6-C_8*	-	350 ± 5
1-butanol	71-36-3	0.086 ± 0.008
Toluene	108-88-3	< 0.01
Ethyl benzene and xylenes	100-41-4, 95-47-6, 108-38-3, 106-42-3	< 0.02
Butyl acetate	123-86-4	55 ± 1
Ethyl acetate**	141-78-6	3.8 ± 0.1
α-pinen	80-56-8	0.126 ± 0.003
β-pinen	127-91-3	0.48 ± 0.02
D-Limonene	5989-27-5	2.7 ± 0.1
Terpene e.g. terpinene**	99-85-4	0.23 ± 0.08
Diethyl phthalate	84-66-2	0.12 ± 0.01
Bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	0.17 ± 0.01

* This group covers e.g heptane and methyl cyclohexane. Calculated against octane.

** Compound calculated against external standard with corresponding chemical character.

Table 6.7 Results of fabric cleaner, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		7
D-Limonene	5989-27-5	0.1 ± 0.1
Nerol acetate, geraniol acetate*	141-12-8, 16409-44-2	0.05 ± 0.04

* Compound calculated against external standard with corresponding chemical character.

Table 6.8 Results of odour remover, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		8
Acetic acid benzylester*	140-11-4	0.005 ± 0.001
Benzyl chloride	100-44-7	0.37 ± 0.05
D-Limonene	5989-27-5	0.0027 ± 0.0003
N,N-dimethyl-1-dodecanamin*	112-18-5	0.54 ± 0.01

N,N-dimethyl-1-tetradecanamin*	129-24-3	0.20 ± 0.01
N,N-dimethyl-1-hexadecanamin*	112-69-6	0.04 ± 0.01
Diethyl phthalate	84-66-2	0.0037 ± 0.01

* Compound calculated against external standard with corresponding chemical character.

Table 6.9 Results of vinyl cleaner, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		10
α-pinen	80-56-8	0.007 ± 0.004
β-pinen	127-91-3	0.007 ± 0.004
D-Limonene	5989-27-5	0.2 ± 0.1
3-caren	13466-78-9	0.09 ± 0.05
Cymen*	99-87-6	0.005 ± 0.003
Citral*	5392-40-5	0.03 ± 0.02
à-Hexylcinnamaldehyd*	101-86-0	0.03 ± 0.02
Diethyl phthalate	84-66-2	0.11 ± 0.04

* Compound calculated against reference standard with corresponding chemical character.

Table 6.10 Results of leather cleaner, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		13
Hydrocarbons, C_8-C_{10}*	-	33 ± 3
Butylhydroxy toluene (BHT)	128-37-0	1.0 ± 0.3

* This group covers e.g. octane, nonane, decane, 2- and 3-methyloctan. Calculated against octane.

Table 6.11 Results of cleaning tissues, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		40
Benzaldehyd*	100-52-7	0.023 ± 0.001
Benzyl chloride	100-44-7	0.077 ±0.006
N,N-dimethyl-1-dodecanamin*	112-18-5	0.14 ± 0.02
Dibutyl phthalate	84-74-2	0.0060 ± 0.0002

* Compound calculated against external standard with corresponding chemical character.

Table 6.12 Results of anti-mist products, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		33
D-Limonene	5989-27-5	0.08 ± 0.004
à-Hexylcinnamaldehyd*	101-86-0	0.11 ± 0.02

* Compound calculated against external standard with corresponding chemical character.

Table 6.13 Results of detergent, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		34
Xylenes	95-47-6, 108-38-3, 106-42-3	0.012 ± 0.002
Allyl heptanoat*	142-19-8	0.013 ± 0.05
Tetralin*	119-64-2	0.027 ± 0.007
4-tert-butyl cyclohexyl acetate*	32210-23-4	0.02 ± 0.01

* Compound calculated against external standard with corresponding chemical character.

Table 6.14 Results of synthetic materials sealant, quantitative GC/MS, mg/g sample

Identification	CAS no.	Sample no.
		38
Hydrocarbons C_{10}-C_{20}*	-	120 ± 20
Ethyl butyric acid ester**	105-54-4	0.13 ± 0.03
Diethyl phthalate	84-66-2	0.11 ± 0.01

* This group covers several different alkanes. Calculated against octane.

** Compound calculated against external standard with corresponding chemical character.

The results of the quantitative analyses are used in Chapter 8 for health assessment of selected compounds. Several of the quantified compounds were

also declared on the label of the product or on the specific safety data sheet while only a few compounds were stated with percentage content, see Table 2.1.

6.2.2 Results of exposure scenarios

Measurements were performed on exposure via inhalation when using product no. 1, 5, 10 and 24 and subsequent evaporation for 5 hours. The results of the measurements appear in the tables below. Some compounds in the result tables have a note stating that the results are minimum values because the results exceed the linear measuring area of the applied analysis method. Therefore, section 8.1.2. gives a theoretic calculation of hydrocarbons that was carried out in product no. 1 on the basis of the quantitative measurements to be compared with the results of the exposure scenarios.

The measurements were carried out during the period stated in the tables (e.g. 45-50 minutes, meaning that the exposure time in this case is 5 minutes), after which the adsorption pipe was removed and a new measurement was carried out in the next interval. The tables state an air amount which is the amount of air collected on the Tenax pipe during the specific measuring period. The air amount is used to calculate the results, which is an expression of the average concentration in the box during the stated measuring period. On the basis of the analyses in duplicate, the analysis uncertainty was calculated to be between 5 and 35% as it varies a lot depending on the product and the individual compound. See section 6.1.2 for further details concerning the measurements.

Table 6.15 Results of exposure when using vinyl make-up, product no. 1

Sampling time (min)		0-5	5-10	10-15	30-35	45-50	60-75
Exposure time (min.)		5	5	5	5	5	15
Air amount (in air)		0.42	0.32	0.33	0.36	0.37	1.09
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air
Sum of C_4-C_7 hydrocarbons*		64300	70800	51800	32500	21500	7500
Sum of C_{10}-C_{14} hydrocarbons*		42600	30600	15500	9200	4300	2800
Sum of hydrocarbons**		106900	101400	67300	41700	25800	10300
α-Pinen	80-56-8	1063	625	276	89	42	23
β-Pinen	127-91-3	2963	2102	1093	423	191	110
Diethylenglycol monoethylether	111-90-0	2069	1140	485	<100	<100	< 25

Comments to Table 6.15: There are traces of toluene and xylenes, less than 100 ng.

* Results are minimum values.

** Sum of results for C_4-C_7 and C_{10}-C_{14}.

Table 6.16 Results of exposure when using vinyl make-up, product no. 1, continued

Sampling time (min.)		120-135	180-195	240-255	300-315
Exposure time (min.)		15	15	15	15
Air amount (in air)		2.49	2.41	2.68	2.55
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air
Sum of C_4-C_7 hydrocarbons*		2550	990	383	197
Sum of C_{10}-C_{14} hydrocarbons*		2540	1951	2094	1557
Sum of hydrocarbons**		5090	2940	2480	1750
α-Pinen	80-56-8	12	8	5	4
β-Pinen	127-91-3	57	33	22	13
Diethylenglycol monoethylether	111-90-0	<25	95	139	85

* Results are minimum values.
** Sum of results for C_4-C_7 and C_{10}-C_{14}.

Table 6.17 Results of exposure when using fabric waterproofing, product no. 5

Sampling time (min.)		0-2	5-8	10-13	15-18	30-34.	45-50	60-65
Exposure time (min.)		2	3	3	3	4	5	5
Air amount (in air)		0.13	0.19	0.2	0.19	0.25	0.31	0.31
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air
Sum of C_5-C_8 hydrocarbons*		160000	103000	84000	85000	60000	43000	35000
Butane*	106-97-8	14000	8700	6600	7600	5000	2700	2000
2-Propanol	67-63-0	1060	612	290	324	196	104	59
Ethyl acetate	141-78-6	11748	6688	4339	3954	2323	1342	662
Butyl acetate*	123-86-4	70000	38000	24000	20000	12000	7300	4200
Allyl acetate	591-87-7	303	124	82	87	< 25	< 25	< 25
α-Pinen	80-56-8	953	363	163	131	67	36	17
β-Pinen	127-91-3	3982	1739	732	598	318	174	76
β-Myrcen	123-35-3	401	173	63	54	31	< 25	< 25
Limonene	5989-27-5	18000*	9000*	4248	3489	1876	997	413
Terpinene	99-85-4	1768	807	285	219	115	61	25

* Results are minimum values.

Table 6.18 Results of exposure when using fabric waterproofing, product no. 5, continued

Sampling time (min.)		120-130	180-190	240-250	300-310
Exposure time (min.)		10	10	10	10
Air amount (in air)		0.64	0.73	0.72	0.7
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air
Sum of C_5-C_8 hydrocarbons		2600	555	161	200
Butane	106-97-8	106	< 25	< 25	< 25
2-Propanol	67-63-0	18	13	< 25	< 25
Ethyl acetate	141-78-6	20	< 25	< 25	< 25
Butyl acetate	123-86-4	277	105	9	29
Allyl acetate	591-87-7	< 25	< 25	< 25	< 25
α-Pinen	80-56-8	< 25	< 25	< 25	< 25
β-Pinen	127-91-3	< 25	< 25	< 25	< 25
β-Myrcen	123-35-3	< 25	< 25	< 25	< 25
Limonene	5989-27-5	18	< 25	< 25	< 25
Terpinene	99-85-4	< 25	< 25	< 25	< 25

Table 6.19 Results of exposure when using vinyl cleaner, product no. 10

Sampling time (min.)		0-5	5-10	10-15	30-35	45-50	60-65
Exposure time (min.)		5	5	5	5	5	5
Air amount (in air)		0.76	0.34	0.40	0.36	0.49	0.39
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air	ng/l air
Butane	106-97-8	762	2074	1830	1630	778	573
2-Propanol*	67-63-0	11000	19000	14000	11000	6000	3800
1-Propanol	71-23-8	148	247	210	234	57	72
α-Pinen	80-56-8	66	70	49	26	13	< 15
β-Pinen	127-91-3	48	45	36	19	< 15	< 15
Limonene	5989-27-5	720	1038	618	340	201	86
Nerol	106-25-2	33	< 15	< 15	< 15	< 15	< 15
Terpineol	98-55-5	35	< 15	< 15	< 15	< 15	< 15
Linalool acetate	115-95-7	24	< 15	< 15	< 15	< 15	< 15
Bornyl acetate or Isobormeol acetate	76-49-3, 125-12-2	92	86	67	41	25	15

* Results are minimum values.

Table 6.20 Results of exposure when using vinyl cleaner, product no. 10, continued

Sampling time (min)		120-135	180-195	240-255	300-320
Exposure time		15	15	15	20
Air amount (in air)		1.18	1.23	1.12	1.60
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air
Butane	106-97-8	48	16	< 4	< 3
2-Propanol	67-63-0	783	166	46	50
1-Propanol	71-23-8	7	5	5	4
α-Pinen	80-56-8	< 4	< 4	< 4	< 3
β-Pinen	127-91-3	< 4	< 4	< 4	< 3
Limonene	5989-27-5	38	< 4	< 4	< 3
Nerol	106-25-2	< 4	< 4	< 4	< 3
Terpineol	98-55-5	< 4	< 4	< 4	< 3
Linalool acetate	115-95-7	< 4	< 4	< 4	< 3
Bornyl acetate or Isobormeol acetate	76-49-3, 125-12-2	<4	13	6	13

Table 6.21 Results of exposure when using glass cleaner, product no. 24

Sampling time (min.)		0-15	15-30	30-45	45-60
Exposure time (min.)		15	15	15	15
Air amount (l)		2.58	2.26	2.61	2.32
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air
2-Propanol*	67-63-0	1000	900	600	369
1-Methoxy-2-propanol*	107-98-2	3300	2200	1100	627
2-Butoxyethanol*	111-76-2	23000	14000	5800	2900
1-Butoxy-2-propanol*	5131-66-8	**	4500	3800	2300
Sek. Butylether	6863-58-7	600*	357	203	110

* Results are minimum values.

** 1-butoxy-2-propanol forms part of 2-butoxyethanol (component coelueting).

Table 6.22 Results of exposure when using glass cleaner, product no. 24, continued

Sampling time		120-135	180-195	240-255	300-315
Exposure time		15	15	15	15
Air amount (l)		2.36	2.41	2.32	2.32
Compound	CAS no.	ng/l air	ng/l air	ng/l air	ng/l air
2-Propanol	67-63-0	20	8	7	5
1-Methoxy-2-propanol	107-98-2	30	6	3	< 2
2-Butoxyethanol	111-76-2	170	64	49	36
1-Butoxy-2-propanol	5131-66-8	160	71	53	32
Sek. Butylether	6863-58-7	5	2	2	< 2

As it appears from the results, the greatest evaporation of the most volatile organic compounds takes place during application of the products and during the first 10-15 minutes after which the concentration declines. It should be expected that some of the product is removed when the cloth used to dry the plate is removed after 15 minutes. The results of the emission tests are used in the exposure calculations in chapter 9.

7 Nano products

It is well-known that aerosols under 2.5 µm form a special health hazardous risk during inhalation. In addition, recent years have focused on the health related risks from airborne nano particles (ultrafine particles)[5] as these particles to a higher degree than larger particles penetrate into the alveolar and tracheobronchial respiratory passages.

Nano aerosols are often created when using spray products. Figure 7.1 illustrates the principles of the creation of aerosols when using spray products. A pump or propellant-based spray mechanism creates primary aerosols in a liquid state consisting of solvent and active substances for spray waterproofing. When the solvent has evaporated, the non-deposited aerosols are transformed to secondary solid-state aerosols consisting of totally or partly polymerized waterproofing spray substances.

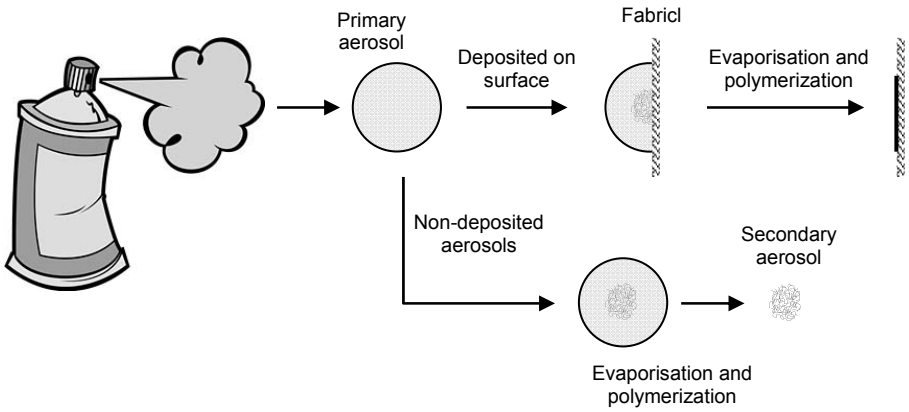


Figure 7.1 Sketch of the creation of fine and ultrafine (nano) particles/aerosols after evaporation of solvent from the fraction of the primary aerosols that are not deposited on the fabric surface.

According to the manufacturers, a number of products for interior car care are based on nano technology. In the project, measurements were carried out of the particle size distribution of aerosols in spray products that are marketed as being based on nano technology (product no. 22, 23, 24 and 41). The distributors of product no. 22, 23 and 24 cannot say what they precisely mean by the products being based on nano technology; however, the manufacturers of all four products inform that they contain nano particles. The chemical composition of the nano particles is not stated and it does not appear if solid-state particles are in question. It is stated that product no. 41 is based on sun-gel-chemistry and therefore it is expected to contain silane compounds, as commercial sun-gel-based surface treatment products to be used at room temperature normally are based on silane chemistry[6]. The composition of the listed nano particles was not informed.

[5] Refer to e.g. ISO/TC 146/SC 2 N 399
[6] Sun-gel group, Centre of Materials Testing, Danish Technological Institute

That means that primary, secondary or possibly added nano particles might be in question. It is also possible that merely products resulting in the creation of a film on the fabric surface with nano size thickness are in question.

Currently, no standardised methods exist for measuring the liberation of nano aerosols from spray products. Therefore, this project has used an analysis method developed in the analysis project of the Danish Environmental Protection Agency concerning spray products for fabric waterproofing (described in chapter 7.1).

7.1 Experimental course for particle measurements

The 4 products were screened for liberation of particles of up to 1 µm in aerodynamic diameter during use on a piece of fabric, in this case undyed cotton. Exposure took place in a purpose-built experimental chamber. Undyed cotton with a pore size of 200-300 µm was covered over a purpose-built, half-closed experimental chamber with a volume of 7.5 litres (Figure 7.2) so the distance from the product to the fabric was 24 cm.

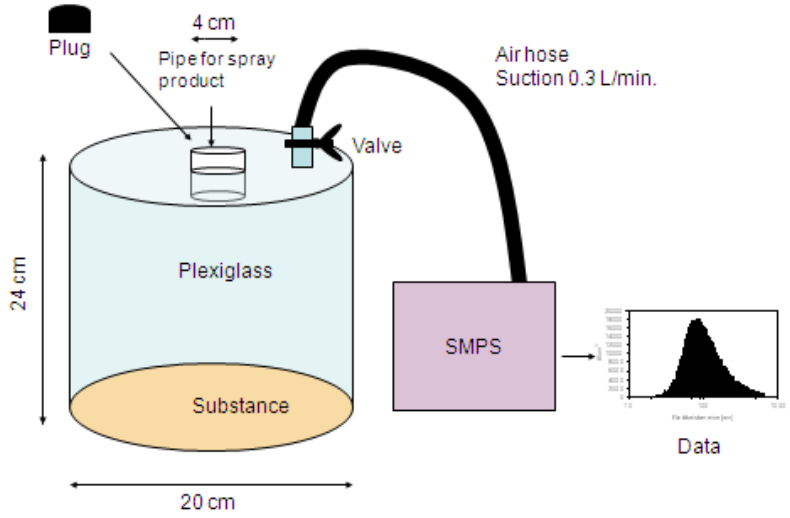


Figure 7.2 Schematic drawing of the experimental setup.

Aerosols created by the spray products were measured behind the product, corresponding to the ordinary application situation where the user directs the spray away from the body. That means that spraying did not take place directly into the measuring device, but measuring took place on aerosols liberated into the air when the products were used. It is estimated that the consumer will not by mistake be able to spray towards the face as the hand of the consumer will protect the face if the spray can is turned the wrong way. The consumer is not expected to be exposed to a larger exposure of aerosols if there is an accident. Damage to the can will probably result in greater exposure in relation to solvents but not in the creation of additional aerosols.

Particle size distribution of the aerosols was measured with a Scanning Mobility Particle Sizer (TSI SMPS 3934 equipped with Differential Mobility Analyzer (DMA model 3081) and ultra fine Condensation Particle Counter (CPC model 3776)). Aerosols were sucked into the device and passed a radioactive source by means of which the aerosols obtained a known charge

distribution. The aerosols were then led in a laminar air flow through an electric field that separates particles according to size.

The particles were counted with a condensation particle counter. Depending on the configuration the instrument can measure particles in the interval of 2-1000 nm. In this project, measuring took place in the interval of 6-650 nm. The instrument counts all aerosols irrespective of composition and form (solid or liquid). As the content of nano particles in the products before use was not determined in this project, it cannot be decided to which extent the aerosols contain nano particles that were present in the liquid phase.

Figure 7.3 gives a schematic presentation of the experimental course. After 10 seconds of waterproofing, the experimental setup was closed with a plug. After 60 seconds, aerosols were measured in the order of magnitude of 20-650 nm. That measurement took 60 seconds. Then another 5 minutes passed and the measurement was repeated. The objective of the follow-up analysis was to investigate if the size distribution changed in the period immediately after use due to solvent evaporation. Then the aerosol flow was increased from 0.3 litre/minute to 1.5 litre/minute in order to measure particles down to 6 nm.

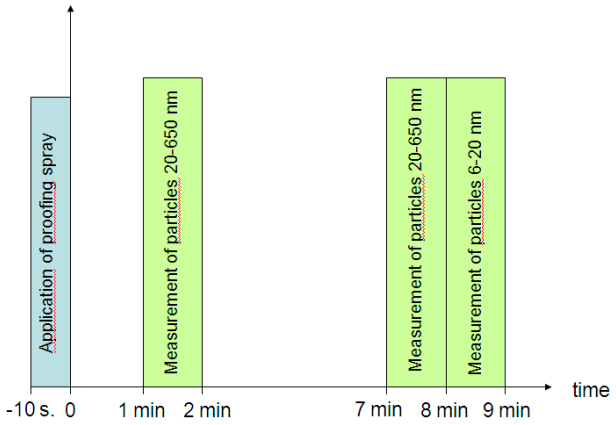


Figure 7.3 Schematic presentation of the experimental course.

Before each measurement, the background level of particles was measured and it demonstrated that the number of background particles varied from 500-4000 particles/cm^3 per minute (a typical background measurement is shown in Figure 7.4) which it a normal level for interior air.

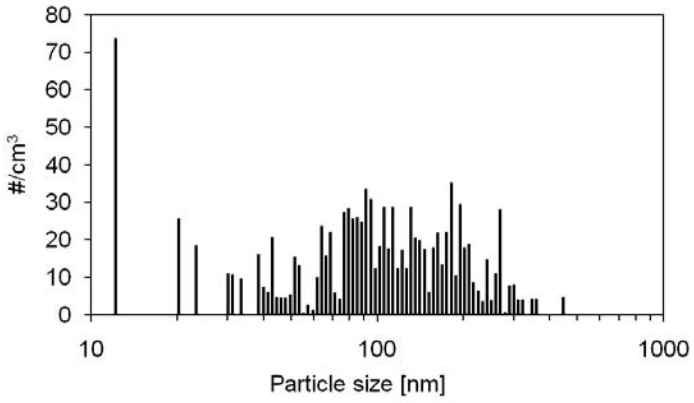


Figure 7.4 Particle size distribution (concentration of particles (number per. cm^3) in each of the 100 logarithmically distributed size intervals) of normal interior air measured with SMPS.

7.2 Results of particle measurements

The measured aerosol concentrations have been collected in Table 7.1. The particle size distribution appears from Figure 7.5. The largest uncertainty on the measurement results is found in the reproducibility of the amount and in the way the waterproofing liquid leaves the products during 10 seconds of continuous use. The uncertainty on the total amount of liberated particles is ±40%. The uncertainty on the mean value of the particle diameter is ± 20%.

The measurements are based on 10 seconds of use in an experimental chamber of 7.5 litres. If the products are used for a longer period of time and over a larger volume, the particle concentrations are expected to change proportionally; if secondary aerosols are in question the particle size distribution is expected to be unchanged.

Table 7.1 Aerosol concentrations

	Aerosol measurement after 1 minute				Aerosol measurement after 7 minutes				
Product no.	Particles 20-650 nm (10^3 per cm^3)	Particles 20-100 nm (10^3 per cm^3)	Particles 100-650 nm (10^3 per cm^3)	Mean particle size (nm)	Particles 20-650 nm (10^3 per cm^3)	Particles 6-20 nm (10^3 per cm^3)	Particles 20-100 nm (10^3 per cm^3)	Particles 100-650 nm (10^3 per cm^3)	Particle size Mean value(nm)
22	120	117	3	36	83	16	82	1	36
23	10	5	6	146	3	1			
24	21	6	16	207	12	0	4	9	194
41	1				1				

As appears from Table 7.1, aerosols are not created at a level above normal interior air when using product no. 41. In connection with product 23 and 24 enough aerosols are created making them measurable in relation to an ordinary background level. For these products, the mean particle size of the measured particles is >100 nm (cf.Table 7.1) and the particle concentrations are lower compared with most propellant-based spray products for fabric waterproofing[7]. Product no. 22 creates ultra fine (<100 nm) aerosols at a level that is more than 100 times above the normal indoor level. The reason for the high level can be the content of nano particles in the product; however, levels of the same size have been observed for spray products that are not marketed as "nano"[7]. The high level of aerosols observed for product no. 22 might be due to the specific construction of the spraying device of the product (propellant pressure and valve design).

[7] Cf. Aerosol measurements carried out in the analysis project of the Danish Environmental Protection Agency about sprays for fabric waterproofing.

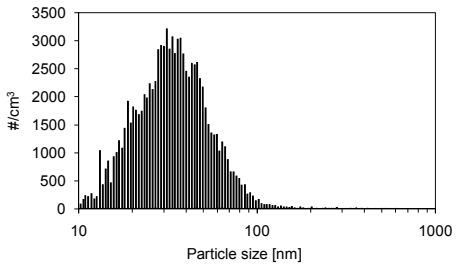
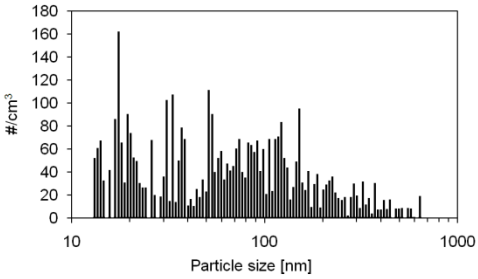
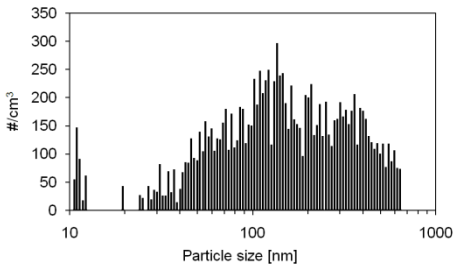
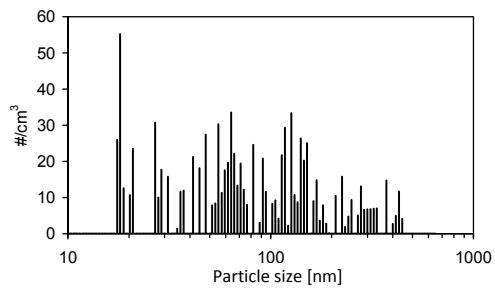
Product no.	Particle size distribution	Product no.	Particle size distribution
22		23	
24		41	

Figure 7.5 Concentration of aerosols (number per cm^3 in each of the 100 logarithmically distributed size intervals) as function of the diameter measured with SMPS in the interval 10-650 nm.

The chemical composition of the measured aerosols has not been determined. As with the aerosol analyses carried out in the project concerning spray products for fabric waterproofing[4] it can by comparing the particle sizes (Table 7.1) after 1 and 7 minutes, respectively, be seen that the solvents evaporate very quickly (< 1 minute). The measured aerosols are therefore expected to consist of completely or partly polymerised waterproofing agent and nano particles that were present in the products (solid state, secondary aerosols, cf. Figure 7.1).

A consumer of product no. 22 (foam spray with propellant) is therefore exposed to ultra fine solid state aerosols (< 100 nm) at a level two sizes above normal indoor air. It is a well-known fact that inhalation of ultra fine aerosols can have negative health effects[8], but in most cases individual tests have to be carried out with each chemical substance in nano form in order to express an opinion about the health effects of nono exposure. Such an evaluation is not comprised by this project.

However, it is clear that caution has to be exercised in general when using spray products. The experiment with this product shows that just as with other spray products for fabric waterproofing[7] airborne particles in nano form appear in connection with normal use of the product.

[8] Refer to e.g. ISO/TC 146/SC 2 N 399

8 Health assessment

In this and the next chapter, health assessments were carried out on the compounds in the analysed products for interior car care. At first, it was assessed if the concentrations measured in the emission tests exceed the occupational threshold limit values that are used in the working environment. The limit values are applicable for the working environment and are put in relation to a whole working day. According to the list of limit values of the Danish Working Environment Authority (DWEA), 2007) the limit values are only advisory when assessing if health hazardous conditions exist and therefore it is in general recommended to keep air pollution as far below the limit values as possible. Therefore, the comparison with the limit values should be regarded as sort of a preliminary screening.

In addition, a ”traditional” health assessment is carried out, i.a. the inhaled amount of substance and the amount of substance absorbed through the skin are put in relation to the critical values. The critical values are the concentrations of substances where literature shows that the substances can result in health effects. The calculations are carried out in chapter 9.

8.1 Assessment of the evaporation of substances in relation to the limit values of the Danish Working Environment Authority

As described in chapter 6 ”Quantitative analyses and exposure” measurements of exposure via inhalation were carried out when using product no. 1, 5, 10 and 24, and subsequent ventilation for five hours. The results are presented in section 6.1.2.

In this section, the measured concentrations of the found substances are put in relation to the limit values of the substances to assess if a person who is in a car during or after application of the interior car care products is exposed to a health risk.

The occupational threshold limit values are determined in the light of the irritative effects of the substances or because of the special harmful effects of the substances (DWEA, 2008). The limit values were determined to protect people who daily work with the substances. A technical/economic evaluation of the limit value level can also form part of the determination of the level. The limit values of the substances have been revised several times through the years. In the working environment the concept “unnecessary exposure” is dealt with. Unnecessary exposure from dangerous substances and material must be avoided. That means, that even though a limit value is observed then additional measures have to be established if exposure is unnecessary (DWEA, 2007). Therefore, a comparison with a working environment limit value can only be advisory.

The definition of limit value and description of how the time-weighted concentration is calculated according to the limit value list of the DWEA is described in box 8.1.

Box 8.1 Definition and description of limit value. Source: The Danish Working Environment Authority, 2007

The limit values in the list of the limit values of the Danish Working Environment Authority (DWEA, 2007) indicate the time-weighted average concentration of a substance in the air breathed at the workplace over an eight-hour working day.

However, even if the time-weighted average concentration does not exceed the limit value, the short-term concentration (15-minute period at the most) must never exceed twice the limit value.

Calculation of time-weighted average
The time-weighted average concentration considers that different concentrations can be measured in different periods. That means that a concentration can exceed the limit value for a shorter period of time, but for a longer of period of time the concentration has to be below the limit value.

The time-weighted average concentration is calculated according to the following formula where t_n is the different periods of time during which the different concentrations c_n are measured. The product of the time and the concentration of the different periods of time are divided by the total period of time (typically an eight-hour working day):

$$Time-weighted\ concentration = \frac{(t_1 \cdot c_1) + (t_2 \cdot c_2) + (t_3 \cdot c_3) + (t_4 \cdot c_4) + \ldots}{t_1 + t_2 + t_3 + t_4 + \ldots}$$

Regarding substances that can be absorbed through the skin (marked with an H in the limit value list) the qualification to use the stated limit value as basis of assessment is that absorption through the skin *does not* take place simultaneously.

Sum formula
When several substances appear at the same time, they can have an intensifying or weakening effect. If no specific information is available about the coordination of the substances, then a sum (additive) effect must be anticipated.

The following formula is used to calculate the total effect::

$$\frac{C_1}{GV_1} + \frac{C_2}{GV_2} + \frac{C_3}{GV_3} + \frac{C_4}{GV_4} + \frac{C_5}{GV_5} + \frac{C_6}{GV_6} + \ldots$$

where C is the air concentration of the respective substances and GV the corresponding limit values. A fraction sum of 1 corresponds to the limit value of the total effect.

Units
The limit values for gases and vapours are normally expressed in ppm, corresponding to the number of cubic metres of pollutant per cubic metre of air. The concentration can also be expressed in mg/m^3. The concentration specifications ppm and mg/m^3 can be mutually converted by using the following formula:

$$Concentration\ in\ mg/m^3 = \frac{M}{24.45} \cdot concentration\ in\ ppm$$

where M is the molecular weight of the substance.

Evaporation of chemical substances from interior car care products were measured at different time intervals during a total time interval of app. 5 hours. (max. measured for 320 minutes). In general, very low substance concentrations were measured in the course of the 5 hours (often values below the detection limit). Therefore it is anticipated that when measurements have stopped evaporation can be set to zero, meaning all evaporation takes place within the 5 hours.

In order to calculate the concentration and the time-weighted concentration it is necessary to know the concentration at all time intervals during the entire measuring period 0-300 minutes (5 hours). For the periods when the concentration was not measured, the concentration is estimated by using the

average concentration of the previous period of time and the concentration of the following period of time. In that way, it is possible to calculate a concentration at different times as stated in Figure 8.1.

The average concentrations measured at a given time are calculated as a sum of the product of the concentration and the time interval divided by the total period of time according to the following formula:

Average concentration at the time n =

$$\frac{(C_1 \cdot t_1) + (C_2 \cdot t_2) + (C_3 \cdot t_3) + \ldots + (C_n \cdot t_n)}{t_1 + t_2 + t_3 + \ldots + t_n}$$

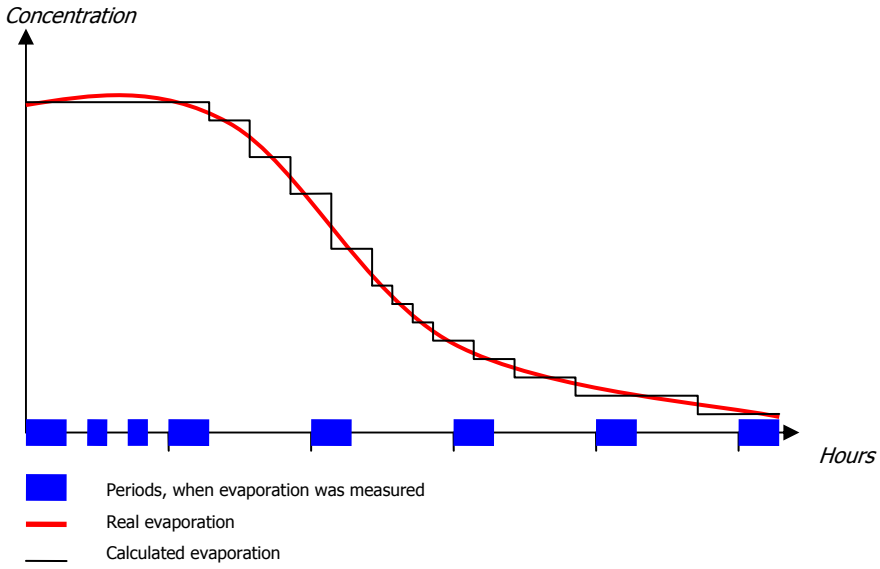


Figure 8.1 Course of evaporation and diffusion of substances after application

The time-weighted concentration is calculated for several periods, around 15, 30, 75, 195 and 315 minutes, respectively, (depending on how it fits with the measurements) to illustrate several situations, i.e.:

1. The car is polished inside (duration 15 min.) at home. The car is not used again the same day.
2. The car is filled with petrol, washed and polished on the outside at the local service station, and finally the car is polished inside (duration 15 minutes) and then the car is driven directly home. A total exposure of 30 minutes (15 minutes application and 15 minute drive home). The car is not used again the same day.
3. Afterwards, a shorter or longer trip is immediately driven in the car. That means exposure during application and stay in the car varies (60, 180 and 300 minute drive, respectively, in the car after application).

That means that an exposure of between 15 and 315 minutes is anticipated. That exposure has to be put into relation with the limit value which is a limit value of a time-weighted concentration over a period of 8 hours. In the calculations it is anticipated that the person in the different situations is exposed between 15 and 315 minutes, after which exposure is set to zero during the remaining time interval up to 480 minutes (= 8 hours), as the

scenario is that the person is exposed x minutes successively during/after application and is not exposed to the substances again. In the same way, it is anticipated that exposure is zero after the 315 minutes as most of the substances has evaporated after that time or as evaporation at that time max. is a few percentage of the initial evaporation.

The measured concentrations refer to the applied amount in relation to the volume of the climate chamber (0.42 m^3). Therefore, it is necessary to correct the measured values of the actual volume of a car (”Factor volume”) and the actually used amount in a car (”Factor used amount”). The volume of a standard car is app. 3.5 m^3 as previously mentioned. Therefore, the measured values have to be divided by a factor 8.3, as the volume of a car is 8.3 times larger than the volume of the chamber.

Correspondingly, the amount of car care product believed to be sufficient to coat a certain plate area was used during the tests. So much car care product was used so it ran down the plate (see detailed description in section 6.1.2). The area of car windows, panels and seats was measured for a standard car. The measured concentrations have therefore been multiplied by a factor 12.2, 8.1 or 17.0 (relation between the car surface area and the sample plate area) depending on the objective of the car care agent. In practice, a greater amount of car care agent is used in a car than during the tests and therefore the actual concentration will also be correspondingly higher.

The time-weighted concentrations of substances with a working environment limit value are shown in Table 8.1 below according to an example of the calculation of stated values in the table.

Example of calculation
The aliphatic hydrocarbons in product 1, vinyl make-up, are used as example.

The average concentration of the hydrocarbons during the first 15 minutes is calculated as described below. Data from Table 6.15 is used from the row ”Sum of hydrocarbons**”. All significant figures are used in the calculations and rounded up values are stated in Table 6.15.

Average concentration at the time n =

$$\frac{(C_1 \cdot t_1) + (C_2 \cdot t_2) + (C_3 \cdot t_3) + ... + (C_n \cdot t_n)}{t_1 + t_2 + t_3 + ... + t_n} \cdot \frac{Factor_{amount}}{Factor_{volume}}$$

Example: Average concentration for the first 15 minutes =

$$\frac{5\ \text{min} \cdot 106900\ ng/l + 5\ \text{min} \cdot 101400\ ng/l + 5\ \text{min} \cdot 67300\ ng/l}{15\ \text{min}} \cdot \frac{8.1}{8.3}$$

$$= 89615\ ng/l$$

$$= 90\ mg/m^3$$

Correspondingly, the ***time-weighted concentration*** at different times was calculated as described in the example below. In this case, it is divided by the total time 480 minutes (= 8 hours) to calculate the time-weighted concentration at an arbitrary time n. If the time-weighted concentration at the time n = 15 minutes has to be calculated, then the concentration is set to zero from minute 15 and up to the 480 minutes. In that way, the time-weighted

concentration for 15 minutes of exposure is obtained – but time-weighted against a period of 8 hours so the value can be compared to the limit value of the DWEA.

Time-weighted concentration at the time n over an 8 hour day =

$$\frac{(C_1 \cdot t_1) + (C_2 \cdot t_2) + (C_3 \cdot t_3) + ... + (C_n \cdot t_n)}{480 \text{ min}} \cdot \frac{Factor_{amount}}{Factor_{volume}}$$

Once again, the aliphatic hydrocarbons in product 1,vinyl make-up, were used as example and the time used was t = 15 minutes. In the time-weighted concentration it is considered that the concentration is zero from 15 minutes and up to the 8 hours which is the time the time-weighted concentration is calculated, The figures originate from ”Sum of hydrocarbons**” in Table 6.15.

Time-weighted concentration at the time 15 minutes =

$$\frac{5 \text{ min} \cdot 106900 \; ng/l + 5 \text{ min} \cdot 101400 \; ng/l + 5 \text{ min} \cdot 67300 \; ng/l}{480 \text{ min}} \cdot \frac{8.1}{8.3}$$

$$= 2800 \; ng/l$$

$$= 2.8 \; mg/m^3$$

The evaporated amount of the substances was measured every 5th minute at the beginning, and then every half hour. A calculation example of the time-weighted concentration of e.g. the time 315 minutes would be too comprehensive and therefore only a calculation example for the time n = 15 minutes was carried out.

Table 8.1 Time-weighted concentrations of compounds from products

Substance	CAS no.	Limit value (mg/m³) DWEA 2007	Factor volumen	Weighed amount (g)	Factor used amount	Average conc. The first 15 min. (mg/m³)	Time-weighted concentration (mg/m³) Time stated in minutes				
Product no. 1: Vinyl make-up			8,3	2,5	8,1		15	30	75	195	315
C_4-C_7 and C_{10}-C_{14} aliphatic hydrocarbons		180**				90	2.8	4.5	6.5	7.8	8.4
Product no. 5: Fabric waterproofing			8,3	4,6	17,0		15	30	65	190	310
Butane	106-97-8	1200				19	0.59	1.01	1.47	1.74	1.75
2-Propanol	67-63-0	490				1.2	0.04	0.06	0.07	0.09	0.10
Ethyl acetate	141-78-6	540				14	0.44	0.65	0.86	0.95	0.96
Heptane[1] / propane/ C_5-C_8 aliphatic hydrocarbons	142-82-5	820 (E) / 1800 / 180				223	6.9	11.7	18.5	23.4	23.5
Butyl acetate	123-86-4	710				80	2.5	3.6	4.8	5.3	5.4
Limonene* [2]	138-86-3	418				19	0.58	0.76	0.92	0.98	0.99
Product no. 10: Vinyl cleaner			8,3	6,4	8,1		15	30	65	195	320
Butane	106-97-8	1200				1.5	0.05	0.10	0.17	0.21	0.21
2-Propanol	67-63-0	490				14	0.45	0.84	1.33	1.66	1.68
1-Propanol	71-23-8	500 (H)				0.2	0.01	0.01	0.02	0.03	0.03
Limonene* [2]	138-86-3	418				0.8	0.02	0.04	0.05	0.06	0.06
Product no. 24: Glass cleaner			8,3	3,1	12,2		15	30	60	195	315
2-Propanol	67-63 -0	490				1.5	0.05	0.09	0.13	0.17	0.17
1-Methoxy-2-propanol	107-98-2	185 (E)				5	0.15	0.25	0.33	0.39	0.40
1-butoxy-2-propanol*	5131-66-8	541				23	1.06	1.36	1.76	2.07	2.09
2-butoxy ethanol	111-76-2	98 (EH)				11	0.34	0.55	0.83	1.08	1.09

* Indicates substances with a tentative limit value. Tentative limit values are temporary and only advisory limit values.

** The limit value of the Danish Working Environment Authority of 180 mg/m³ applies to petroleum redistilled C_9-C_{14} with < 5% aromatic compounds. The limit value is therefore not fully adequate for the found fractions of aliphatic hydrocarbons, but a precautionary approach has been chosen, i.e. the lowest limit value has been chosen.

E Indicates that there is an EU limit value. The tentative limit value is stated in ppm and converted to mg/m³ according to the instructions in the Danish Working Environment Authority limit value list, 2007.

H Indicates that the substance can be absorbed by the skin.

1 According to the evaporation tests in the box, C_5-C_8 aliphatic hydrocarbons were measured in large amounts. According to the safety data sheet it contains up 40% heptane and 20-40% butane/propane. It is therefore anticipated that the measured aliphatic hydrocarbons are a mixture of heptane and propane as butane is identified separately. Therefore, it is the limit value of 820 mg/m³ the measured values have to be compared with.

2 The limit value of Limonene covers the D as well as the L version (CAS 138-86-3). D as well as L-Limonene was identified in the analyses. D-Limonene (CAS 5989-27-5) is used as standard for identification.

Table 8.2 Calculation of the additive effect, calculated on the basis of the time-weighted concentrations for 5 hours (sum formula for limit value – see box 8.1)

	Product 1 Vinyl make-up	Product 5 Fabric waterproofing	Product 10 Vinyl cleaner	Product 24 Glass cleaner
Sum formula limit value (must not exceed 1)	0.0009	0.021	0.004	0.012

It appears from Table 8.1 that none of the evaporated substances have problems regarding the limit values of the substances. In addition, the limit

values are not exceeded when regard is given to the additive effect of the substances (Table 8.2), i.e. if for instance fabric waterproofing as well as vinyl cleaner is used when the same substance forms part of both products. Finally, there are no problems when the measured concentration of the substances during the first 15 minutes exceeds 2 x limit value of the substances (rule concerning the limit values, see page 11 in "Arbejdstilsynet", 2007).

The four investigated products for interior car care contain some of the same substances. Even if the car care products are applied simultaneously the limit limits will not be exceeded in the scenarios that are set up.

8.1.1 Which amount should be used in order to reach the limit value of the Danish Working Environment Authority?

During the climate chamber tests, the amount was applied that is anticipated to be used during normal use of the products. If it is anticipated that twice the applied amount would give the corresponding double measured concentration of each substance, it can be calculated which amount of the products has to be used to reach the limit value of the working environment. In the calculations, regard is not given to additive effects. The amount is calculated on the basis of the relation between the limit value and the measured average concentration. That factor is multiplied by the amount that is estimated to be used for a car.

The results are calculated for each compound with a limit value for 5 hours and 30 minutes. See the results in Table 8.3. The 5 hours and 30 minutes, respectively, correspond to the two scenarios where the person applies the products in a closed car and then remains in the car, so the total time spent in the car becomes 5 hours or 30 minutes, respectively. The latter scenario corresponds to a situation where the car care product is applied, e.g. at a service station and the car is then driven directly home.

Table 8.3 Product amount required to obtain the limit value of the working environment

Substance	CAS no.	Limit value (mg/m^3) DWEA 2007	Weighed amount product (g)	Factor used amount	Amount used each time for a car (g)	5 hour scenario		30 minutes scenario	
						Average conc. during 315 min. (mg/m3)	Amount required to exceed GV (g)	Average conc. during 30 minutes (mg/m3)	Amount required to exceed GV (g)
Product no. 1: Vinyl make-up			2.5	8.1	*20.3*				
C_4-C_7 and C_{10}-C_{14} aliphatic hydro-carbons		180**				8.4	434	4.5	817
Product no. 5: Fabric waterproofing			4.6	17.0	*78.2*				
Butane	106-97-8	1200				1.7	53.663	1.0	93.149
2-Propanol	67-63-0	490				0.1	391.835	0.1	693.783
Ethyl acetate	141-78-6	540				1.0	43.802	0.7	64.646

Substance	CAS no.	Limit value (mg/m³) DWEA 2007	Weighed amount product (g)	Factor used amount	Amount used each time for a car (g)	5 hour scenario		30 minutes scenario	
						Average conc. during 315 min. (mg/m3)	Amount required to exceed GV (g)	Average conc. during 30 minutes (mg/m3)	Amount required to exceed GV (g)
Heptane[1] / propane/ C_5-C_8 aliphatic hydro-carbons	142-82-5	820				23.5	2.725	11.8	5.446
Butyl acetate	123-86-4	710				5.3	10.380	3.6	15.405
Limonene*	5989-27-5	418				1.0	32.913	0.8	42.835
Product no. 10: Vinyl cleaner			6.4	8.1	*51.8*				
Butane	106-97-8	1200				0,2	296.633	0,1	620.947
2-Propanol	67-63-0	490				1,7	15.157	0,8	30.263
1-Propanol	71-23-8	500				0,0	948.171	0,0	2.005.637
Limonene*	5989-27-5	418				0,1	334.822	0,0	558.924
Product no. 24: Glass cleaner			3.1	12.2	*37.8*				
2-Propanol	67-63-0	490				0,2	108.512	0,1	213.381
1-Methoxy-2-propanol	107-98-2	185				0,4	17.711	0,3	27.894
1-butoxy-2-propanol*	5131-66-8	541				2,1	9.800	1,4	15.086
2-butoxy-ethanol	111-76-2	98				1,1	3.386	0,6	6.724

* Indicates substances with a tentative limit value. Tentative limit values are temporary limit values and are only advisory limit values.

** The limit value of the Danish Working Environment Authority of 180 mg/m³ applies to petroleum redistilled C_9-C_{14} with < 5% aromatic compounds. The limit value is therefore not fully adequate for the found fractions of aliphatic hydrocarbons, but a precautionary approach has been chosen, i.e. the lowest limit value has been chosen.

It appears from the table that in connection with most of the substances a total product amount exceeding 1 kg by far has to be used before the limit value of the individual substance is reached if the person as worst-case scenario remains in the car 5 hours after application of the product. A substantially smaller amount only has to be used in connection with hydrocarbons in the vinyl make-up to reach the limit value. The 434 g that have to be used corresponds to a consumption of 1.7 cans (estimated for the volume and density of the product) or 21 times the amount anticipated to be used for one car in this project. When staying 30 minutes in the car, an even larger amount has to be used to reach the limit value (3.2 cans of the product).

In the light of the measured values of the measured products, observing the limit values of the compounds of the products is not assessed to be a problem. Even if several products are used simultaneously (e.g. vinyl make-up, fabric waterproofing and glass cleaner), there will be no problems related to observing the limit values of the compounds of the investigated products. Furthermore, it must be anticipated that there will be some kind of air change in the car when driving in it, unless the fan is switched off and the recirculation of air is switched on.

8.1.1.1 Theory of calculations: Product 1 – Vinyl make-up

According to the safety data sheet, product 1 contains a number of petroleum products:

- Distillates (crude oil), hydrogen treated light
- Naphtha (crude oil), hydro desulphurized light, dearomatized (benzene content < 0.1%)
- Crude oil gases, condensed, sweetened (does not contain 1.3-butadien).

In the climate chamber tests, these products were identified as C_4-C_7 and C_{10}-C_{14} aliphatic hydrocarbons. The Danish Working Environment Authority has a limit value of 180 mg/m^3 for petroleum distillates with the chain length C_9-C_{14} (< 5% aromatic compounds). In the calculations it was assumed that the petroleum products described in the safety data sheets have this limit value (which also is stated by the manufacturer on the safety data sheet). That assumption was chosen as a precautionary approach as it is the lowest of the different petroleum fractions of the Danish Working Environment Authority. Calculations on the basis of the limit values of each compound in C_4-C_7 (pentane, hexane or heptane) were not carried out in this project.

The calculations show that 434 and 817 g, respectively, of vinyl make-up has to be used to reach the limit value of the petroleum distillates for staying in the car for a total of 5 hours and 30 minutes, respectively (incl. application time). As this vinyl make-up has a density of 0.636 kg/l and 400 ml of the product is sold each time that corresponds to having to use app. 1.7 cans and 3.2 cans before the limit value is reached.

8.1.1.2 Theory of calculations: Product 5 – Fabric waterproofing

According to the safety data sheet, product 5 contains:

- Propane/butane 20-40%
- Heptane 30-40%
- Butyl acetate
- Ethyl acetate.

The climate chamber tests i.a. identified butane and C_5-C_8 aliphatic hydrocarbons which in this case are anticipated to cover propane as well as heptane. Heptane has the limit value 820 mg/m^3 and propane has the limit value 1800 mg/m^3. During the first 15 minutes, the measured concentration did not exceed 2 x the limit value, if the C_5-C_8 aliphatic hydrocarbons are regarded as heptanes as stated in the safety data sheet.

The quantitative analyses (section 6.2.1) show that heptane is not necessarily pure but in the calculations it has been anticipated that pure heptane is in question and the limit value of heptane has been used.

8.1.1.3 Theory of calculations: Product 10 – Vinyl cleaner

The substance 1-propanol can be absorbed through the skin which means that exposure increases if the product is applied without using gloves. Exposure to 1-propanol that takes place through the skin has not been taken into account in this case, but, of course, it has to be added to exposure by inhalation. Exposure through the skin is anticipated to be min., as the product is not applied with the bare hands but a cloth is used.

8.1.1.4 Theory of calculations: Product 24 – Glass cleaner

It should be noted that during the first 15 minutes of the analysis it was not possible to distinguish 1-butoxy-2-propanol and 2-butoxy ethanol from each other with the chosen analysis method. Therefore, the amount measured during the first 15 minutes is the sum of the two substances. Therefore, it was

in the calculations anticipated that the condition found between the two substances after the 15 minutes also exists between the two substances during the first 15 minutes.

The substance 2-butoxy ethanol can be absorbed through the skin which means that exposure increases if the product is applied without using gloves. Exposure to 2-butoxy ethanol that takes place through the skin has not been taken into account in this case, but it has to be added to exposure by inhalation. Exposure through the skin is anticipated to be min., as the product is applied with a cloth.

8.1.2 Calculated total concentration of hydrocarbons

The emission tests in the box did in a few cases give problems with overexposure of the pipes used to collect the substances for analysis, and therefore especially the measured hydrocarbons are uncertain and must be regarded as minimum values. However, the same concentrations of hydrocarbons were not measured during the first measuring periods (the first few minutes), which indicates that the problem with overexposure was not necessarily very big.

Therefore, a theoretical calculation of the concentration of hydrocarbons was also carried out for product no. 1 (the product closest to the limit value). According to Table 6.4, hydrocarbons in product 1 were quantified in a total amount of 250 mg/g sample (110 + 140 mg/g sample). According to Table 6.2, 20 g of product 1 is typically used for application in a car. That will result in an amount of 5000 mg hydrocarbons in a car volume of 3.5 m^3, i.e. a concentration of 1429 mg/m^3 if it is anticipated that all hydrocarbons evaporate immediately when used.

If it is anticipated that the hydrocarbon concentration is kept constant, i.e. no decay and no ventilation in the car, then a person can stay 60.5 minutes in the car before the working environmental limit value of petroleum distillates is exceeded.

$$GV = \frac{C_1 \cdot t_1}{480\,\text{min}} \quad \Rightarrow \quad t_1 = \frac{GV \cdot 480\,\text{min}}{C_1} = \frac{180\,mg/m^3 \cdot 480\,\text{min}}{1429\,mg/m^3} = 60.5\ \text{min}$$

If for instance twice the amount is used, then the concentration becomes twice as large and the time before the limit value is reached is halved.

In that way, it is theoretically possible to exceed the limit value, but it requires the use of a large amount of vinyl make-up and that the person remains seated in a completely closed car (with the application cloth) for a longer period of time before the limit value is exceeded. Finally, it should be stressed that a theoretical maximum value is in question as it is anticipated that evaporation takes place spontaneously and that the concentration is kept constant (unrealistic as a car is not tight and as the substances are decomposed in air).

The theoretical maximum calculated concentration of hydrocarbons in the car cabin will exceed 2 x theoretical value and therefore it is recommended to apply vinyl make-up with doors open.

A person can remain in the car without the limit value being exceeded (based on the theoretical maximum concentration) for a longer period of time, than

the time the pipes were overexposed in the emission tests, and therefore it is assessed that the conclusions made on the basis of the emission tests are still valid as long as the largest concentration/evaporation takes place within the first half hour. There is no great difference between exposure during the first half hour and exposure during all 5 hours, as the concentration declines substantially after the first half hour.

8.2 Selection of substances for health assessment

In the light of the conversations with the staff in the shops, which formed part of the survey, and the information from the product labels, relevant exposure scenarios were drawn up for using products for interior car care (see chapter 4). Based on these exposure scenarios, actual application tests were carried out in climate chambers for four of the selected products for interior car care. In climate chambers it was measured which substances evaporate in the chamber when using realistic amounts of the selected products for interior car care (see detailed description of climate chamber tests in section 6.1.2).

The chemical substances that evaporate the most in the climate chambers and that have a relevant health classification (i.e. effects in relation to inhalation or skin contact, etc.), are the substances on which it is most obvious to carry out detailed health assessments.

In addition, quantitative analyses were carried out of the total content of chemical substances in 15 selected products for interior car care. In connection with these products it is relevant to assess the risk related to absorption through the skin if e.g. gloves are not used when applying the car care products. The products are typically applied with a cloth and therefore there is no direct skin contact, however, a smaller amount of the car care products must be expected to penetrate the cloth and could be absorbed through the skin. Therefore, it is also relevant to have a closer look at absorption through the skin of the danger classified substances that appear in the highest concentrations in the investigated products.

The substances that evaporate from the four investigated products for interior car care in the highest concentrations and at the same time have a relevant health classification/and or limit values are:

- Petroleum distillates (Xn; R65 (and CARC2; R45[9] where the content of benzene is ≥ 0.1%))
- Butyl acetate (R10, R66, R67)
- 2-butoxy ethanol (Xn; R20/21/22; Xi; R36/38)
- Limonene (R10, Xi; R38, R43, N; R50/53)
- Butane (E.g.: R12 (and CARC1; R45 and Mut2; R46 at content of 1.3-butadien > 0.1%[10]))

[9] According to the List of Dangerous Substances, some of the petroleum destillates identified in the investigated products have to be classified as carcinogenic (Carc2) with R45 unless the benzene content is < 0.1%. In connection with two of the products it has not been stated if the benzene content is < 0.1% so the classification Carc2 can be omitted. According to the safety data sheet the products are not classified as Carc2, R45, i.e. the benzene content is presumably below 0.1%, but as mentioned earlier that has not been stated.

[10] On the safety data sheets of some of the investigated products it is not stated if the content of butadiene is < 0.1%. According to the safety data sheets the products are not classified as Carc1, R45, i.e. the content of butadiene is presumably below 0.1% but as mentioned earlier that has not been stated.

- Ethyl acetate (F; R11, Xi; R36, R66, R67)
- 2-propanol (F; R11, Xi; R36, R67)
- 1-butoxy-2-propanol (Xi; R36/38)
- 1-methoxy-2-propanol (R10).

The substances are listed chronologically, so the substances from which the largest amounts evaporate are stated first. Among those substances, health assessments on butyl acetate, 2-butoxy ethanol, limonene, 2-propanol and 1-butoxy-2-propanol were carried out in previous analysis projects of the Danish EPA.

In order to assess absorption through the skin, focus is placed on substances with a concentration exceeding 10 mg/g (i.e. >1% of the product) and substances that simultaneously have a health classification. However, benzyl chloride is also included although the max. concentration in one product was measured to 0.37 mg/g (i.e. 0.037%) as it is classified as carcinogenic (Carc 2). The substances are:

- Petroleum distillates (Xn; R65 (and Carc2; R45[11] if content of benzene is ≥ 0.1%))
- 1-methoxy-2-propanol (R10)
- 2-butoxy ethanol (XN; R20/21/22; Xi; R36/38)
- Xylenes (R10, Xn; R20/21, Xi R38)
- 1-butoxy-2-propanol (Xi; R36/38)
- Benzyl chloride (Carc2 R45, Xn; R22-48/22, T; R23, Xi R37/38-41).

The substances are listed chronologically, so the substances with the largest quantitative amounts are stated first. Among the substances, health assessments on 2-butoxy ethanol, xylenes and 1-butoxy-2-propanol were carried out in previous analysis projects of the Danish EPA. The NOEL values (No Observed Effect Level) of these previously assessed substances are stated in Table 9.1.

The five substances selected for health assessment were:

- Petroleum distillates (Xn; R65 (and Carc2; R45[10] if content of benzene is ≥ 0.1%))
- Butane (E.g.: R12 (and Carc1; R45 at content of 1.3-butadien >0.1%[12])
- Ethyl acetate (F; R11, Xi; R36, R66, R67)
- 1-methoxy-2-propanol (R10)
- Benzyl chloride (Carc2 R45, Xn; R22-48/22, T; R23, Xi R37/38-41).

[11] According to the List of Dangerous Substances, some of the petroleum distillates identified in the investigated products have to be classified as carcinogenic (Carc2) with R45 unless the benzene content is < 0.1%. In connection with two of the products it has not been stated if the benzene content is < 0.1% so the classification Carc2 can be omitted. According to the safety data sheet the products are not classified as Carc2, R45, i.e. the benzene content is presumably below 0.1%, but as mentioned earlier that has not been stated.

[12] On the safety data sheets of some of the investigated products it is not stated if the content of butadiene is < 0.1%. According to the safety data sheets the products are not classified as Carc1, R45, i.e. the content of butadiene is presumably below 0.1% but as mentioned earlier that has not been stated.

8.2.1 Objective of health assessment

The objective of the health assessment is to describe the health effects of the assessed substances and to describe the critical effect. The critical effect of a substance is the effect that appears when exposed to the lowest dose where an effect is observed. That dose is also called NO(A)EL – No Observed (Adverse) Effect Level. The NOEL value is stated in mg/kg body weight.

On the basis of the safety factors, NOEL is converted to a TDI value (Tolerable Daily Intake). The calculated values for consumption (based on actual emissions or worst-case considerations on absorption through the skin) divided by the TDI value must not exceed 1 – if that is the case, and then there is a health related risk.

A safety factor of 100 is often used for conversion between NOEL value and TDI value. A factor 10 is used for species differences (between animals and humans) and a factor 10 is used to take particularly sensitive individuals into consideration. In some cases, a higher safety factor is used, as e.g. consideration can be given to experiments on animals not being long-term tests (chronic), but merely sub-chronic studies which is why yet another safety factor is added depending on the conditions.

In connection with the calculations concerning absorption through the skin, absorption is generally estimated due to lacking data. If no other information is available, a dermal absorption of 100% is used, however, a dermal absorption of 10% is used for substances with a molar weight larger than 500 g/mol that at the same time has a log K_{OW} less than -1 or larger than 4 (as stated in TGD, 2003). That is because large molecules in general have greater difficulties in permeating the skin just as very lipophilic substances do.

8.3 Health assessment of petroleum distillates

The term petroleum distillates, covers a wide range of organic compounds that are very similar - actually so similar, so it has not been possible to distinguish between the different petroleum distillates during the quantitative analyses. The petroleum distillates found during the quantitative analyses are therefore stated as C_6-C_8, C_8-C_{10} and C_{10}-C_{12}/C_{10}-C_{14}, respectively.

In connection with products, in which petroleum distillates were identified, we have to put our trust in the information stated on the safety data sheets of the products. According to the safety data sheets the following types of petroleum distillates form part of the products. Table 8.4 also states what the petroleum distillates have been identified as through the quantitative analyses and the box analyses.

Table 8.4 Petroleum distillates forming part of the analysed products for interior car care (according to safety data sheets (MSDS))

Product no.	CAS no.	Name	Classification according to LODS* and safety data sheet	Conc. according to MSDS	Identified as
Product 1 Vinyl make-up	64742-47-8	Distillates (crude oil), hydrogen treated light	LOFS: Xn; R65 MSDS: Xn; R65	25-50%	
	92045-53-9	Naphtha (crude oil), hydro desulphurized light, dearomatized (benzene content < 0.1%)	LOFS: Xn; R65 MSDS: Xn; R65, N; R51/53	25-50%	C_4-C_7/C_6-C_8* and C_{10}-C_{14}
	68476-86-8	Crude oil gases,	LOFS: Fx; R12	25-50%	

Product no.	CAS no.	Name	Classification according to LODS* and safety data sheet	Conc. according to MSDS	Identified as
		condensed, sweetened (does not contain1.3-butadiene)	MSDS: Fx; R12		
Product 2 Vinyl make-up	64742-49-0	Naphtha (crude oil), hydrogen treated light	LOFS: Carc2; R45[1] Xn; R65 MSDS: Xn; R38 R65, R67; F; R11	12.5-35%	C_6-C_8 and C_{10}-C_{12}
	64742-48-9	Naphtha (crude oil), hydrogen treated heavy	LOFS: Carc2; R45[1] Xn; R65 MSDS: Xn; R65	0.1-1%	
Product 37 Glass cleaner	64742-48-9	Naphtha (crude oil), hydrogen treated heavy	LOFS: Carc2; R45[1] Xn; R65 MSDS: Xn; R65, R67; Xi R66, R10	30-50%	C_8-C_{10}
Product 38 Synthetic materials sealant	64742-47-8	Distillates (crude oil), hydrogen treated light	LOFS: Xn; R65 MSDS: Xn; R65, R66	No information	C_{10}-C_{20}

* For analyses carried out in the box, a solvent was not used in connection with the analyses and therefore it is possible to identify compounds way down to C_4. Therefore, this difference between quantitative analyses and analyses in the box appears.
LODS = List of Dangerous Substances.
1 In this case it is not stated that the benzene content is below 0.1% and if that is not stated the labelling of the product should in principle be Carc2, R45. It is anticipated that the content of benzene is below 0.1%.

In English, petroleum distillates are also called TPH – Total Petroleum Hydrocarbons and the term covers a large family of several hundred chemicals that originate from crude oil (ATSDR, 1999a).

Petroleum products are complex mixtures of hundreds of different hydrocarbon compounds ranging from light, volatile, short chained organic compounds to heavy, long chained branched compounds. The exact composition depends on the source the crude oil comes from and the refining method (ATSDR, 1999a).

In the following, the health properties of petroleum products are described as a group because the data available for each compound as stated on the safety data sheet is extremely limited.

The identified petroleum products have all been identified as aliphatic hydrocarbons (i.e. no cyclic or ring-shaped organic compounds, and in addition it is anticipated that the aromatic content is insignificant or that the benzene content is below 0.1%).

In the following, the definition EC (Equivalent Carbon Number) Index is used. The EC Index represents the corresponding boiling points of hydrocarbons and is based on the equivalent retention times of a boiling point in a gas chromatographic column normalized in relation to ***n***-alkane. In other words, the EC number of a compound represents the number of carbon atoms that an imaginary ***n***-alkane would have in order to have exactly the same boiling point as the mentioned compound (Baars et al., 2001).

In connection with the short chained hydrocarbons, the health effects of ***n***-hexane are quite unique compared to petroleum products and petroleum mixtures. Therefore, ***n***-hexane specifically appears in the following text as some places refer to ***n***-hexane in the selected studies.

Occurrence and application

Almost all crude oil that is produced is prepared in refineries through distillation and pressure distillation for different fuel or non-fuel fractions (WHO, 1982).

Petroleum products are used for a wide range of applications such as heating, lighting, industrial solvents and detergents (Wikipedia, 2007a).

Limit value in working environment

The occupational threshold limit value of petroleum distillates with the chain length C_9-C_{14} (< 5% aromatic compounds) is 180 mg/m^3 (25 ppm) (The Danish Working Environment Authority, 2007). The limit values of hydrocarbons with shorter chain lengths, C_4 –C_8, can be found under either solvent naphtha (tentative) or for the actual hydrocarbons (pentane, hexane, heptane, octane, etc.).

Identification

Chemical name	Distillates (crude oil), hydrogen treated light	Naphtha (crude oil), hydrogen treated heavy	Naphtha (crude oil), hydrogen treated light	Crude oil gases, condensed, sweetened	Naphtha (crude oil), desulphur-ized light, dearoma-tized
Synonyms	Exxsol Kerosine Petroleum distillates	Exxsol Naphtha White spirit (type 3)	Exxsol Naphtha	Fuel gas Petroleum product	Exxsol heptane
CAS No.	64742-47-8	64742-48-9	64742-49-0	68476-86-8	92045-53-9
EINECS No.	265-149-8	265-150-3	265-151-9	270-705-8	295-434-2
Gross formula	-	-	-	-	-
Molecule structure	Chemical mixture	Chemical mixture	Chemical mixture	Chemical mixture	Chemical mixture
Legislation: List of Dangerous Substances (Executive Order 923, 2005)	Xn; R65	Xn; R65 (and Carc2; R45, if content of benzene > 0.1%)	Xn; R65 (and Carc2; R45, if content of benzene > 0.1%)	Fx; R12 (and Carc1; R45 Mut2; R46, if content of 1.3-butadien > 0.1%)	Xn; R65 (Carc2; R45, if content of benzene > 0.1%)
List of undesirable substances (Information from the Danish EPA no. 8, 2004)	No, not the specific CAS number, but other oil diverted substances				
MST Self classification (Danish EPA project no. 635, 2001)	No				

R12 Very inflammable
R45 Can be carcinogenic
R46 Can cause hereditary genetic damage
R65 Dangerous: Can give pulmonary damage when consumed

Physical-chemical properties

CAS No.	64742-47-8	64742-48-9	64742-49-0	68476-86-8	92045-53-9
State of matter	Liquid	Liquid	Liquid	Gas	Liquid
Molar weight (g/mol)	-	-	-	-	-
Melting point	< 0 °C	< 0 °C	< -60 °C	-183- -20°C	< -60 °C
Boiling point	150-290°C (1013 hPa)	155-217°C (1013 hPa)	55-140°C (1013 hPa)	-162- -0.5 °C (1013 hPa)	94-99°C (1013 hPa)
Vapour pressure	0.01-0.6 hPa (20°C)	0.35-145 hPa (20°C)	App. 26-246 hPa (20°C)	600-39000 hPa (20°C)	App. 53.7 hPa (20°C)
Octanol/water Distribution coefficient (log P_{OW})	App. 3.4-8.7 (calculated)	App. 2.1-6 (calculated)	App. 2.1-6 (calculated)	< 2.8 (calculated)	App. 4.4 (calculated)
Solubility in water	15 mg/l at 20°C	< 1000 mg/l at 20°C	< 1 mg/l at 20°C	24-61 mg/l at 20°C	< 0.1 vol% at 20 °C
Reference	IUCLID, 2000a	IUCLID, 2000b	IUCLID, 2000c	IUCLID, 2000d	IUCLID, 2000e

Absorption

Studies on humans who inhale ***n***-hexane vapours indicate that 20-25% of the inhaled amount is absorbed and remains in the body (ATSDR, 1999b). In ATSDR (1999a) it is concluded that the value prevails for aliphatic EC_5-EC_8-fractions. On the other hand, aliphatic $EC_{>8}$-EC_{16}-fractions can easily be absorbed in the body when inhaled (ATSDR, 1999a). Therefore, 100% absorption is anticipated for these fractions and that is also consistent with log P_{ow} typically being between -1 and 4 for hydrocarbons (meaning 100% absorption). In case of fractions with higher EC index, absorption during inhalation declines considerably.

Studies with rats show, that oral intake of aliphatic hydrocarbons declines when the molecular weight increases. There is complete absorption at low molecular weight, 60% absorption for C_{14}-hydrocarbons, 5% for C_{28}-hydrocarbons and hardly any absorption for $C_{>32}$-hydrocarbons (Albro and Fishbein (1970); Miller et al. (1996) in ATSDR (1999a)). However, that does not comply with information in Baars et al. (2001), who write that petroleum distillates with low molecular weight are absorbed poorly from the gastrointestinal tract.

Limited studies exist on the absorption of aliphatic hydrocarbons through the skin. The aliphatic EC_5-EC_8 fractions and EC_{16}-EC_{35} fractions seem to have very low potential for skin absorption (ATSDR, 1999a). According to an article on skin absorption of jet fuel[13] skin absorption is also very limited and it is not expected that absorption through the skin is considerable enough for this hydrocarbon fraction to give systematic effects (McDougal et al., 2000). No existing sources indicate percentage absorption – only that it is small. However, descriptions do exist of the hydrocarbons being able to be absorbed through the skin and in connection with the exposure calculations a 10% value is used for worst-case dermal absorption.

Distribution

When aliphatic hydrocarbons in the fraction EC_5-EC_8 have been absorbed, they are to a large degree distributed to tissue (especially fatty tissue) and organs in the body. Aliphatic $EC_{>8}$-EC_{16} fractions are also distributed to tissue and organs and can accumulate in fat (ATSDR, 1999a). Compared to aromatic hydrocarbons, aliphatic hydrocarbons tend to result in lower

[13] Jet fuels are medium distillates of petroleum crude oil with a boiling point between 150-300 °C (ATSDR, 1999a).

concentrations in the blood, higher concentrations in the brain and other organs when inhaled and they have a high potential for accumulating in fat. The hydrocarbon concentration in tissue ((blood, brain, kidneys, liver and fat) normally increases when the carbon number increases (Zahlsen et al. (1992) in ATSDR (1999a)).

Studies on humans and animals show that the low aliphatic hydrocarbon fractions EC_5-EC_8 (tests with ***n***-hexane) mainly are liberated through urine and only a small part is liberated through the expiratory air. When exposed to larger concentrations, the importance of the liberation through the expiratory air increases (ATSDR, 1999b). The higher aliphatic hydrocarbon fractions $EC_{>8}$-EC_{16} are only liberated slowly from the body (Pedersen et al. (1984) in ATSDR (1999a)).

Acute toxicity
Inhalation of vapours from petroleum products can result in central nervous system (CNS) depression (e.g. dizziness, intoxication, headache and tiredness) and cardiac arrhythmias (Baars et al., 2001).

Tests with 19 different petroleum products on rats resulted in oral LD_{50}-values from 4700 mg/kg bw to 17500 mg/kg bw, but six petroleum products did not result in death at concentrations of 23000 mg/kg bw (Baars et al., 2001).

Local irritation
Hydrocarbon mixtures (EC_5-EC_8 and $EC_{>8}$-EC_{16}) are irritating for skin as well as eyes (ATSDR, 1999a). An old study (Klauder & Brille (1947) in WHO (1982)) demonstrated that irritation from hydrocarbon mixtures declines when the boiling point increases. Mainly hydrocarbon mixtures with boiling points below 230 ºC are irritating. Hydrocarbon mixtures with aromatic content are more irritating than aliphatic hydrocarbons (WHO, 1982).

Skin tests with petroleum in mineral oil carried out on 34 persons showed that all test persons reacted (with irritated skin) at an 80% solution and nobody reacted at 40% solution (Tagami & Ogino (1973) in WHO (1982)). Petroleum distillates have a degreasing effect on the skin and repeated or long-term exposure can lead to dry and cracked skin (WHO, 1982).

According to the IUCLID documents of the mentioned petroleum distillates as stated on the safety data sheet of the products, the petroleum distillates are moderately irritating to irritating to the skin and not irritating to slightly irritating to the eyes (IUCLID, 2000 – a, b, c, d and e).

Allergy
According to the IUCLID documents of the mentioned petroleum distillates stated on the safety data sheet of the products, the petroleum distillates are non-sensitising (IUCLID, 2000 – a, b and c).

During tests on rats with 19 different types of petroleum products, only one single type of petroleum (heavy fuel oil with 0.8% sulphur content) demonstrated sensitising properties (Baars et al., 2001).

Long-term, repeated exposure and mutagenic effects
Consumption or long-term inhalation of petroleum can result in chemically conditioned pneumonia (ATSDR, 1999a).

Inhalation studies with rats show that petroleum products can result in kidney and lung effects. A 90-day study with rats and mice that constantly were exposed to marine diesel vapour in concentrations of 150-750 mg/m^3 resulted in dose dependent nephropathy (kidney disease) but only in male rats. Other corresponding or long-term tests show the same effect (Baars et al., 2001). According to ATSDR (1999a) it is mainly ***n***-hexane that seems to result in nephropathy whereas other compounds in the EC_5-EC_6 fraction do not seem to result in nephropathy by inhalation. Correspondingly it is stated in ATSDR (1999a) that exposure to the higher hydrocarbons $EC_{>8}$-EC_{16} also resulted in nephropathy in male rates but the effect is regarded to be of doubtful relevance to humans.

Petroleum products (heavy fuel oils) have demonstrated effects of hereditary genetic damage in rats, in the dam as well as foetus at doses of 8 and 30 mg/kg bw/day (LOAEL) through exposure of the skin. In another study with rats that was to demonstrate effects of hereditary genetic damage a NOAEL (No Observed Adverse Effect Level) of > 250 mg/kg bw/day was demonstrated by exposure on the skin (for both sexes) (Baars et al., 2001). According to ATSDR (1999a) commercial hexane (i.e. mixture of ***n***-hexane, 3-methyl pentane, methyl cyclopentane, 2-methyl pentane, cyclo hexane, 2,3-dimethyl butane etc.) demonstrated effects of hereditary genetic damage in chronic studies with mice. In addition, liver tumours were developed in the female mice, which indicates carcinogenic potential.

In 1997, TPHCWG (Total Petroleum Hydrocarbon Criteria Working Group) determined specific reference doses (RfD) for petroleum products. RfD stands for Reference Dose and is the maximum acceptable dose of a chemical. Normally, RfD (or TDI) appears by dividing the NOAEL value with a safety factor of 1000, 100 or 10, respectively, depending on the quality of the data from the NOAEL value.

The reference dose for C_5-C_8 aliphatic hydrocarbons was determined in the light of ***n***-heptane and commercial hexane. According to TPHCWG (1997), the reference dose of ***n***-hexane is 0.06 mg/bw kg/day with neurotoxicity as the critical effect. TPHCWG (1997) states, that ***n***-hexane has unique toxic properties compared to petroleum products and petroleum mixtures, and therefore it is concluded that the reference dose for ***n***-heptane should be used instead. It is calculated to be 2 mg/kg bw/day as ***n***-heptane on the basis of tests seems to be 38 times less neurotoxic than ***n***-hexane. However, tests with commercial hexane (mixture as mentioned above with 53% hexane) result in a reference dose of 5 mg/kg bw/day. TPHCWG states the value to be the recommended reference dose for petroleum mixtures for C_5-C_8, of course, if the total hexane amount is below 53%.

Correspondingly, TPHCWG (1997) states a reference dose of 0.1 mg/kg bw/day for $C_{>8}$-C_{16} aliphatic petroleum products in the light of calculations from several studies. In this case, the critical effect is hepatic and hematologic changes (i.e. cell changes in liver and blood). Three studies state the same reference dose of 0.1 mg/kg bw/day.

Baars et al. (2001) discuss TDI values (Tolerable Daily Intake) for a long range of substances. Among them are petroleum distillates (TPH). Baars et al. (2001) state a TDI value of 2 mg/kg bw/day for the C_5-C_8 fraction and a TDI value for the $C_{>8}$-C_{16} fraction of 0.1 mg/kg bw/day.

IARC (IARC 47, 1998 and IARC 45, 1998) state the following assessments of a number of petroleum distillates:

- Petroleum distillates – non-classifiable with regard to carcinogenicity in humans (IARC group 3)
- Petroleum – non-classifiable with regard to carcinogenicity in humans (IARC group 3)
- Benzine – may be carcinogenic to humans (IARC group 2B)
- Jet fuel – non-classifiable with regard to carcinogenicity in humans (IARC group 3)
- Marine diesel fuel – may be carcinogenic to humans (IARC group 2B)
- Light diesel fuel – non-classifiable with regard to carcinogenicity in humans (IARC group 3)
- Heavy fuel oils – may be carcinogenic to humans (IARC group 2B).

As stated in Table 8.4, most of the petroleum products stated on the safety data sheets of the products for interior car care have to be labelled with R45 according to the List of Dangerous Substances, i.e. may cause cancer. However, there are notes to the substances describing that the classification carcinogenic can be left out for the petroleum distillates if it can be demonstrated that the substance contains less than 0.1% (w/w) benzene. However, none of the petroleum products are market with R45 according to the safety data sheets and therefore it must be anticipated that they contain less than 0.1% benzene (only a few safety data sheets directly state that the content of benzene is less than 0.1%).

Critical effect

On the basis of Baars et al. (2001), who reassessed TDI for petroleum products, the found TDI values of 2 and 0.1 mg/kg bw/day are used for the C_5-C_8 fraction and $C_{>8}$-C_{16} fraction, respectively. The critical effect of the C_5-C_8 fraction is neurotoxic effects and hepatic and haematological changes (cell changes in liver and blood) for the $C_{>8}$-C_{16} fraction.

8.4 Health assessment of butane

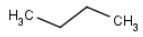
Occurrence and application

Butane is used widely and for many applications. Butane is used as lighter gas, as propellant in aerosol containers/spray cans, in small blowtorches. Butane is also used for organic synthesis (e.g. for the production of ethylene) and as raw material for the production of synthetic rubber. Pure butane is used to calibrate instruments and as additive in foodstuffs (IPCS, 1997), (TOXNET HSDB).

Limit value in working environment

The occupational threshold limit value of butane is 1200 mg/m^3 (500 ppm), (DWEA, 2007).

Identification

Chemical name	Butane
Synonyms	*n*-butane butylhydrid methylethylmethane
CAS No.	106-97-8
EINECS No.	203-448-7
Gross formula	C_4H_{10}
Molecule structure	
Legislation: List of Dangerous Substances (Executive Order 923, 2005) List of Undesirable Substances (Information from DEPA no. 8, 2004) DEPA Self classification (DEPA project no. 635, 2001)	 Fx; R12 (Extremely flammable) When pure butane is in question i.e.content of 1.3-butadien < 0.1%, Otherwise also Carc1 R45 (May cause cancer) and Mut2 R46 (May cause heritable genetic damage). No No

Physical-chemical properties

State of matter	Colourless gas	Chemfinder
Molar weight (g/mol)	58.123	Chemfinder
Melting point	-138 °C	TOXNET ChemIDplus
Boiling point	- 0.45 °C	Chemfinder
Vapour pressure	1820 mmHg	TOXNET ChemIDplus
Octanol/water distribution coefficient (log P_{OW})	2.89	TOXNET ChemIDplus
Solubility in water	61.2 mg/L (at 25 °C)	TOXNET ChemIDplus

Absorption and distribution

Inhalation studies with mice and rats that were given lethal butane doses show that butane is absorbed and distributed to i.a. fatty tissue, brain, spleen, liver and kidney (TOXNET HSDB), (IUCLID, 2000f).

Dermal absorption of butane vapours has not been reported. Dermal absorption of butane is not expected to take place to a large degree as skin contact only is brief due to the volatility of butane (TOXNET HSDB).

Butane is very volatile and therefore it must be expected that butane also can be exhaled with the expiratory air (TOXNET HSDB).

Studies have not been found that show the absorption of butane in percent for skin absorption or inhalation. In connection with the exposure calculations 100% absorption via inhalation is therefore used and 10% is used for skin contact (based on butane being volatile) as worst-case.

Acute toxicity

Butane mainly shows health damaging effects by displacing oxygen, i.e. large concentrations of butane can result in suffocation. Concentrations of 15% butane in the air can result in sensitisation of the heart muscles and dysrhythmias (seen in humans) (IPCS, 1997).

Exposure to smaller amounts of butane can result in symptoms such as i.a. euphoria, psychic excitement, dimmed sight and speech, coughing and vomiting (IPCS, 1997). Butane is used as lighter gas and the effects of butane have made it popular to sniff lighter gas. Exposure to larger amounts of butane can give rise to hallucinations, delusions, tinnitus, CNS depression, lethargy, headache, coma and, finally, sudden death due to lack of oxygen (IPCS, 1997).

Tests with rats exposed to different concentrations of butane for 4 hours demonstrated a LC_{50} value of 658 mg/l (corresponding to 658.000 mg/m^3). After exposure it was ascertained that butane accumulates in several organs. A similar test with mice exposed to different concentrations of butane for 2 hours gave a LC_{50} value of 680 mg/l (corresponding to 680.000 mg/m^3) (IUCLID, 2000f). In comparison, the limit value of butane is 1200 mg/m^3 (DWEA, 2007).

Local irritation
According to IUCLID (2000f), butane does not irritate the eyes. IPCS (1997) states that butane vapours can seem irritating to the throat if condensed butane gas is sprayed directly into the throat. Butane sprayed directly on the skin from a spray can result in frostbite (TOXNET HSDB).

Analysis project no. 49 of the Danish Environmental Protection Agency "Emission of chemical substances from products made of exotic wood" (Witterseh, 2004) states a LCI value (Lowest Concentration of Interest) of 200 mg/m^3 for butane. That LCI value is developed especially for indoor climate considerations. The critical effect from that value is irritation.

Allergy
No information was found about possible sensitising properties of butane.

Long-term, repeated exposure and mutagenic effects
In a 90-day inhalation test with rats, rats were exposed to a concentration of 1017 and 4489 ppm, respectively, (corresponding to 2.417 and 10.670 mg/m^3 according to the conversion formula shown in Box 8.1). No deaths or other significant toxicological effects were observed. NOAEL was determined to 4489 ppm (or 10.670 mg/m^3). The subsequent check of the animals showed mild hydrocarbon kidney effects, but there were no signs of kidney effects. The test was not carried out with pure butane but with two gas mixtures of 50% pentane and 50% butane, respectively, and 50% isopentane and 50% isobutane (IUCLID, 2000f).

In a 21-day inhalation test with rats, no significant toxic effects were observed at concentrations of 0.12 mg/l, 1, 15 mg/l and 11.8 mg/l, respectively, of a mixture consisting of 25% butane and the rest isobutane, pentane and isopentane. The duration of exposure was 6 hours per day, 5 days a week. In the light of the study, NOAEL is determined to 11.8 mg/l (or 11.800 mg/m^3) (IUCLID, 2000f).

Ames test with butane is negative i.e. that butane does not show genetic effects (IUCLID, 2000f).

No information was found about tests showing hereditary genetic damage.

IARC has not assessed butane in relation to carcinogenicity. If the content of 1.3-butadien is more than 0.1%, then butane will have to be classified as carcinogenic.

Critical effect
The critical effect of butane seems to be CNS depression. However, no information has been found about levels concerning when damages arise (besides death). Only a few long-termed tests are described in literature. The tests were not carried out with butane only, but with a mixture of butane, pentane, isobutane and isopentane.

The tests stated a NOAEL of 11.8 mg/l (highest dose applied during tests – none of the tests gave toxic effects). The value is not stated per kg body weight. If it is anticipated, that a rat weighs max. 520 g[14] and that the respiratory volume of a rat is max. 130 ml/min[15], then that will correspond to a NOAEL of 4.248 mg/kg bw/day (Ace Animals Inc., 2007), (Rat Forum, 2007). Corrections have not been made for the fact that the rats, as described in the test, only inhaled the mixture 6 hours per day and 5 days a week.

If a safety factor of 1000 is used (10 for interspecies variation, 10 for intraspecies variation and 10 for sub-chronic to chronic), then that gives a tolerable dose of 4.2 mg/kg bw/day. That TDI value is used in the exposure calculations.

8.5 Health assessment of ethyl acetate

Occurrence and application
Ethyl acetate appears as a natural flavouring agent in i.a. sugar cane, rum and whisky (Jensen, 2003). In addition, it also appears naturally in wine (Department of the Environment and Water Resources Australia, 2006). The most important application of ethyl acetate regarding amount is as technical solvent in varnish and lacquer products for surface treatment. Besides, it is also used as solvent for plastics, fatty substances, nitrocellulose, synthetic resin and colours, e.g. for serigraphy. A smaller amount is used in laboratories or for chemical synthesis of perfume, medicine, photo chemicals and artificial silk and leather (Jensen, 2003).

Other consumer products that contain ethyl acetate comprise car paint, ink, lubricating oils, moisturizing lotion, nail varnish, nail varnish remover, paint diluents and artificial flavour additives (Department of the Environment and Water Resources Australia, 2006) and products for interior car care.

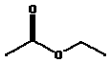
In 1985, global production of ethyl acetate amounted to app. 300.000 tons. The annual consumption of ethyl acetate in Denmark has declined from 3.370 tons in 1984 to 1.140 tons in 1999, but due to a reduced limit value for other solvents over recent years it is possible that the consumption of ethyl acetate might increase again (Jensen, 2003).

[14] Weight of Sprague Dawley rats which the test is based on is 250-300 g for female rats and 450-520 g for male rates according to http://aceanimals.com/SpragueDawley.htm.
[15] Found on http://gray.hmgc.mcw.edu/pipermail/rat-forum/2000-April/000531.html. 130 ml/min corresponds to app. 2% of the respiratory volume of a human at rest.

Limit value in working environment

According to the Danish Working Environment Authority limit values for air pollution the limit of ethyl acetate is 540 mg/m^3 (150 ppm) (Danish Working Environment Authority, 2007).

Identification

Chemical name	Ethyl acetate
Synonyms	Ethyl acetate ester Acetoxy ethane Acetidin
CAS No.	141-78-6
EINECS No.	205-500-4
Gross formula	$C_4H_8O_2$
Molecule structure	
Legislation: List of Dangerous Substances (Executive Order 923, 2005) List of Undesirable Substances (Information from DEPA no. 8, 2004) DEPA Self classification (DEPA project no. 635, 2001)	 F; R11: Highly flammable XI: R36: Irritating to eyes; R66: Repeated exposure may cause skin dryness or cracking; R67: Vapours may cause drowsiness and dizziness. No No

Physical-chemical properties

State of matter	Colourless liquid with a pleasant fruity smell.	Chemfinder
Molar weight (g/mol)	88.106	Chemfinder
Melting point	-83.6 °C	Chemfinder
Boiling point	77.1 °C	Chemfinder
Vapour pressure	93 hPa at 20 °C 124.79 hPa at 25 °C	IUCLID
Octanol/water distribution coefficient (log P_{OW})	0.71	IUCLID
Solubility in water	Moderately water-soluble. 8 g/100 ml	Chemfinder

Absorption and distribution

Ethyl acetate is easily absorbed through the skin, lungs and the gastrointestinal tract. However, a considerable amount of ethyl acetate as liquid on the skin will evaporate before it passes through the skin as the substance in volatile (Jensen, 2003).

Ten men and women (between 18 and 25 years) were in a test exposed to 344-501 mg ethyl acetate/m^3 air for 4 hours. The results demonstrated intake via the respiratory passages of 63.2% (men) and 56.7% (women) and elimination through the respiratory passages of 3% (men) and 2.5% (women). In addition, there was a respiratory retention of 60.2% (men) and 54.1% (women). According to the authors of the study, the results indicated that ethyl acetate quickly is transformed in the body (IUCLID, 2000g). That is confirmed by Jensen (2003) who states that ethyl acetate is an ester that

decomposes (hydrolyzed) quickly in the body by means of enzymes to ethanol and acetic acid which again can be degraded to CO_2 and water.

A 63.2 % absorption of ethyl acetate via inhalation is used as worst-case in the calculations. No immediate data exists on absorption via skin contact. The only existing information is, that it is "easily" absorbed through the skin (Jensen, 2003), and that a considerable amount of ethyl acetate evaporates from the skin before absorption. However, in the calculations a value of 100% is used as worst-case.

Acute toxicity

Short-term exposure of high concentrations of ethyl acetate first of all results in irritation of eyes, nose and throat. Then come headache, nausea, vomiting, sleepiness and unconsciousness (Department of the Environment and Water Resources Australia, 2006).

According to Jensen (2003) the acute toxicity of ethyl acetate in humans and animals is very low and therefore ethyl acetate does not have to be classified as harmful. Nevertheless, the toxicity should not be underestimated as intake through the mouth can cause inflammation of the throat, stomach ache and diarrhea. Exposure to very high concentrations can result in liver damages (Jensen, 2003) and anaesthesia (Department of the Environment and Water Resources Australia, 2006).

The U.S. National Toxicology Program has made the below summary of LC_{50} values related to acute toxicity of ethyl acetate. The values are based on information in NTP (2006).

Study type	Rute	Type	Result	Unit
LC50	Inhalation	Mouse	45	$mg/m^3/2H$
LC50	Inhalation	Rat	1.600	ppm/8H
LCLo	Inhalation	Cat	61	gm/m^3
LCLo	Inhalation	Guinea pig	77	$mg/m^3/1H$
LD50	Intraperitoneal	Mouse	709	mg/kg
LD50	Oral	Guinea pig	5.500	mg/kg
LD50	Oral	Mouse	4.100	mg/kg
LD50	Oral	Rabbit	4.935	mg/kg
LD50	Oral	Rat	5.620	mg/kg
LD50	Subcutaneous (hypodermic needle)	Cat	3.000	mg/kg
LD50	Subcutaneous (hypodermic needle)	Guinea pig	3.000	mg/kg
LDLo	Subcutaneous (hypodermic needle)	Rat	5.000	mg/kg

Local irritation and allergy

Ethyl acetate has degreasing properties and therefore it is moderately irritating to skin, mucous membrane and respiratory passages. Toxic as well as allergic skin eczema can appear. At air concentrations of 200 ppm (720 mg/m^3) the smell of the vapour is unpleasant, while at 400 ppm (1440 mg/m^3) mild irritation of the eyes, nose and throat appeared (Jensen, 2003). According to IUCLID (2000g) a study showed irritation of the eyes in humans exposed to 400 ppm for 72 hours. However, humans will typically experience considerable irritation at that concentration and therefore they will not remain exposed to such a concentration for a very long time (TOXNET, HSDB).

According to HSDB (TOXNET), a study did not demonstrate irritation or sensitisation during a skin test on 25 persons (exposure of a 10% ethyl acetate solution in petroleum).

Long-term, repeated exposure and mutagenic effects
Long-term exposure to ethyl acetate can result in "misty vision" and damages on lungs, heart, liver and kidneys (Department of the Environment and Water Resources Australia, 2006). In addition, long-term dermal exposure to ethyl acetate can make the skin dry out and crack (NTP, 2006).

Very limited knowledge exists on the possible long-term effects of ethyl acetate at low exposure; however, the substance does not seem to have reproduction damaging effects but many good long-term tests exist that could clarify possible hereditary genetic damage or cancer risks. As ethyl acetate is quickly transformed in the body to rather harmless compounds (ethanol and acetic acid) it is not likely that the substance under normal working environment conditions would have substantial chronic effects (Jensen, 2003). According to HSDB (TOXNET) and Dutia (2004) ethyl acetate also has the reputation of being one of the least toxic of the volatile organic solvents.

A study on rats was reported in IRIS and it demonstrated an oral reference dose of 0.9 mg/kg bw/day based on a NOEL value of 900 mg/kg bw/day and a safety factor of 1000 as it is a sub-chronic study (extra safety factor of 10 from sub-chronic study to chronic). The investigated factors were i.a. body weight and food intake, clinical signs of toxicity, mortality and influence on blood and urine. The study took 90 days and involved 120 rats that (in groups of 30) were exposed to 0, 300, 900 and 3600 mg, respectively, of ethyl acetate/kg/day. At doses of 3600 mg/kg/day there were significant toxic effects that resulted in weight loss, at doses of 900 mg/kg/day there were no effects.

In another study with mice, reference is made to a NOAEL value of 0.02 mg/L air. For a period of 90 days the mice were exposed to ethyl acetate via inhalation (doses: 0; 0.002; 0.01; 0.043 mg/L air). At 0.01 and 0.043 mg/L there were after 15 and 30 days effects related to muscular activity and the internal organs. Therefore, a NOAEL value of 0.02 mg/L air was determined.

Critical effect
The critical effect of ethyl acetate is effects on blood, urine, body weight and food intake. The described NOEL value of 900 mg/kg bw/day above (reference dose of 0.9 mg/kg bw/day) is used in the subsequent calculations.

8.6 Health assessment of 1-methoxy-2-propanol (PGME)

Occurrence and application
In 2003, a total of 188.000 tons of PGME was produced in Europe. From 2001- 2003 production increased - mainly due to increased export. The superior demand in the EU is constant (EU Risk Assessment, 2006).

In the EU, PGME is mainly used as solvent in paint and coatings (38.5%), printer colours (8.5%), washing powder and detergents (5.3%), leather agents (1.3%), the electronic industry (1%), agriculture (0.8%), cosmetics/personal care (0.7%), adhesives (0.2%), metal cleaning (0.2%) and oil dispergents (0.1%). In addition, a large amount is used (42%) in synthesis of other chemicals. The figures are based on information from the year 2001 to 2003 (EU Risk Assessment Report, 2006).

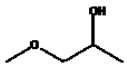
Other consumer products containing PGME, i.a. comprise paint, varnish, car care products, window cleaning agents, oven cleaner, pesticides, dyes and ink, and swimming pool cleaners (OECD SIDS, 2001). A study of 150.000 products in Switzerland demonstrated that 1.5% of the products contained PGME, and the largest part of the products contained between 1 and 10% PGME, while a few contained up to 10-50% (EU Risk Assessment Report, 2006).

It should be mentioned that PGME typically is found in two isomers: 1-methoxy-2-propanol and 2-methoxy-1-propanol, of which the latter is anticipated to be more toxic as it can be transformed to 2-methoxy propionic acid. However, commercial PGME typically consists of 95% of the non-toxic ismers (Tobiassen et al., 2003). The main part of toxicological studies concerning PGME, concern the non-toxic isomer to which the below studies refer unless otherwise stated.

Limit value in working environment

According to the limit value list of the Danish Working Environment Authority concerning air pollution the limit for 1-methoxy-2-propanol is 50 ppm (185 mg/m^3) (DWEA, 2007). According to HSDB the odour limit of PGME is 10 ppm (37 mg/m^3).

Identification

Chemical name	Propylene Glycol Monomethyl ether
Synonym	1-methoxy-2-propanol 1-methoxy-2-hydroxy propane 1-methoxypropan-2-ol Polypropylene glycol methyl ether PGME
CAS No.	107-98-2
EINECS No.	203-539-1
Gross formula	$C_4H_{10}O_2$
Molecule structure	
Legislation: List of Dangerous Substances (Executive Order 923, 2005) List of Undesirable Substances (Information from DEPA no. 8, 2004) DEPA Self classification (DEPA project no. 635, 2001)	 R10: S(2-)24 No No

Physical-chemical properties

State of matter	Clear, colourless liquid with ether-like smell	EU Risk Assessment Report (2006)
Molar weight (g/mol)	90.1218	Chemfinder
Melting point	-97 °C	Chemfinder
Boiling point	119.6 °C	Chemfinder
Vapour pressure	11.5 hPa at 20 °C 16.4 hPa at 25 °C	IUCLID (2000h) EU Risk Assessment Report (2006)
Octanol/water distribution coefficient (log P_{OW})	-0.437 -0.49	IUCLID (2000h) EU Risk Assessment Report (2006)
Solubility in water	10 g/100 ml at 19 °C	Chemfinder

Absorption and distribution

A report from the Danish Environmental Protection Agency (Tobiassen et al., 2003) on health hazardous effects of selected pesticide compounds, among them PGME, states that PGME seems to be absorbed via all ways of exposure. Toxicological studies have not indicated that an accumulation of the substance takes place. Elimination mainly takes place by demethylation and oxidation to CO_2, which subsequently is exhaled. Conjugation and liberation via the urine also take place but are less important (Tobiassen et al., 2003).

The above is confirmed by a test on rats that received one single dose radioactively marked PGME. Within 48 hours, the rats liberated 50-60% PGME as CO_2 in the expiratory air, while 20% was liberated via the urine as glucoronid conjugators, sulphate conjugators and propylene glycol (Miller et al., 1983 i OECD SIDS, 2001). Another study has demonstrated that after 10 tests with 6 hours of exposure to PGME (inhalation, 3.000 ppm), PGME was completely eliminated in rats 24 hours after the last exposure (Margot and Nolan, 1987 i OECD SIDS, 2001).

A study (Johansson, 1990) mentions a test where drugged rats absorbed 87% of PGME by inhalation. The rats were exposed to 1000 ppm.

Other studies concerning absorption via inhalation do not immediately exist and therefore it is as worst-case considered to be 100%. It should be noted that the studies mentioned above indicate that PGME is liberated from the body completely within 24-48 hours (however, based on tests with rats).

In relation to skin absorption, a study with human skin demonstrated an absorption rate of 1.17 mg/cm^2/hour for undiluted PGME (Dugard et al., 1984). According to Johansson (1990) a test has been reported with percutaneous intake (through the skin) of PGME ***in vitro*** (isolated epidermis from humans), where intake through the skin was 1.2 mg/cm^2 per hour. That value is not immediately applicable in the exposure calculations and therefore a dermal absorption of 100% is used as worst-case.

PGME vapours that are exposed to sunlight are decomposed rather quickly as a result of reactions with photo chemically created hydroxyl radicals. The half-life period of PGME is in the air estimated to 3.1 hour (OECD SIDS, 2001).

Acute toxicity

The acute toxicity of PGME is anticipated to be low. Oral LD_{50} values for PGME in experiments with rats were found from >5.000 mg to 6.100 mg/kg (BASF AG, 1964, 1979; Rowe et al., 1954; Smyth et al., 1941, 1962 in

OECD SIDS, 2001). Oral LD_{50} values for other animal studies have turned out to be 10.800 mg/kg (mice), 1.840-5.300 mg/kg (rabbits) and 4.600-9.000 mg/kg (dogs). LD_{50} values for PGME conveyed via the skin on rabbits was 13-14 g/kg (OECD SIDS, 2001). The study by Tobiassen et al. (2003) confirms that PGME has a low acute toxicity.

Investigations where two people inhaled 50-1000 ppm (2050 ppm in one single test) PGME were carried out. Exposure duration for concentrations of up to 250 ppm took up to 7 hours, while exposure took max. 2 hours for concentrations of up to 2050 ppm. The investigations showed that at 10 ppm the smell was noticeable. At concentrations exceeding 100 ppm the test persons experienced a temporary odour irritation, but after 2 hours they experienced minor irritation in the eyes. At concentrations exceeding 300 ppm the persons experienced mild eye and nose irritation within the first 5 minutes, but after 1 hour the irritations were almost unbearable. Severe irritation was measured at 750 ppm, whereas 1000 ppm indicated CNS depression. Neurological, clinical, chemical and general medicine studies have not shown significant abnormalities. However, all test persons experienced a quick "odour habituation" which can result in a risk for people who are exposed to high doses without being conscious about it. In the meantime, PGME vapours are believed to contain sufficient warnings (heavy smell) and therefore that should not happen (IUCLID, 2000h).

Human exposure to PGME in a concentration exceeding 150 ppm is expected to be self-regulating due to irritation effects (OECD SIDS, 2001). According to a study from the United States and Canada, it is recommended that the use of PGME should not exceed 100 ppm in an 8 hour period, while the limit according to the Danish WEA is 50 ppm.

Local irritation and allergy

In animal studies (rabbits) PGME was found to be non-irritating for the skin and less irritating for the eyes (OECD SIDS, 2001). According to IUCLID (2000h) less irritation of the eyes has been reported after exposure (of rabbits) with PGME (no values stated).

IUCLID (2000h) reports one single test with guinea pigs where PGME is non- sensitising.

Long-term, repeated exposure and mutagenic effects

Laboratory animals exposed to PGME via inhalation developed effects such as CNS depression (anaesthesia), adapted changes in the liver, and reduced weight increase. The NOAEL values range from 300 to 5.000 ppm in tests with rats that took from 11 days to 6 months (OECD SIDS, 2001).

Tests with monkeys that inhaled PGME during a period of 6 months resulted in NOEL values of 800 ppm (Rowe et al., 1954 in OECD SIDS, 2001).

With regard to reproductive effects a NOAEL value of 300 ppm (adult rats) and 1000 ppm (rat offspring) was reported in a two-generation study with exposure to PGME via inhalation (Liberacki et al., 1997[16]; Carney et al, 1999 in OECD SIDS, 2001). The 300 ppm corresponded to 396 mg PGME/kg

[16] Original source could not be procured but a description of the test method was found on the following site:
http://www.americanchemistry.com/s_acc/sec_directory.asp?CID=1478&DID=5629

bw/day (the figures are stated in the source). At that value, there were no effects in the parent rats. A NOEL value of 1.325 mg/kg/day is stated for effects on rat offspring. However, it should be mentioned that a solution of PGME was used where 2% consisted of the previously mentioned ß-isomer of PGME that can be transformed to 2-methoxy propionic acid (2-MPA, which is a known animal teratogenic agent, i.e. causes malformation on foetuses).

Another study demonstrated a NOEL of 200 to 600 ppm for inhalation of PGME, 6 hours a day for 10 days. The study has not been further described (Doe et al., 1983 in OECD SIDS, 2001).

A study with rats exposed to PGME via inhalation showed a NOAEL value of 1.500 ppm (for dam), 1.500 ppm (teratogenically) and 3.000 ppm (embryotoxic, i.e. harmful to the foetus) (Hanley et al., 1984 in OECD SIDS, 2001). The effects observed at 3.000 ppm were minor CNS depressions and reduced appetite and weight.

Laboratory animals exposed to dermal exposure of PGME developed skin effects such as peeling, minor inflammation and thickening of the skin. In addition, large dermal doses can result in narcosis (narcosis of the body up to anaesthesia) and death. Two studies in which PGME was applied to the skin showed a NOEL value of < 1000 mg/kg (3 week study) and a NOEL value of 2 ml/kg (corresponding to app. 2000 mg/kg) (90-day study) (Calhoun and Johnson, 1984; Rowe et al., 1954 in OECD SIDS, 2001). Another study demonstrated a NOEL of 1000 mg/kg for systematic effects, while a LOEL of 4 ml/kg turned out to give a weak narcotic effect.

In general, studies with laboratory animals demonstrated that PGME is neither teratogenic nor embryotoxic when it is inhaled or after intake. In addition, PGME is not assumed to be carcinogenic (OECD SIDS, 2001). Furthermore, the study by Tobiassen et al. (2003) concludes that PGME is anticipated to have low systematic toxicity and that the critical values are irritation of eyes, CNS depression and effects on mucous membrane and respiratory passages.

Critical effect
An inhalation effect related to irritation effects on the eyes after two hours of exposure is 100-150 ppm (374-560 mg/m^3 value converted according to the formula in Box 8.1).

As further information concerning the study that states a NOAEL value of 200 ppm cannot be found, focus is on the study that demonstrates a NOAEL value of 396 mg/kg/day (determined from 300 ppm) for reproductive effects in a rat test as other studies also have stated effects at values around 300 ppm.

If a safety factor of 100 is used (10 for interspecies variation and 10 for intraspecies variation) that gives a tolerable dose of 3.96 mg/kg bw/day. That TDI value is used in exposure calculations.

8.7 Health assessment of benzyl chloride

Occurrence and application
Benzyl chloride is used as intermediate substance in organic synthesis for the production of benzyl alcohol, dyes, perfumes, resin, softening agents

(phthalates), pesticides and as a preliminary stage to penicillin (OECD SIDS, 1998), (TOXNET HSDB).

In 1993, the production of benzyl chloride in Japan was app. 7.800 tons (OECD SIDS, 1998), in 1982 the production in the USA was estimated to be 49.900 tons and in 1989 the industry capacity in the Western world was estimated to be 144.200 tons/year (TOXNET HSDB).

Limit value in working environment

The occupational threshold limit value of benzyl chloride is 5 mg/m^3 (1 ppm), (Danish Working Environment Authority, 2007).The limit value is a threshold value that never must be exceeded. Benzyl chloride is marked as carcinogenic on the limit value list of the Danish Working Environment Authority.

Identification

Chemical name	Benzyl chloride
Synonyms	Chloromethyl benzene chlorophenylmethane α-chlor toluene α -tolyl chloride
CAS No.	100-44-7
EINECS No.	202-853-6
Gross formula	C_7H_7Cl
Molecule structure	
Legislation: List of Dangerous Substances (Executive Order 923, 2005) List of Undesirable Substances (Information from DEPA no. 8, 2004) DEPA Self classification (DEPA project no. 635, 2001)	 Carc2;R45 (May cause cancer) Xn;R22-48/22 (Harmful if swallowed. Harmful: danger of serious damage to health by prolonged exposure if swallowed) T;R23 (Toxic by inhalation) Xi;R37/38-41 (Irritating to respiratory system and skin. Risk of serious damage to eyes) Yes No

Physical-chemical properties

State of matter	Colourless to slightly yellow liquid with unpleasant smell	TOXNET HSDB
Molar weight (g/mol)	126.9	TOXNET HSDB
Melting point	-45 °C -43 °C	TOXNET ChemIDplus OECD SIDS, 1998
Boiling point	179 °C	TOXNET ChemIDplus
Vapour pressure	1.23 mmHg at 25 °C	TOXNET ChemIDplus
Octanol/water distribution coefficient (log P_{OW})	2.3 2.66	TOXNET ChemIDplus OECD SIDS, 1998
Solubility in water	525 mg/l at 25 °C App. 1.2 g/l	TOXNET ChemIDplus OECD SIDS, 1998

Absorption and distribution

Tests with rats, where radioactive marked benzyl chloride was given orally, demonstrated that benzyl chloride is absorbed through the gastrointestinal

tract. The concentrations were highest in the stomach, stomach content, ileum and the duodenum. 76% of the intake amount was liberated through the kidney in the course of 72 hours. Around 7% was liberated through the expiratory air as CO_2, while less than 1.3% existed as benzyl chloride or benzyl chloride metabolic in the expiratory air in the course of the 72 hours. Benzyl alcohol, benzaldehyde and acetylsysteine were found as metabolic of benzyl chloride in the urine (Saxena and Abdel-Rahman (1989) in OECD SIDS, 1998).

No information was found about the absorption of benzyl chloride through the skin or during inhalation. Therefore, 100% dermal absorption and 100% absorption during inhalation is anticipated in the exposure calculations which also is consistent with the molar weight and log P_{ow} of benzyl chloride that are below 500 g/mol and between -1 and 4, respectively.

Acute toxicity
Benzyl chloride is labelled toxic by inhalation (R23) and Harmful: danger of serious damage to health by prolonged exposure if swallowed (R48/22).

Oral LD_{50} values are 1231 mg/kg bw for rats and 1500 mg/kg bw for mice. In connection with inhalation, the LC_{50} values are 740 mg/m^3 and 390 mg/m^3 for rats and mice, respectively (OECD SIDS, 1998).

Local irritation and allergy
Benzyl chloride is regarded as irritating for skin, eyes and respiratory organs. 0.5 ml benzyl chloride on rabbit skin for 24 hours resulted in a considerable blush, swelling and subsequent cell damage. Rabbits and cats exposed to 462 mg/m^3 (95 ppm) 8 hours/day for 6 days gave symptoms of eye and respiratory irritation. Irritation of mucous membrane and infection in the conjunctivitis of the eye appeared when exposed to benzyl chloride for 2 hours in concentrations from 100-1000 mg/m^3 (21-205 ppm) (however, it has not been stated for which animals) (OECD SIDS, 1998).

IUCLID (2000i) as well as OECD SIDS (1998) refer to certain animal tests that all indicate that benzyl chloride is sensitising. IUCLID (2000i) reports of minimum sensitising doses of 0.0006 mg/kg bw for rats (given as 30 daily oral doses).

Long-term, repeated exposure and mutagenic effects
In a test that took 26 weeks, rats were orally given concentrations of between 6.4 and 107.1 mg benzyl chloride/kg bw/day. Doses were given 3 times a week. All rats that were given doses of 53.6 and 107.1 mg/kg bw/day, respectively, died within two-three weeks. The cause of death was mainly acute and chronic infection in the gastritis but edema of the heart and acute cell death in the heart muscles was also observed - often in the dead rats. At lower doses, hyperplasia also appeared in the stomach after new cell formation and cell death in the hearth muscles (resulted in death). NOEL was set to 12.9 mg/kg bw/day for male rats and 6.4 mg/kg bw/day for female rats (OECD SIDS, 1998).

Reproduction studies with rats, where doses of 50 and 100 mg/kg bw/day, respectively, were given to the dam from day 6 to 15 of the pregnancy showed no toxic effects in the dam. The number of live born foetuses and the average birth weight were not influenced. The only substantial change was a reduced birth length at doses of 100 mg/kg bw/day. NOEL was therefore set to 50 mg/kg bw/day for foetus toxicity (OECD SIDS, 1998).

Benzyl chloride has demonstrated genotoxic effects in Ames test (IUCLID, 2000i).

IARC (1999) assesses that there is sufficient waterproof in experimental animals of the carcinogenic properties of benzyl chlorides. However, the IARC assessment only covers a simultaneous exposure of chlormethyl benzene (benzyl chloride), dichlormethyl benzene, trichlormethyl benzene and benzoyl chloride. Therefore, IARC assesses that a combined exposure to the above-mentioned substance probably is carcinogenic to humans (group 2A) although there is no clear obviousness for humans (OECD SIDS, 1998).

Critical effect
The critical effect of benzyl chloride is acute and chronic infection in the gastritis. NOEL was set to 6.4 mg/kg bw/day.

If a safety factor of 1000 is used (10 for interspecies variation, 10 for intraspecies variation and 10 for sub-chronic to chronic) that gives a tolerable dose of 0.006 mg/kg bw/day. That TDI value is used in the exposure calculations.

9 Exposure scenarios - calculations

In the light of the analysed four products for interior car care and limit value considerations, the following compounds were selected for the exposure calculations as it was assessed that they might have a potential health effect on the consumer.

The selected compounds in focus during the exposure calculations are:

- Hydrocarbons C_5-C_8
- Hydrocarbons C_{10}-C_{14}
- Butane
- 2-propanol
- Ethyl acetate
- Butyl acetate
- Limonene
- 1-propanol
- 1-methoxy-2-propanol
- 2-butoxy ethanol
- 1-butoxy-2-propanol
- Xylenes
- Benzyl chloride.

The exposure calculations represent the use of interior car care products in a closed car cabin (worst-case situation). The exposure scenarios comprise inhalation and intake through the skin.

9.1 Method

The exposure scenarios comprise a number of hypothetical cases where the consumer can be exposed to compounds in products for interior car care. The calculations are based on the following scenario that is described closer in chapter 4:

An adult applies car care agent inside his car (generally speaking with closed doors) and then goes for a car drive. Minimum exposure is set to 30 minutes as it is anticipated that application takes place at the local service station where the car is filled with petrol, the car is washed and finally car care products are applied on the interior, after which the car is driven home. Maximum exposure is set to 5 hours, because after that time measurable values of the substances in the car no longer exist for most substances. The measured values were applied in (almost) closed chambers to illustrate a more or less closed car. During the tests a certain amount of car care product was applied to a plate. Application took place quickly (in a few minutes) and then the test chamber was closed to illustrate the worst-case (application during almost closed car). The cloth with car care product remained in the test chamber for 15 minutes. After the 15 minutes the cloth was removed from the test chamber to illustrate that the user throws the cloth away or removes it to be washed. During application and afterwards, the person was exposed to the compounds via the air (substances that evaporate and are sprayed into the car

cabin (for waterproofing spray)) and via the skin (direct skin contact during application).

In connection with the exposure calculations, a starting point was taken in the EU Technical Guidance Document (TGD) that describes methods for risk assessment of chemical substances (TGD, 2003).

It is anticipated that the consumer of interior car care products is an adult. The body weight of the person is set to 70 kg (men) which is the standard weight of an adult male in TGD, 2003.

In connection with the calculations a starting point was taken in the formulas in the TGD of the EU, 2003.

9.1.1 Inhalation

The calculation of the amount of substance the consumer inhales is described in the below formula. In the calculations it is anticipated that as worst-case there is no air change of importance in the car i.e. application of the interior car care products takes place when the doors are closed.

$$I = \frac{f_{resp} \cdot C_{luft} \cdot Q_{inh} \cdot t}{BW} \cdot n$$

I	Inhaled amount of substance (mg substance/kg body weight/day)
f_{resp}	Inhalable or respirable part of the substance
C_{luft}	Substance concentration in the air (mg substance/m^3)
Q_{inh}	Inhalation speed of user (m^3/hour)
t	Duration of exposure (hours)
n	Number of times a day the user is exposed (day^{-1})
BW	Body weight of the user (kg)

The number of times the user is exposed to the substance per day was set to 1. The inhalable or respirable part of the substance was set to 1 as worst-case unless information in the health assessments says something else.

The speed of inhalation during application was set to 1.75 m^3/hour based on the EU TGD, 2003, of an adult male with light activity (upper limit for light activity applied (42 m^3/day)), as it was anticipated that only a light activity is required to apply interior car care products. In the subsequent period in the car (irrespective of it being 15 minutes or 5 hours) the speed of inhalation is set to 0.45 m^3/hour based on the EU TGD of an adult male at rest (upper limit for rest is applied (10.8 m^3/day)). The speed of inhalation for resting was used for car driving, as light activity is not in question when sitting and driving the car. However, the upper limit was used which is specified for resting.

9.1.2 Absorption through the skin

Absorption through the skin was calculated by means of the below equation.

$$U_{der,pot} = \frac{A_{der}}{BW} \cdot n \cdot f_{der} \cdot D_f \cdot R_f = \frac{q \cdot w_f}{BW} \cdot n \cdot f_{der} \cdot D_f \cdot R_f$$

$U_{der,pot}$	Substance amount absorbed through the skin (mg substance/kg body weight/day)
A_{der}	Amount of applied substance (mg)
q	Amount of applied car care product (mg)
w_f	Substance part in the car care product (weight-%)
n	Number of times per day the consumer is exposed (day^{-1})
f_{der}	Part of substances that can be absorbed through the skin
D_f	Factor describing how large a percent of the product ends on the skin (%)
R_f	Retention factor (%) that considers that the product is rinsed off
BW	Body weight of the user (kg)

The number of times the user was exposed to the substance per day was set to 1. The retention factor R_f was introduced by SCCNFP (Scientific Committee on Cosmetic Products and Non-Food Products) to consider ”rinse-off” products (SCCNFP 0690, 2003) (cosmetics). The retention factor was set to 0.01 by SCCNFP when the products are rinsed off after use. The corresponding factor was used in this connection as it must be anticipated that the user washes hands after application. All the car care products have an oil-like smell and/or are greasy and therefore it is anticipated that the user will wash hands if he/she gets some of the car care product on the hands. If hands are not washed after use the calculated absorption will be 100 times higher (retention factor = 1 instead of 0.01).

The factor D_f is introduced as it is not the entire applied amount of the product that ends on the skin. The products for interior car care will typically be applied with a cloth and therefore there is no direct skin contact with the entire applied amount. It is anticipated that max. 5% of the applied amount will end on the skin (D_f = 0.05). In connection with fabric waterproofing products it is anticipated that the amount that ends on the skin will be negligible and therefore exposure calculations for skin contact were only carried out for products applied with a cloth.

By using the formula, it was not considered that volatile substances to a certain degree are liberated to the air instead of penetrating the skin. Besides, 100% permeability for the skin is assumed for the applied substances unless other values are found in the health assessments or the log P_{ow} values indicate something else. Regard has not been given to the fact that car care products applied in a thick layer will not give the same exposure as the same amount of car care product applied to a larger area in a thin layer. Therefore, it is possible that exposure via the skin is overestimated in the exposure scenarios that were carried out.

9.2 Exposure scenarios

In connection with the calculations, a starting point was taken in the measured and calculated concentrations stated in chapter 6. For each substance, the highest concentration/amount was determined under the chemical analyses selected for the exposure scenarios. Therefore, the scenarios will state the worst possible exposure with each individual focus substance that realistically can be expected in the light of the measured and calculated values.

The values applied in the exposure calculations are described under the health assessments for each individual substance and are repeated in the table below (Table 9.1). In connection with substances that were not assessed in this project, values of the health assessments in previous analysis projects carried out by the Danish EPA were applied. The reference from which the values were taken is stated in parenthesis under the individual substances.

Table 9.1 Outline of values used in the exposure calculations

Substance name	CAS no.	Dermal absorption	Absorption by inhalation	NOAEL-value[1] (mg/kg bw/day)	TDI or RfD[2] (mg/kg bw/day)
Aliphatic hydrocarbons EC_5-EC_8		10%	25%		2
Aliphatic hydrocarbons $EC_{>8}$-EC_{16}		10%	100%		0.1
Butane	106-97-8	10%	100%	4.200*	4.2*
Ethyl acetate	141-78-6	10%	100%	900	0.9
1-methoxy-2-propanol	107-98-2	100%	100%	396	3.96
Benzyl chloride	100-44-7	100%	100%	6.4	0.006
Previously implemented assessments					
Butyl acetate (Glensvig and Pors, 2006)	123-86-4	No information 100%	No information 100%	7.230 mg/m^3	4.5*
2-butoxy ethanol (Svendsen et al., 2006)	111-76-2	100%	100%		0.5
D-limonene (Svendsen et al., 2006)	5989-27-5	No information 100%	No information 100%		0.1
2-propanol (Engelund and Sørensen, 2005)	67-63-0	100%	100%	420	42
1-butoxy-2-propanol (Svendsen et al., 2004)	5131-66-8	100%	No information 100%	350	0.35
Xylenes (Svendsen et al., 2006)	1330-20-7	No information 100%	60%	6.4	0.150

* The values were calculated in this report.

1 NOAEL stands for No Observed Adverse Effect Level, i.e. the highest exposure value/concentration where no serious effect is observed.

2 TDI stands for Tolerable Daily Intake and is the max. tolerable dose of a chemical. RfD stands for Reference Dose and is the max. acceptable dose of a chemical. Normally, TDI/RfD appears by dividing the NOEAL value with a safety factor of 1000, 100 or 10, respectively, depending of the quality of the data from the NOAEL value.

Comments to the previously assessed substances

For butyl acetate, a NOAEL value of 7.230 mg/m^3 is stated in Glensvig and Pors (2006) in a 16 day gestation test with rats. The value is not stated per kg. body weight. If it is anticipated that a female rat weighs max. 300 g[17] and that

[17] Weight of Sprague Dawley rats which the test is based on is 250-300 g for female rats and 450-520 g for male rats according to http://aceanimals.com/SpragueDawley.htm.

the respiration volume of a rat is max. 130 ml/min[18] then that will correspond to a NOAEL of 4.512 mg/kg bw/day. Corrections have not been made for the rats only inhaling the mixture 7 hours per day, as described in Glensvig and Pors (2006). If a safety factor of 1000 is used (10 for interspecies variation, 10 for intraspecies variation and 10 for sub-chronic to chronic) that gives a tolerable dose of 4.5 mg/kg bw/day. This TDI value was used in the exposure calculations.

For 2-propanol, one NOAEL value of 420 mg/kg bw/day for humans is stated in Engelund and Sørensen (2005). It is supposed to be the human dose that will not result in reproductive toxic or development effects in foetuses. If a safety factor of 10 is used (10 for intraspecies variation) that gives a tolerable dose of 42 mg/kg bw/day. This TDI value was used in the exposure calculations.

9.2.1 Exposure by inhalation when applying products for interior car care

In connection with the four products for interior car care, where measurements were carried out in the box to find out which chemicals evaporate to the air, the substances listed in Table 6.15-Table 6.22 were identified. Of the identified substances, exposure calculations were carried out of the substances that are on the List of Dangerous Substances.

Scenario: 5-hour drive immediately after application
In the exposure calculations, a scenario was anticipated where the car care products are applied – duration 15 minutes. The application cloth is thrown away /washed and the person immediately goes for a longer 5-hour drive in the car (without ventilation). That gives the following amount of inhaled substance of the different analysed products for interior car care (see Table 9.2). Consideration has been given to volume as well as the amount factors i.e. the concentration is calculated for the amount of car care product that is used in the car and for the typical volume of a car.

In the calculations, the values stated in Table 8.1 of the concentration during the first 15 minutes and over the 5 hours are used. Table 8.1 states the total concentration of hydrocarbons whereas the concentration in Table 9.2 is divided into the individual hydrocarbon fractions. The column "Conc. first 15 min (mg/m^3)" the values have been taken directly from the column in Table 8.1 with corresponding headline whereas the values in the column "Conc. over 5 hours (mg/m^3)" are calculated values that are not stated anywhere else.

For instance, the calculation of TDI/I_{pot} was carried out for Product 1 vinyl make-up for hydrocarbons C_{10}-C_{14}:

$$TDI\ /\ I_{pot} = \frac{0{,}1\ mg\ /\ kg\ \ legemsvægt\ \ \ per\ \ dag}{\frac{((29\ mg\ /\ m^3 \cdot 1{,}75\ m^3\ /\ time\ \cdot 0{,}25\ timer\ ) + (3\ mg\ /\ m^3 \cdot 0{,}45\ m^3\ /\ time\ \cdot 5\ timer\ )) \cdot 1}{70\ kg}} = 0{,}4$$

[18] Found at http://gray.hmgc.mcw.edu/pipermail/rat-forum/2000-April/000531.html.130 ml/min corresponds to app. 2% of the respiratory volume of a human at rest.

Table 9.2 Calculated inhaled amount of chemicals for application and subsequent 5-hour drive in the car (without ventilation)

Product ID	Product type	Substance name	CAS no.	Conc. first 15 min (mg/m^3)	Conc. over 5 hours (mg/m^3)	Respirable part f_{resp}	Inhaled amount during 5 hours in car (mg/kg bw/day)
1	Vinyl make-up	Hydrocarbons C_4-C_7	-	61	6	0.25	0.143
1	Vinyl make-up	Hydrocarbons C_{10}-C_{14}	-	29	3	1	0.276
5	Fabric waterproofing	Hydrocarbons C_5-C_8	-	223	27	0.25	0.565
5	Fabric waterproofing	Butane	106-97-8	19	1.9	1	0.178
5	Fabric waterproofing	2-propanol	67-63-0	1.2	0.1	1	0.011
5	Fabric waterproofing	Ethyl acetate	141-78-6	14	0.8	1	0.116
5	Fabric waterproofing	Butyl acetate	123-86-4	80	4.6	1	0.651
5	Fabric waterproofing	Limonene	138-86-3	19	0.7	1	0.138
10	Vinyl cleaner	Butane	106-97-8	1.5	0.3	1	0.018
10	Vinyl cleaner	2-propanol	67-63-0	14	1.9	1	0.151
10	Vinyl cleaner	Limonene	138-86-3	0.8	0.06	1	0.007
24	Glass cleaner	2-propanol	67-63-0	1.5	0.2	1	0.016
24	Glass cleaner	1-methoxy-2-propanol	107-98-2	5	0.4	1	0.042
24	Glass cleaner	2-butoxyethanol	111-76-2	23	2.2	1	0.214
24	Glass cleaner	1-butoxy-2-propanol	5131-66-8	11	1.2	1	0.107

For the calculations the following values were used and they are the same for all products and substances:
Inhalation speed Qinh during application = 1.75 m^3/hour
Inhalation speed Qinh when driving = 0.45 m^3/hour
Duration exposure application = 0.25 (i.e. 15 minutes)
Duration exposure driving = 5 hours
Body weight (BW) = 70 kilo
The respirable part F_{resp} is as stated in Table 9.1 set to 1 (=100% intake by inhalation), however, with exception of the low hydrocarbon fractions where existing data indicates max. 25% absorption (i.e. a factor 0.25 is used in the calculations).

With the values listed in Table 9.1 for tolerable daily intake the following calculated safety margins are obtained (see Table 9.3).

Table 9.3 Calculated safety margins for the scenario application and subsequent 5-hour car drive (no ventilation)

Product ID	Product type	Substance name	CAS no.	Inhaled amount I_{pot} during 5 hours in car (mg/kg bw/day)	TDI (mg/kg bw/day)	TDI/I_{pot}
1	Vinyl make-up	Hydrocarbons C_4-C_7	-	0.143	2	14.0
1	Vinyl make-up	Hydrocarbons C_{10}-C_{14}	-	0.276	0.1	0.4
5	Fabric waterproofing	Hydrocarbons C_5-C_8	-	0.565	2	3.5
5	Fabric waterproofing	Butane	106-97-8	0.178	4.2	23.6
5	Fabric waterproofing	2-propanol	67-63-0	0.011	42	3928
5	Fabric waterproofing	Ethyl acetate	141-78-6	0.116	0.9	7.8
5	Fabric waterproofing	Butyl acetate	123-86-4	0.651	4.5	6.9
5	Fabric waterproofing	Limonene	138-86-3	0.138	0.1	0.7

Product ID	Product type	Substance name	CAS no.	Inhaled amount I_{pot} during 5 hours in car (mg/kg bw/day)	TDI (mg/kg bw/day)	TDI/I_{pot}
10	Vinyl cleaner	Butane	106-97-8	0.018	4.2	237
10	Vinyl cleaner	2-propanol	67-63-0	0.151	42	277
10	Vinyl cleaner	Limonene	138-86-3	0.007	0.1	14.5
24	Glass cleaner	2-propanol	67-63-0	0.016	42	2696
24	Glass cleaner	1-methoxy-2-propanol	107-98-2	0.042	3.96	93.4
24	Glass cleaner	2-butoxy ethanol	111-76-2	0.214	0.5	2.3
24	Glass cleaner	1-butoxy-2-propanol	5131-66-8	0.107	0.35	3.3

As it appears from Table 9.3 most of the substances have a safety margin of more than 1, which means that there is no health risk involved when applying the analysed products for interior car care and subsequent stay in the car for 5 hours (where the concentration of the substances has declined substantially).

In connection with the longer hydrocarbons in product 1, vinyl make-up, and for D-limonene in product 5, fabric waterproofing agent, the safety margin is below 1 which is tantamount to a health risk. However, it should be noted that the calculations were carried out with n (number of occurrences per day) = 1, i.e. that the same product for interior car care has to be applied every day for a longer period of time before exposure will constitute a health effect.

For hydrocarbons C_{10}-C_{14} the safety margin is below 1 (TDI/I_{pot} = 0.4). The calculation is carried out per day. That means the safety margin is below 1 if interior car care is used on the car every day. The safety margin will exceed 1 as long as the car care agents only are used every third day (0.4*3 > 1). In that case, the tolerable daily intake (TDI) exceeds the inhaled amount per day (I_{pot}) which is tantamount to a safety margin exceeding 1 and therefore no health risk.

No measurements were carried out on the worst-case scenario where all four analysed products for interior car care are used immediately after each other and it is not immediately possible to calculate the situation. Therefore, the individual measurements have been added up, corresponding to a worst-case situation, where all four analysed products are used at the same time (in practice not possible, but is anticipated to be theoretically possible). The concentration of the individual substances will increase as the same chemical substances appear in several of the analysed products. This hypothetical situation will not give rise to a health risk as long as the car care products at a maximum only are used every third day. Adding up the concentration of the substances that appear in several of the four analysed products will not change the relation between the tolerable daily intake and the inhaled amount per day (TDI/I_{pot}). See Table 9.4 below.

Table 9.4 Calculated safety margins of the scenario application of all four products at the same time and subsequent 5-hour car drive (no ventilation)

Product ID	Substance name	CAS no.	Inhaled amount I_{pot} during 5 hours in car (mg/kg bw/day)	TDI (mg/kg bw/day)	TDI/I_{pot}
1 +5	Hydrocarbons C_4-C_7	-	0.143 + 0.565 = 0.708	2	2.8
1	Hydrocarbons C_{10}-C_{14}	-	0,276	0.1	0.4
5 +10	Butane	106-97-8	0.178 + 0.018 = 0.196	4.2	21.4
5 + 10 +	2-propanol	67-63-0	0.011 + 0.151 + 0.016 = 0.178	42	236

Product ID	Substance name	CAS no.	Inhaled amount I_{pot} during 5 hours in car (mg/kg bw/day)	TDI (mg/kg bw/day)	TDI/I_{pot}
24					
5	Ethyl acetate	141-78-6	0.116	0.9	7.8
5	Butyl acetate	123-86-4	0.651	4.5	6.9
5 + 10	Limonene	138-86-3	0.138 + 0.007 = 0.145	0.1	0.7
24	1-methoxy-2-propanol	107-98-2	0.042	3.96	93.4
24	2-butoxy ethanol	111-76-2	0.214	0.5	2.3
24	1-butoxy-2-propanol	5131-66-8	0.107	0.35	3.3

If it is anticipated that not an adult male but a child is exposed to the substances, then all inhaled amounts per day (I_{pot}) will amount to app. 140-235% of the calculated inhaled amounts of an adult male (see calculation example below). That is because children have a lower weight, but a larger respiratory volume per weight unit compared to adults. Under normal conditions, the car care products will not be applied by children but they could e.g. be exposed to the substances if the family gets into the car and drives on holiday immediately after application of car care products. Therefore, a calculation has been carried out where it is anticipated that a child also is present during application of the car care products.

However, some of the substances (butane and ethyl acetate – butane which was found in nearly all spray products and ethyl acetate that mainly was found in fabric waterproofing (product no. 5) (see Table 2.1)) can be liberated in concentrations where irritative effects on the respiratory tracts can appear and therefore it is recommended to apply car care products with open car doors and to turn on the ventilation in the car if going for a car drive immediately after application.

Calculation example – children

The inhalation speed of children is anticipated to be 0.5 m^3/hour during application and when driving in a car (corresponding to a light activity as defined in TGD, 2003).

Inhaled amount per day I_{pot} =

$$\frac{(C_{første 15\,\min} \cdot IH_{første 15\,\min} \cdot t) + (C_{5timer} \cdot IH_{5timer} \cdot t)}{BW} =$$

$$\frac{(29\ mg/m^3 \cdot 0{,}5\ m^3/time \cdot 0{,}25\ timer) + (3\ mg/m^3 \cdot 0{,}5\ m^3/time \cdot 5\ timer)}{20\ kg}$$

= 0.55 mg/kg bw/day.

If that figure is compared to the tolerable daily intake (TDI) of 0.1 mg/kg bw/day for medium chained hydrocarbons, then TDI/I_{inh} of 0.18 is obtained, i.e. a value below 1.

When a child, as worst-case, also is present in the car during the entire application process, then the relation TDI/I_{pot} will be above 1 in most cases, however, values for the relation TDI/I_{pot} will be below 1 for hydrocarbons C_{10}-C_{14} and for limonene where the calculated values are 0.18 and 0.5,

respectively. The lowest value of hydrocarbons C_{10}-C_{14} gives a calculated safety margin below 1 (TDI/I_{pot} = 0.18). The calculation is carried out per day. That means that the safety margin is below 1 if interior car care products are used in the car every day. The safety margin will exceed 1 as soon as the car care products only are used once a week (0.18*7 > 1). Here the tolerable daily intake (TDI) exceeds the inhaled amount per day (I_{pot}) which results in a safety margin above 1 and therefore there is no health risk.

Scenario: 15 minute drive immediately after application

In the exposure calculations a scenario is anticipated in which the car care products are applied at the local service station – duration 15 minutes. The application cloth is thrown away/washed and the person then drives directly home in the car (without ventilation) – duration 15 minutes. Table 9.4 shows the amount of inhaled substance that will result in for the various analysed products for interior car care. Consideration has been given to volume as well as the amount factors, i.e. the concentration is calculated for the amount of car care that is used in the car and for the typical volume of a car.

Table 9.5 Calculated inhaled amount of chemicals for application and subsequent 15-minute car drive (no ventilation)

Product ID	Product type	Substance name	CAS no.	Conc. first 15 min. (mg/m^3)	Conc. minute1 5-30 (mg/m^3)	Respirable part f_{resp}	Inhaled amount during 30 minutes in car (mg/kg bw/day)
1	Vinyl make-up	Hydrocarbons C_4-C_7	-	60.8	41.1	0.25	0.112
1	Vinyl make-up	Hydrocarbons C_{10}-C_{14}	-	28.8	12.0	1	0.199
5	Fabric waterproofing	Hydrocarbons C_5-C_8	-	222.6	154.2	0.25	0.410
5	Fabric waterproofing	Butane	106-97-8	18.8	13.5	1	0.139
5	Fabric waterproofing	2-propanol	67-63-0	1.2	0.6	1	0.008
5	Fabric waterproofing	Ethyl acetate	141-78-6	14.1	6.8	1	0.099
5	Fabric waterproofing	Butyl acetate	123-86-4	80.5	34.8	1	0.559
5	Fabric waterproofing	Limonene	138-86-3	18.6	5.8	1	0.126
10	Vinyl cleaner	Butane	106-97-8	1.5	1.7	1	0.012
10	Vinyl cleaner	2-propanol	67-63-0	14.3	12.6	1	0.109
10	Vinyl cleaner	Limonene	138-86-3	0.77	0.47	1	0.006
24	Glass cleaner	2-propanol	67-63-0	1.5	1.3	1	0.011
24	Glass cleaner	1-methoxy-2-propanol	107-98-2	4.8	3.3	1	0.035
24	Glass cleaner	2-butoxyethanol	111-76-2	22.9	20.5	1	0.176
24	Glass cleaner	1-butoxy-2-propanol	5131-66-8	11.0	6.6	1	0.079

For the calculations the following values were used and they are the same for all products and substances:
Inhalation speed Qinh during application = 1.75 m^3/hour
Inhalation speed Qinh when driving = 0.45 m^3/hour
Duration exposure application = 0.25 (i.e. 15 minutes)
Duration exposure driving = 0.25 (i.e. 15 minutes)
Body weight (BW) = 70 kg
The respirable part F_{resp} is as stated in Table 9.1 set to 1 (=100% intake by inhalation), however, with exception of the low hydrocarbon fractions where existing data indicates max. 25% absorption (i.e. a factor 0.25 is used in the calculations).

With the values listed in table 9.1 for tolerable daily intake, the following calculated safety margins are obtained (see Table 9.6).

Table 9.6 Calculated safety margins for the scenario application and subsequent 15-minute car drive (no ventilation).

Product ID	Product type	Substance name	CAS no.	Inhaled amount$_{pot}$ at 30 minutes in car (mg/kg bw/day)	TDI (mg/kg bw/day)	TDI/I$_{pot}$
1	Vinyl make-up	Hydrocarbons C_4-C_7	-	0.112	2	17.9
1	Vinyl make-up	Hydrocarbons C_{10}-C_{14}	-	0.199	0.1	0.5
5	Fabric waterproofing	Hydrocarbons C_5-C_8	-	0.410	2	4.9
5	Fabric waterproofing	Butane	106-97-8	0.139	4.2	30.2
5	Fabric waterproofing	2-propanol	67-63-0	0.008	42	4969
5	Fabric waterproofing	Ethyl acetate	141-78-6	0.099	0.9	9.1
5	Fabric waterproofing	Butyl acetate	123-86-4	0.559	4.5	8.0
5	Fabric waterproofing	Limonene	138-86-3	0.126	0.1	0.8
10	Vinyl cleaner	Butane	106-97-8	0.012	4.2	344
10	Vinyl cleaner	2-propanol	67-63-0	0.109	42	384
10	Vinyl cleaner	Limonene	138-86-3	0.006	0.1	17.9
24	Glass cleaner	2-propanol	67-63-0	0.011	42	3729
24	Glass cleaner	1-methoxy-2-propanol	107-98-2	0.035	3.96	113
24	Glass cleaner	2-butoxy ethanol	111-76-2	0.176	0.5	2.8
24	Glass cleaner	1-butoxy-2-propanol	5131-66-8	0.079	0.35	4.4

As it appears from Table 9.6 there is no great difference in the safety margins from the scenario with 5-hour drive and merely 15-minute drive. That is because the largest exposure takes place within the first half hour as that is when the substance concentration is greatest. Then the concentration declines subsequently.

A similar picture develops as when driving 5 hours: The majority of the substances have a safety margin that is larger than 1, but for the longer hydrocarbons in product 1, vinyl make-up, and for D-limonene in product 5, fabric waterproofing agent, the safety margin is below 1, which is tantamount to a health risk. In that case, exposure can result in liver and blood changes (e.g. cell increases). However, changes seen in the liver of experimental animals were reversible, i.e. the changes might return to normal again. It should be noticed that the calculations were made with n (number of incidences per day) = 1, i.e. that the same product for interior car care has to be applied every day for a longer period of time before exposure will constitute a health effect.

As soon as the car care products only are used every other day (n = ½), the tolerable daily intake (TDI) exceeds the inhaled amount per day (I_{pot}), which results in a safety margin above 1 and therefore there is no health risk.

In worst-case, when all four analysed car care products for interior car care are used simultaneously (in practice not possible but anticipated to be theoretically possible), the concentration of some substances will increase as the same chemical substances appear in several of the analysed products. In this hypothetical case there will be no health risk as long as the car care products only are used max. every other day.

It must be anticipated that in practice products for interior car care are only used once or max. twice a month by the most punctilious people. In that case, the analysed products for interior car care will not give rise to health concern.

Discussion of duration of application and applied amounts

In connection with the above calculations it is assumed that application takes 15 minutes per product that is used. If a person is very careful and spends e.g. 30 minutes on applying one car care product, then the amount of used car care product might increase and the time during which the person is exposed to a higher concentration of vapours from chemical substances will increase.

Therefore, the inhaled amount per day has been calculated in relation to TDI for one substance (the hydrocarbon fraction C_{10}-C_{14}). That compound was chosen because in the calculations it gives the lowest safety margin (below 1) and therefore it is the most critical compound.

If an adult instead spends 30 minutes applying vinyl make-up (product 1) – and uses the same amount (assumed that the concentration measured during the first 5 minutes appears for 30 minutes) then the relation between the inhaled amount per day/TDI can be calculated to 0.16. That means there is a health risk related to using the product every day (30 minute application and subsequent 5-hour drive). However, if the product is used max. once a week the relation inhaled amount per day/TDI will exceed 1, which is tantamount to no health effects.

If an adult spends 30 minutes on applying vinyl make-up (product 1) and uses twice the amount (assumed that the measured concentration has to be doubled when using twice the amount and assumed that the concentration measured during the first 5 minutes appears for 30 minutes), then the relation between inhaled amount per day/TDI can be calculated to 0.08. That means that there is a health risk when using the product every day (30 minute application and subsequent 5- hour drive). However, if the product is used max. once every fortnight the relation inhaled amount per day/TDI will exceed 1, which is tantamount to no health effects.

The calculated safety margin for the hydrocarbon fraction C_{10}-C_{14} will also be below 1 if the application time and amount is doubled. If the product is used max. once every fortnight, then the relation inhaled amount per day/TDI will also exceed 1 which is tantamount to no health effects.

The calculations are based on tests with ”almost closed ” cabin, i.e. during ventilation (open car doors) one person will during application be exposed to substantially smaller concentrations.

Remarks to substances labelled with R67 – Vapours may cause drowsiness and dizziness

Several substances are labelled with the risk phrase R67 (Vapours may cause drowsiness and dizziness) which can be regarded as an especially interesting effect when car driving is in question. The following is a short summary of the knowledge collected in this project concerning the substances with that effect simultaneously measured in the box tests:

- Ethyl acetate
- 2-propanol
- Butyl acetate

The health assessment of ethyl acetate in this project shows that the measured concentrations of ethyl acetate (max. 11.7 mg/m^3) at no time exceeds the concentrations where the substance causes inconvenience (at 720 mg/m^3 the smell of the vapours is unpleasant while mild irritation of eyes, nose and throat was ascertained at 1440 mg/m^3 (Jensen, 2003)).

Health assessments of 2-propanol and butyl acetate were carried out in previous analysis projects of the Danish Environmental Protection Agency. According to the safety data sheets of the products 2-propanol appears in eight different products (product 3, 4, 10, 21, 24, 29, 31 and 33). In three products, the content of 2-propanol is so large that they are labelled with R67 " Vapours may cause drowsiness and dizziness". Two of the products have that labelling. That means that one product has not been labelled with R67 although this should appear. The remaining products have a 13% or less content of 2-propanol which does not result in labelling with R67. That means that when using product 10 (vinyl cleaner), 31 (glass cleaner) and 33 (anti-mist product), lethargy might appear during use (no ventilation) – however, measurement of the concentration of 2-propanol during actual use of these products were not carried out in the project. According to the health assessment of 2-propanol, described in Engelund and Sørensen (2005), an air concentration of 980 mg/m^3 can result in light irritation of nose, eyes and throat, and at concentrations of 1960 mg/m^3 the symptoms are intensified without being serious. The highest labelled concentration of 2-propanol was 11 mg/m^3, i.e. not in a concentration that should give irritative effects.

According to the safety data sheets of the products, butyl acetate appears in two products (product 5 and 12). None of the products has a content of butyl acetate that exceeds 10% and therefore labelling with R67 is not necessary. Butyl acetate is in Glensvig and Pors (2006) stated to have a LCI value of 7 mg/m^3, which is the lowest amount that can give locally irritating effects when inhaled. The highest measured concentration of butyl acetate is 70 mg/m^3, i.e. local irritation will only appear when using product no. 5, fabric waterproofing agent. No values are mentioned in Glensvig and Pors (2006) that state at which concentration butyl acetate vapours can give lethargy and dizziness.

9.2.2 Exposure during skin contact in connection with application of products for interior car care

In the light of the quantitative analyses carried out on 15 selected products for interior car care (see Table 6.4 - Table 6.14), exposure calculations were carried out for skin contact with the substances found in the products in concentrations of 1% or more and that simultaneously have a relevant health classification. However, benzyl chloride was also selected due to the carcinogenic properties of the substance.

Table 9.7 Calculated absorbed amount of chemicals through the skin during application of the products.

Product ID	Product ype	Substance name	CAS no.	Highest measured quantitative conc. (mg/g)	Amount applied to product (g)	Factor D_f – How much ends on the skin?	Skin absorption	$U_{der, pot}$ (mg/kg bw/day)	TDI (mg/kg bw/day)	TDI/U_{der}
2	Vinyl make-up	Hydrocarbons C_6-C_8	-	160	20	0.05	0,1	0.0023	2	864
2	Vinyl make-up	Hydrocarbons C_{10}-C_{14}	-	59	20	0.05	0,1	0.0009	0.1	117
37	Glass cleaner	Hydrocarbons C_8-C_{10}	-	130	38	0.05	0,1	0.0035	2	569
37	Glass cleaner	Xylenes	95-47-6, 108-38-3, 106-42-3	24	38	0.05	1	0.0065	0.15	23
1	Vinyl make-up	Hydrocarbons C_6-C_8	-	110	20	0.05	0,1	0.0016	2	1257
1	Vinyl make-up	Hydrocarbons C_{10}-C_{14}	-	140	20	0.05	0,1	0.0020	0.1	49
23	Glass cleaner	1-methoxy-2-propanol	107-98-2	50	38	0.05	1	0.0135	3.96	293
24	Glass cleaner	2-butoxy-ethanol	111-76-2	47	38	0.05	1	0.0127	0.5	39
24	Glass cleaner	1-butoxy-2-propanol	5131-66-8	21	38	0.05	1	0.0057	0.35	62
8	Odour remover	Benzyl chloride	100-44-7	0.37	50	0.05	1	0.0001321	0.006	45
40	Cleaning tissue	Benzyl chloride	100-44-7	0.077	6	1	1	0.0000616	0.006	97

For the calculations, the following values were used and they are the same for all products and all substances:
Retention factor R_f = 0.01
Body weight (BW) = 70 kg

As it appears in Table 9.7, all of the listed substances have a safety margin of min. 23 (>> 1), which is tantamount to no health risk during application of the analysed products for interior car care although the products are applied without using gloves. However, in the calculations a retention factor of 0.01 has been used by SCCNFP (Scientific Committee on Cosmetic Products and Non-Food Products) to take ”rinse-off” products (SCCNFP 0690, 2003) in cosmetics into consideration. If hands are not washed after use it means that the calculated absorption will be 100 times higher (retention factor = 1 instead of 0.01) and the calculated safety margins will therefore be between 0.2 and 12 and the safety margin will in six cases be below 1 (i.e. health risk). It should be noted that the calculations were carried out with n (number of occurrences per day) = 1, i.e. the same product for interior car care has to applied every day for a longer period of time before exposure will contribute to a health effect.

It is recommended to use gloves as the compounds may degrease skin and result in dry skin.

9.2.3 Total exposure

The inhaled amount and the absorbed amount by skin contact have to be added up for each substance to obtain the total exposure. However, exposure during skin contact is substantially smaller than during inhalation of the same substances (a factor 3 – 177) and therefore the conclusion remains the same: As long as the analysed products for interior car care only are used every third day or less then there is no health risk when using the products.

9.2.4 Overall conclusion

The exposure calculations for inhalation of the chemical substances that evaporate from the four analysed products show that no matter if you go for a short drive (15 minutes) or a long drive (5 hours) in the car immediately after application of the car care product (duration 15 minutes), then there is no health risk when using the analysed products for interior car care unless the products are used every day for a longer period of time. In that case, exposure can result in changes in liver and blood (e.g. increased cells). However, changes seen in the liver of test animals were reversible, i.e. the changes can go back to normal again. As long as the products are only used once a week – or a couple of times a year, which probably is most realistic, then there is no health risk when using the products that have been investigated closer in this project. The products must be used in double amounts and more frequent than every second week before a long term risk is possible.

The exposure calculations for skin contact show that even though the products for interior car care are applied without using gloves (but with an application cloth), then there will be no health risk connected with using the analysed product as long as the user washes hands after use or only uses interior car care products every fortnight. That also goes for cleaning tissues when there is direct contact with the compounds.

The inhaled amount and the amount absorbed via skin contact have to be added up for each compound in order to obtain total exposure. However, exposure during skin contact is much less than during inhalation of the same substances and therefore the conclusion remains the same: As long as the analysed products for interior car care during normal use only are used max. twice a week or less, then there is no health risk when using the products investigated in this project.

No substances evaporate in concentrations that exceed the individual work threshold limit values of the compounds. Calculations show, that in worst-case more than one full can has to be used (in this case vinyl make-up) at once in order to exceed the limit value of the compounds. Even though no limit values are exceeded, some of the compounds can be liberated in concentrations where irritating effects may appear and therefore it is recommended to apply car care products with the car door open and to ensure good ventilation in the car if going for a drive in the car immediately after application. It is also recommended to use gloves as the compounds may degrease the skin and result in dry skin.

In general, the following is recommended when using interior car care products:

- Ensure proper ventilation during application of products (open the car doors).
- Use as small an amount as possible.
- When using spray products – spray away from the inhalation area and avoid inhalation of spray mist.
- Wash hands after using the products or use gloves.

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Photo 1: Picture of the box.

Photo 2: Picture of location of item to which the product is applied. The lid is pulled down before the product is applied and during measurements.

The 26 allergenic substances

Table 1.1. List of the 26 allergenic substances which must be labelled on the packaging of detergents if added at concentrations exceeding 0,01% w/w

Substance	CAS-no.
Amyl cinnamal	122-40-7
Amylcin-namyl alcohol	101-85-9
Anisyl alcohol	105-13-5
Benzyl alcohol	100-51-6
Benzylbenzoat	120-51-4
Benzyl cinnamate	103-41-3
Benzyl salicylate	118-58-1
Cinnamyl alcohol	104-51-1
Cinnamal	104-55-2
Citral	5392-40-5
Citronellol	106-22-9
Coumarin	91-64-5
d-Limonene	5989-27-5
Eugenol	97-53-0
Farnesol	4602-84-0
Geraniol	106-24-1
Hexyl cinnam-aldehyd	101-86-0
Hydroxy-citronellal	107-75-5
Hydroxy-methylpentylcyclohexenecarboxaldehyd	31906-04-4
Isoeugenol	97-54-1
2-(4-tert-Butylbenzyl)propionaldehyd	80-54-6
Linalool	78-70-6
Methyl heptin carbonate	111-12-6
3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	127-51-5
Oak moss and treemoss extract	90028-68-5
Treemoss extract	90028-67-4