

Survey of chemical substances in consumer products

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Mapping of stain removers

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Summary and conclusions

The project "Mapping of stain removers" has carried out a mapping of existing products for stain removal on the Danish retail market. This mapping has been supplemented by an Internet search to identify any further products available to Danish consumers. In addition, a mapping has been carried out of "DIY advice" from literature and the internet and an estimate of the sale of stain removers in Denmark has been prepared.

The ingredients in the stain removers have been identified through information on the product packaging and other information material. This information has been supplemented by chemical analysis of selected products and an exposure evaluation has been carried out for the substances estimated to be the critical ingredients.

The mapping found a total of 35 products of which one consisted of two components. The products can be divided into all-round, bleaching and special agents as well as "natural/green products". 14 all-round products, 3 bleaching agents, 13 special agents and 5 products in the category "natural/green products" were found.

The mapping of ingredients resulted in the products being divided 5 categories:

1. Products based on surfactants
2. Products based on surfactants and enzymes
3. Products containing bleach
4. Products containing solvents
5. Products based on "natural/green" ingredients

The sales estimate was based on information from large Danish supermarket chains and showed that approximately 800,000 unites of stain removers are sold annually corresponding to approximately 147,000 litres (liquid and paste) and approximately 176,000 kg (powder).

Based on the mapping of ingredients, 6 products were selected for chemical analysis. The purpose of the analyses was partly to control the amount of certain ingredients and partly to identify selected ingredients that are problematic with regard to environment and health, including perfume substances, preservatives and octyl-/nonylpolyethoxylates. The analyses showed a.o. that 4 of the 6 products contained perfume and that the product with the biggest perfume content was one of the so-called "green" products.

It was estimated that the critical substances were: D-limonen, benzyl alcohol, NTA and dibutylphthalat and an exposure evaluation was carried out for these substances.

It is concluded that the risk of damaging effects when using the products is very small. However, due to the seriousness of the effects (allergy, potential risk of cancer and damages to reproduction), precautions should still be taken to avoid inhalation or skin contact with the products.

It is also concluded that the most efficient way of avoiding the damaging effects from the use of stain removers is to follow the household remedies mentioned in the report instead of the advanced special agents that can be bought retail.

Sammenfatning og konklusioner

I projektet "Kortlægning af pletfjernere" er der foretaget en kortlægning af eksisterende produkter til pletfjerning på det danske detailmarkedet. Denne kortlægning blev suppleret med en søgning på Internettet for at identificere eventuelle yderligere produkter tilgængelige for danske forbrugere. Der er desuden foretaget en kortlægning af "gør-det-selv råd" i litteraturen og på Internettet, og et estimat over salget af pletfjernere i Danmark.

Indholdsstofferne i pletfjerningsmidlerne blev identificeret ved hjælp af oplysninger på produkternes emballage og andet informationsmateriale. Disse oplysninger blev suppleret med kemiske analyser af udvalgte produkter, og for de stoffer, der blev vurderet at være de kritiske indholdsstoffer, blev der foretaget en eksponeringsvurdering.

Der blev ved kortlægningen fundet i alt 35 produkter, hvoraf et bestod af to komponenter. Produkterne kan inddeles i allround-, blege- og specialmidler samt "naturprodukter/grønne produkter". Der blev fundet 14 allround produkter, 3 blege-midler, 13 specialmidler samt 5 produkter i kategorien "naturprodukter/grønne produkter".

Kortlægningen af indholdsstoffer resulterede i, at produkterne kunne inddeles i 5 kategorier:

1. Produkter baseret på overfladeaktive stoffer
2. Produkter baseret på overfladeaktive stoffer og enzymer
3. Produkter der indeholder blegemidler
4. Produkter der indeholder opløsningsmidler
5. Produkter baseret på "naturlige/grønne" ingredienser.

Estimatet over salget blev baseret på oplysninger fra store danske supermarkeds-kæder og viste, at der sælges omkring 800.000 enheder pletfjernere pr. år, svarende til ca. 147.000 liter (væske og pasta) og ca. 176.000 kg (pulver).

På baggrund af kortlægningen af indholdsstoffer blev der udvalgt 6 produkter til kemisk analyse. Analyserne havde til formål dels at kontrollere mængden af visse indholdsstoffer, dels at identificere udvalgte miljø- og sundhedsmæssigt problematiske indholdsstoffer, herunder visse parfume stoffer, konserveringsmidler og octyl-/nonylpolyethoxylater. Analyserne viste blandt andet, at 4 ud af de 6 produkter indeholdt parfume, og at det produkt, der havde det største indhold af parfume, var et af de såkaldte "grønne" produkter.

Det blev vurderet, at de kritiske stoffer var: D-limonen, benzylalkohol, NTA og dibutylphthalat, og der blev foretaget en eksponeringsvurdering for disse stoffer.

Det konkluderes at risikoen for skadevirkninger ved anvendelse af produkterne er meget lille, men at der på grund af alvorligheden af effekterne (allergi, potentiel kræftisiko og risiko for reproduktionsskader) alligevel bør tages forholdsregler mod indånding eller hudkontakt med produkterne.

Endelig konkluderes det, at den mest effektive måde, hvorpå skadevirkninger fra anvendelsen af pletfjerningsmidler kan undgås er at anvende nogle af de husråd, der nævnes i rapporten i stedet for avancerede specialmidler, der kan købes i detailhandlen.

1 Introduction

Throughout time, the removal of stains from textiles and other materials has generated much interest with consumers. This can be seen in particular in an article from Consumer Information ("Forbrugerinformationen 1 år", 1 February 2001), which presents statistics of enquiries to the Consumer Information hotline. "Stains" are number one on the top 10 list of household enquiries with 1738 out of 7532 telephone enquiries corresponding to 23 %.

In addition to those stain removers marketed in the retail business, there is a large number of old household remedies for stain removal. These household remedies, applied through time, includes substances such as spirits, benzine and ammonium spirits as well as a number of substance mixtures. The description of these household remedies often uses old-fashioned designations for the substances, which may be difficult to understand today.

In the EPA introduction to the project "Mapping of stain removers", it is stated that quite a large number of stain removers are presumed to contain organic solvents and other "fierce" things. This is supported by a search in the Nordic product registers' SPIN database in which a search for the stain remover code yields a result of 31 different ingredients. Among the ingredients found in the search are solvents (such as ethanol, 2-propanol, ammonia, benzene, diethyleneglycolmono-n-butylether) and surfactants. In addition, a number of fragrances are found (such as terpinol, lemon extract, cumarin) as well as preservatives (2,6-di-tert-butyl-p-cresol, benzylbenzoat).

The EPA project "Kortlægning af kemiske stoffer i rensede tekstil fra Rynex- og kulbrinterenseri, 2002" (Mapping of chemical substances in cleaned textile from a Rynex and hydrocarbon cleaner, 2002) identifies a number of chemical substances in cleaning fluids including hydrocarbon mixtures, halogenated substances and glycolethers. It is likely that the same type of substances can be found in stain removers for consumers.

The project focuses on ingredients in stain removers, both in marketed products and in do-it-yourself solutions and is aimed at consumer risks through skin contact with and inhalation of aerosols or volatile ingredients in the products.

The project provided an overview of the stain remover ingredients in both products that can be bought retail and in DIY solutions described in books, magazines, pamphlets etc. In addition, the project led to an evaluation of the impact on the consumer as well as which precautions the consumer should take when using stain removers in the home.

The target group can be largely defined as users of stain removers as well as the authorities responsible for regulating the content and use of the products.

Producers/retailers have had an opportunity of commenting on the report and the results before publication. They have been very interested in the report result. Regarding the products for which the report stated violation of the rules of labelling the producers have declared they will bring this in order. The

producers of product no. 7 and product no. 35 had already before they received the report changed the labelling on their products. Other comments and corrections from these are included in the report.

2 Purpose

The overall purpose of the project is to get an overview of which stain removers can be bought retail as well as of the various DIY solutions for private use. In addition, it aims at identifying the ingredients and evaluate which effects from health hazardous substances the consumer is exposed to when using stain removers in the home.

The project will also result in an estimate of the consumption of the products and will illuminate which precautions the consumers should take when using the different kinds of stain removers in the home.

The project is divided into 3 phases: mapping, analysis and exposure evaluation.

The purpose of phase 1 has been to create an overview of marketed stain removers and DIY remedies.

Phase 1 comprises 3 sub-activities:

- Mapping of stain removers marketed retail.
- Mapping of DIY remedies including a list of the meaning of old designations.
- Estimate of consumption of the products.

The mapping is based on:

- Visits to the retail stores.
- Contact to dealers and suppliers.
- Information searches on the internet.
- Literature searches (magazines, pamphlets, books).
- Product and safety data sheets.

Phase 2 comprises qualitative and quantitative analyses of selected products as different types of stain removers are evaluated for further identification of ingredients and the amount of these ingredients in the products.

Phase 3 sets up exposure scenarios for selected health hazardous substances to evaluate the effects on consumers when using the stain removers in the home. In addition, an evaluation is given of which precautions the consumer should take when using the different kinds of stain removers.

3 Mapping of the market

3.1 Mapping of products on the retail market

The purpose of this sub-activity has been to identify and create an overview of the stain removers marketed on the retail market. In addition, a registration has been carried out of the ingredients stated on the product packaging and in other product information.

A number of stores were visited and a number of stain removers were identified. Table 1 contains an overview of which products were found in which stores. In addition, there are products which are sold only over the internet and/or in specialty stores.

The mapping of products on the retail market was carried out through visits in selected grocery stores, DIY centres, cleaners, service stations and carpet stores as well as through contact with dealers and suppliers.

As internet trade is a growing market, it was also checked which stain removers were sold on the internet.

3.1.1 The products

The list of products was based on a previous investigation described in an article in "Råd og Resultater, Teknik & Miljø nr. 2, 1999", which identified 13 products for stain removal on clothes. Of these 13 products, 8 were still on the market while 4 had been discontinued and could not be found on the market or identified in any other way.

Visits to grocery stores added 13 products to the list as products for stain bleaching and stain removal from carpets and other types of mats were included. Internet searches and telephone contact to health stores and suppliers identified an additional 11 products of which 2 can be bought in clothing stores and 3 in health stores while the rest can only be bought on the internet. Visits and contact to carpet stores yielded an additional 3 products.

Visits to timber yards, DIY centres, service stations and cleaners did not result in any additional products. The result of the mapping of stain removers on the retail market and on the internet is a list of a total of 35 products of which 1 product consists of 2 components.

In addition to the products sold specifically as stain removers, ordinary washing agents are commonly used for soaking. Dishwashing liquids are also commonly used as stain removers. These products have not, however, been included in the mapping.

Table 1 is an overview of the products indicating where they were found.

Trade name	Irma	Super Brugsen	KvicklyExtra	Fakta	Føtex	BILKA	ISO	IC Dalgaard Supermarked	Prima	Gobi SuperStore	Matas	Clothing stores	Carpet stores	Health stores	Internet
Product 1													x		
Product 2															x
Product 3	x	x	x		x		x	x	x	x	x				
Product 4	x	x	x		x			x	x	x	x				
Product 5	x		x	x	x		x		x						
Product 6	x		x		x		x	x	x	x	x				
Product 7	x	x	x		x	x	x	x	x	x	x				
Product 8					x			x		x	x				
Product 9												x			x
Product 10								x	x	x	x				
Product 11								x	x	x	x				
Product 12								x	x	x	x				
Product 13											x				
Product 14											x				
Product 15											x				
Product 16							x								
Product 17													x		
Product 18															x
Product 19								x	x	x	x				
Product 20			x					x			x				
Product 21								x			x				
Product 22															x
Product 23 – 2 components					x						x				
Product 24															x
Product 25					x										
Product 26													x		
Product 27			x				x	x	x		x				
Product 28			x				x	x	x		x				
Product 29														x	
Product 30														x	
Product 31														x	
Product 32												x			x
Product 33													x		x
Product 34						x				x					
Product 35	x	x	x		x	x	x		x		x				
Products total per store	6	4	9	1	9	3	8	13	12	10	18	2	3	3	8

Table 1 – Stain remover assortment in selected grocery stores

As can be seen from the table, a materialist is the type of store with the absolute widest selection of stain removers as no fewer than 18 different products are marketed while the large grocery stores carry approximately 10 different products.

The products can be divided into all-round, bleaching and specialty agents as well as natural products. The specialty agents can furthermore be sub-divided into products for different types of stains such as stain removers for red wine stains and products for specific kinds of mats such as silk, wool or carpets.

The products that belong to each of the 5 categories are listed in table 2.

Trade name	Suitable for*
1. All-round products	
Product 3	Food stuffs, fruit, gravy, blood, vomit, grass etc. Ideal for shirt collars and cuffs
Product 7	Chocolate, grass, sweat, grease, oil, gravy
Product 5	Hand cleaning, soaking removes milk, egg, blood and sweat at low temperatures
Product 9	Tea, coffee, red wine, oil, asphalt, dog accidents, blood, chocolate, gum, beetroot, grass, fruit, ballpoint pen, grease, lip stick
Product 11	Fruit, coffee, tea, red wine and vegetables, grease stains, blood, milk and cocoa. Bactericidal
Product 12	Grease, oil, blood, milk, fruit, ketchup and vegetables
Product 18	For removal of stains from carpets and fabric furniture
Product 19	Oil and grease stains on clothes, upholstered furniture, carpets etc.
Product 22	Universal stain remover
Product 24	Contains bacterial strains. Removes stains and odours from drinks, grease, ketchup, food, milk, urine, blood, vomit, pet stains etc.
Product 25	Textiles and skins. All waterproof materials
Product 32	Tea, coffee, red wine, oil, asphalt, dog accidents, blood, sauce, chocolate, gum, beetroot, grass, fruit, ballpoint pen, grease, lip stick
Product 33	Waterproofs
Product 35	Food, gravy, red wine, fruit juice, grass, water-based ink, cola, tea, coffee
2. Bleaches	
Product 8	Discolouring and soaking
Product 10	Discolouring and bleaching
Product 16	Bleaching of stains from tea, coffee, juice, grass. To prevent greying of white clothes
3. Speciality products	
3a. Specific types of stains	
Product 4	Oil, stearin, Indian ink, grease, make-up
Product 13 – Washable fabrics	Oils, grease, make-up, ink, chocolate, grass, gravy, shoe polish
Product 14 – Washable fabrics	Coffee, wine, blood, mud, meat juice, milk, collar and cuff stains
Product 15 – For dry-cleaning	Textiles that are not water-proof. Removes: Oils, grease, make-up, ink, chocolate, shoe polish, glue, wax
Product 20	Rust
Product 21	Red wine
Product 23	Mouldy stains
Product 34	Rust

3b. Specific types of mats	
Product 1	For coconut and sisal natural flooring
Product 6	For wool and silk. Effective against grease, make-up, gravy, dressing, chocolate etc.
Product 17	Water-based carpet stains
Product 26	Textile stain remover. Approved for wool
Product 27	Dirt and stains in carpets. Also suitable for smaller surfaces and hallways
Product 28	For carpets
4. Natural/green products	
Product 2	For all textiles, carpets and furniture
Product 29	For all types of stains except peptides that have been heated to more than 50°C
Product 30	For stains from ballpoint pens, ink, blood, grease, fruit etc.
Product 31	For stains from fruit, blood, ink, ballpoint pens, grass, grease etc.

Table 2 – Overview of products in each category.

* According to supplier information

3.1.2 Content and state

The content of the products varies from only 17 ml to 2000 g. Generally speaking, the products for special stains contain the least, which is logical as you probably do not often need a product for rust removal.

Trade name	State	Content
Product 19	Aerosol	100 ml
Product 33	Aerosol	590 ml
Product 31	Solid	90 g
Product 9	Paste	150 ml
Product 20	Paste	17 ml
Product 32	Paste (pump)	175 ml
Product 8	Powder	360 g
Product 5	Powder	600 g
Product 10	Powder	75 g
Product 11	Powder	500 g
Product 16	Powder	250 g
Product 22	Powder	2000 g
Product 23 Component 1	Powder	200 g
Product 23 Component 2	Powder	20 g
Product 28	Powder	750 g
Product 35	Powder	500 g
Product 6	Foam	150 ml
Product 1	Spray	200 ml
Product 7	Spray	375 ml
Product 17	Spray	250 ml
Product 18	Spray	1000 ml
Product 25	Spray	500 ml
Product 27	Spray	500 ml

Trade name	State	Content
Product 2	Liquid	500 ml
Product 3	Liquid	200 ml
Product 4	Liquid	250 ml
Product 12	Liquid	250 ml
Product 13	Liquid	75 ml
Product 14	Liquid	75 ml
Product 15	Liquid	75 ml
Product 21	Liquid	17 ml
Product 26	Liquid	650 ml
Product 29	Liquid	500 ml
Product 30	Liquid	120 ml
Product 34	Liquid	100 ml

Table 3 – Overview of state and content of stain removers

3.1.3 Labelling

As every other chemical product, stain removers are covered by the EPA regulations on classification and labelling /1/. This means that for some of the hazard labelled products, there will be information on the label on hazardous ingredients along with any hazard symbols as well as risk and safety phrases.

In addition, there is a recommendation from EU on declaration of ingredients in washing and cleaning agents /3/ with further specified regulations for declaration of the content. They are, however, only recommendations and thus not actual legislation. An Order has just been passed which introduce these regulations as legislation from October 2005. /31/

Trade name	Labelling	Safety data sheet	EU declaration
Product 1	Not labelled	No	Yes
Product 2	Not labelled	Yes	No
Product 3	Not labelled	No	Yes
Product 4	Xi;R10-41 S26-28-2	Yes	Yes
Product 5	Not labelled	No	Yes
Product 6	Not labelled	No	Yes
Product 7	Not labelled	Yes	Yes
Product 8	Xi;R36 S22-26-2	No	Yes
Product 9	Not labelled	No	No
Product 10	Xn, R7-22-31 S7/8-26-38-43	No	Yes
Product 11	Xi; R36 S2-22-26	No	Yes
Product 12	Not labelled	No	Yes
Product 13	Xi R10-36/38 S2-26-37-46 *	Yes	Yes
Product 14	Xn, R22 S2-23-45-63 *	Yes	No
Product 15	F, Xi R11-36-67 S2-7-16-24/25-26 *	Yes	No
Product 16	Xi;R36 S2-7/?-26-17	No	Yes
Product 17	Not labelled	Yes ***	No
Product 18	Xi; R36	Yes	No
Product 19	Fx, S2-16-23-51	Yes ****	No
Product 20	Not labelled	Yes	No
Product 21	Not labelled	Yes	No

Trade name	Labelling	Safety data sheet	EU declaration
Product 22	Xn; R22-36/38 S2-26-46	Yes	No
Product 23, Component 1	O, Xn, N R8-22-50/53 S2-60-61	No	No
Product 23, Component 2	Xn; R22-41-31S2-26-39-46	No	No
Product 24	**	**	**
Product 25	Not labelled	No	Yes
Product 26	Xi, R10-43 S24-37	Yes	Yes
Product 27	Not labelled	No	Yes
Product 28	Not labelled	No	Yes
Product 29	Not labelled	Yes ***	No
Product 30	Not labelled	No	No
Product 31	Not labelled	No	No
Product 32	Not labelled	No	No
Product 33	F; R11 S2-16-23-51	Yes	No
Product 34	Not labelled	No	No
Product 35	O, Xn R8-22-36/38 S1/2?-17?-25-26-46	No	Yes

Table 4 – Overview of the labelling of the products

* The packaging content is < 125 ml and the labelling has been reduced according to current regulations. Full labelling (as stated here) can be found in the safety data sheets for the products.

? Not correct S-phrase

** Omitted from examination, see page 18

*** Safety data sheet in English

**** The supplier did not wish to forward a safety data sheet

18 of the 35 products had an EU declaration on the packaging, 17 did not – at least not in a correct version.

3.1.4 Ingredients

As mentioned in the previous section, you can find some information on ingredients on the product labels if they are hazard labelled and/or equipped with a declaration according to the EU recommendation. If the products are used commercially, there is a demand for the supplier to obtain a safety data sheet for the product if it is considered hazardous according to the Danish Working Environment Authority (DWEA) regulations. Section 2 of the safety data sheet must state the hazardous ingredients in the product if the content exceeds certain limits /2/.

The information on ingredients are found on the product labels and safety data sheets. As most of the agents are intended for use in the home – and thus not commercially – it has not been possible to obtain safety data sheets for all products. Safety data sheets have been received for 12 out of 35 products.

Based on the known ingredients, the products can be roughly divided into 5 categories:

1. Products based on surfactants
2. Products based on surfactants and enzymes
3. Products containing bleaches
4. Products containing solvents as well as possible surfactants and/or enzymes
5. Products which are marketed as based on natural/green ingredients

3.1.4.1 Category 1 – Products based on surfactants

Table 5 is an overview of the products that fall into this category.

Based on the available information on ingredients, 5 products fall into the category of products based on surfactants without a content of enzymes, solvents and bleaches. All 5 products are stain removers for carpets and none of the products have been hazard labelled according to the EPA regulations according to the packaging and the supplier information. Based on the information in table 5, it is estimated that there are no demands for labelling of products 1, 27, 28 and 17.

Two of the products (products 17 and 18) contain the complex binder NTA (nitrilo-triacetic acid). NTA is included on the DWEA list of substances considered to be carcinogenic /16/. Products that contain more than 0.1 % NTA and are used commercially are covered by the regulations in the Order on precautions to prevent the cancer risk when working with substances and materials /17/. From the table it can be seen that the suppliers classify NTA differently. As the substance is not included on the list of unwanted substances it is the responsibility of the supplier to evaluate the classification based on existing data. According to a report from the Nordic Council of Ministers, the classification should be Carc. cat2 T;R45 Xn;R22 Xi;R38 /22/.

As ordinary consumers are not protected by the regulations in the above-mentioned Order, it is unfortunate that products on the retail marked contain this type of substances.

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (product)
Product 1		Anionic surfactants	< 5		Not labelled
		Preservative	-		
		Fragrances	-		
Product 27		Anionic surfactants	< 5		Not labelled
		Polymers	< 5		
		Perfume	< 5		
		Preservative	< 5		
Product 28		Anionic surfactants	< 5		Not labelled
		Cellulose	< 5		
		Perfume	< 5		
		Preservative	< 5		
Product 17		Anionic surfactants	< 5	Xi;R36/38	Not labelled
		NTA	< 5	Xi;R36/38	
		Phosphonate	< 5	Xi;R36/38	
		Phosphate	< 5	Xi;R36/38	
		Perfume	-		
Product 18	7758-29-0	Sodium tripolyphosphate	-		Xi;R38
	68439-50-9	Alcohol ethoxylat	-	Xn;R22 Xi;R41	
	6834-92-0	Sodium metasilikate	-	C;R34-37	
	18662-53-8	NTA	-	Xi;R36	
	2492-26-4	Sodium 2-mercap-tobenzothiazol	-		

Table 5 – Products based on surfactants
 * According to supplier information

The composition of the products, as it has been stated, is very similar to ordinary washing agents without enzymes. For all products, except product 17, it has been stated that they contain a preservative. For product 18, the preservative sodium-3-mercaptobenzothiazol has been declared. Product 17 has not been declared according to the EU recommendation.

3.1.4.2 Category 2 – Products based on surfactants and enzymes

This category is represented by 8 products stated in table 6. The chemical composition of these products is very similar to the composition of ordinary washing agents with enzymes. However, the two products purchased in clothing stores (products 9 and 32) stand out by containing sodiumoleat and natural fragrances. None of the products have been hazard labelled according to the EPA regulations according to the packaging and supplier information.

It should be noted that, according to the information in the safety data sheet, product 7 contains 5-15 % of a non-ionic surfactant classified Xn;R22 Xi;R41 N;R50. The classification of this substance with Xi;R41 leads to a classification of the product with R36 if the content is greater than or equal to 5 % but less than 10 % and R41 if the content is larger than or equal to 10 %. Thus, it is not correct that the product should not be classified and labelled since it should, as a minimum, be classified with Xi;R36 and labelled with the hazard symbol for irritant and the risk phrase R36 "Irritating to the eyes" based on the information in the safety data sheet.

For the remaining products, the information available is insufficient to establish whether or not it is correct that the products should not be classified and labelled.

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (Product)
Product 3		Non-ionic surfactants	5-15		Not labelled
		Phosphonates	< 5		
		Enzymes	-		
		Preservative	-		
		Perfume	-		
Product 7		Non-ionic surfactants; Fedtalkoholethoxylat-7	5-15	Xn;R22 Xi;R41 N;R50	Not labelled
		Citrate	-		
	10043-52-4	Calcium chloride	-	Xi;R36	
		Phosphonates	< 5		
		Enzymes	< 5		
		Preservative	-		
		Perfume	-		

Product no.	CAS-no.	Substance name	Content %	Classification (substance) *	Labelling (Product)
Product 6		Non-ionic surfactants	5-15		Not labelled
		Phosphonates	< 5		
		Perfume	-		
		Enzymes	< 5		
		Preservative	-		
Product 5		Zeolites	15-30		Not labelled
		Anionic surfactants	5-15		
		Soap	< 5		
		Polycarboxylates	< 5		
		Phosphonates	< 5		
		Enzymes	< 5		
		Non-ionic surfactants	< 5		
Product 9		Anionic surfactants	-		Not labelled
	7732-18-5	Demineraliseret vand	-		
	143-19-1	Sodiumoleat	-		
		Real perfume	-		
		Citrus extract	-		
		Enzymes	-		
Product 12		Soap	< 5		Not labelled
		Non-ionic surfactants	15-30		
		Enzymes	-		
		Preservative	-		
Product 25		Anionic surfactants	5-10		Not labelled
		Enzymes	< 5		
		Fruit acid	< 5		
Product 32		Non-ionic surfactants	-		Not labelled
		Enzymes	-		
	143-19-1	Sodiumoleat	-		
	56-87-1	Glycerol	-		
		Citrusterpener	-		

Table 6 – Products based on surfactants and enzymes
* According to supplier information

3.1.4.3 Category 3 – Products containing bleaches

This category contains 6 products of which 3 contain sodium percarbonat, 2 contain sodium dithionit and 1 contains an unnamed oxygen-based bleach.

All products are powders and can be used in the washing machine.

The products in this category are all labelled according to the EPA regulations. However, there seems to be some disagreement between the producers about how a product that contains > 30 % sodium percarbonat should be classified, as can be seen from table 7.

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (Product)
Product 8		Anionic surfactants	5-15		Xi;R36
	1318-02-1	Zeolites	< 5		S22-26-2
	497-19-8	Sodium carbonate	-	Xi;R36	
	7775-14-6	Sodium dithionie	-	R7 Xn;R22 R31	
		Optic white	-		
		Perfume	-		
Product 10	775-14-6	Sodium dithionite	> 30	R7 Xn;R22 R31	Xn, R7-22-31 S7/8-26-38-43
Product 11		Non-ionic surfactants	< 5		Xi;R36
		Soap	< 5		S2-22-26
		Enzymes	< 5		
		Oxygen-based bleaches	15-30		
Product 16	15630-89-4	Sodium percarbonate	> 30		Xi;R36 S2-7/?-26-17
Product 22	15630-89-4	Sodium percarbonate	> 30	O;R8 Xn;R22 Xi;R36/38	Xn;R22-26/38 S2-26-46
		Carbonates	5-15	Xi;R36	
		Sulphates	5-15		
		Non-ionic surfactants	< 5	Xi;R41-38	
		Zeolites	< 5		
Product 35	15630-89-4	Sodium percarbonate	> 30		O, Xn R8-22-36/38 S1/2?-17?-25-26-46

Table 7 – Products containing bleaches

* According to supplier information

? Not correct S-phrase on the packaging, the stated phrase is the one that comes closest to the correct text

It should be noted that product no. 16 and 35 has been supplied with non-regulation S-phrases. For example "Store cool, locked up and inaccessible to children" which is a hybrid of sorts between S1/2: "Keep locked up and out of the reach of children" and S3: " Keep in a cool place" as well as the phrase "The product should be kept away from flammable substances", which is almost similar to S17 "Keep away from combustible material". Likewise for product 16 with "Keep container tightly closed and not to warm" which is like a compile of S7 and S15 or S3. Even though the message in the uses S-phrases are correct you must according to the law, use the official S-phrase formulations, and the products have thus not been labelled completely correctly. In addition, the product has been supplied with an EU declaration, but the substance name has been stated in a language other than Danish.

3.1.4.4 Category 4 – Products containing solvents

This category contains 9 products and includes a number of the so-called special agents which is perhaps not surprising as these products have been specifically designed for especially difficult stains which it takes "tougher" substances to dissolve.

The category also includes the 2 registered aerosol products (products 19 and 33). All products, except products 21 and 20, have been hazard labelled according to the EPA regulations. Of these, 6 products are labelled for fire hazard.

In addition, this category contains the only product out of all of them classified for allergens as product 26 contains d-Limonen in an amount which leads to a classification with R43 " May cause sensitisation by skin contact".

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (Product)
Product 4	67-63-0	Isopropanol	-	F;R11 Xi;R36 R67	Xi;R10-41
		Propylenglycolether	-		S26-28-2
	628-63-7	Amylacetat	-	R10 R66	
	3088-31-1	Anionic surfactants, Sodium laurethsulphate	10-30	Xi;R38-41	
		Non-ionic surfactants; Fedtalkoholethoxylat-7	5-15	Xn;R22 Xi;R41 N;R50	
		Preservative			
Product 13	102-71-6	Triethanolamin (TEA)	5-10		** Xi R10-36/38
	61827-42-7	Polyethylenglycolisoddecylether	5-10		S2-26-37-46
	68584-24-7	Benzenesulfonsyre, C10-16 alkyl derivatives, compounds with 2-propanamin	10-30		
	68647-72-3	Terpenes and terpenoides, sweet orange oil	30-60		
Product 14	111-46-6	Diethylenglycol	20-30	Xn;R22	**Xn;R22
		Non-ionic surfactants	< 1		S2-23-45-63*
	61827-42-7	3-hydroxy-5-methylisoxazol	1-5		
	9073-77-2	Proteinase, Bacillus alkaline	1-5		
Product 15	67-63-0	Propan-2-ol	75-100	F;R11 Xi;R36 R67	**F Xi R11-36 S2-7-16-24/25-26
Product 19		Aliphatic hydrocarbons	> 30		**Fx;R12
	108-08-7	Heptane		F;R11 Xi;R38Xn;R65 R67 N;R50/53	S2-16-23-51
	109-66-0	Pentane		Fx;R12 Xn;R65 R66 R67 N;R51/53	
	106-97-8	Butane		Fx;R12	
	74-98-6	Propane		Fx;R12	
		Cationic surfactants	< 5		
		Perfume	< 5		
	1318-02-1	Zeolites	5-15		

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (Product)
Product 21		Glycerol			Not labelled
		Alkali			
		Glycoether			
		EDTA			
		Phosphate			
		Cationic surfactants			
		Non-ionic surfactants			
Product 20		Salt of sorrel			Not labelled
	144-62-7	Oxalic acid		Xn;R21/22	
	77-92-9	Citric acid			
		Traganth			
	64-17-5	Denatured spirits			
Product 26	8052-41-3	White spirit (Benzene content < 0.1%)	1-5	R10 Xn;R48/20-65	Xi;R10-43 S24-73
	5989-27-5	d-Limonen	1-5	R10, Xi;R38-43, N;R50/53	
	111-76-2	Butylglycol	1-5	Xn;R20/21/22Xi;R37	
Product 33	115-10-6	Dimethylether	10-30	Fx;R12	F;R11
	107-98-2	Propylenglycolmono-methylether	1-5	R10	S2-16-23-51
	-	Styrene/maleinanhydrid polymer	1-5	Xn;R20/22	

Table 8 – Products containing solvents

* According to supplier information. ** The packaging contains less than 125 ml which means that full labelling is not required.

3.1.4.5 Category 5 – Products based on natural/”green” ingredients

This category is represented by 4 products as stated in table 9 of which 3 can be purchased via health stores and 1 (product 2) for now is only sold over the internet. The supplier has informed us that product 2 contains micro-organisms and the product will be described further in the project ”Kortlægning af lugtfjernere” (Mapping of odour removers). None of the products have been labelled according to the EPA regulations. In this category, exotic ingredients such as ox bile are found.

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (product)
Product 2		Kokosdiethanolamin	5-10		Not labelled
		Cetylalkohol	5-10		
		Fruit acids	1-5		
		Silica	1-5		
		Kieselsyreanhydrid	0-1		
Product 29		Vegetable oil-based soap	< 5		Not labelled
		Citrusterpener	< 5		
		Alcohol	< 5		
		Ethereal oil	< 5		

Product no.	CAS-no.	Substance name	Content %	Classification (substance)	Labelling (product)
Product 30		Sugar surfactant	5-10		Not labelled
		Fedtalkoholsulfat	1-5		
		Orange peel oil	< 1		
		Ethereal oil	< 1		
Product 31		Palm oil and coconut grease soap	> 30		Not labelled
		Ox bile	10-15		
		Chlorophyll	5-10		

Table 9 – Products based on natural/“green” ingredients

3.1.4.6 Products that are not covered by the above categories

This category contains the remaining products, a total of 3. Product 23 cannot be immediately placed in the above-mentioned categories. The product consists of 2 components of which one is 100 % potassium permanganate and the other is 100 % dinatriumdisulfit. The clothes are treated first with one agent and then with the other. Both components are labelled “Harmful” with risk phrase R22 “Harmful if swallowed”.

Product no.	CAS-no.	Substance name	Classification	Labelling
Product 23 a - 2 components	7722-64-7	Potassium permanganate	O;R8 Xn;R22 N;R50/53	O,Xn,N R8-22-50/53 S2-60-61
Product 23 b - 2 components	7681-57-4	Dinatriumdisulfit	Xn;R22 Xi;R41 R31	Xn; R22-41-31 S2-26-39-46
Product 34		Oxalic acid	Xn;R21/22	Not labelled
		Potassium carbonate		
		Citric acid		
Product 24*				

Table 10 – Products that are not covered by the above categories

* The product has been cancelled from the investigation

Product 34 is based on oxalic acid. The product is not labelled according to the EPA regulations. If the content of oxalic acid exceeds 5 %, the product must be classified with Xn;R21/22, but as no interval has been stated for the content of this substance, it is not possible to evaluate whether it is correct that the product should not be labelled. However, analysis have shown that the content is below the classification limit of 5 % (see section 5.2.4). Product 24 differs from the other products in that it contains a “mixture of specific, natural, highly active bacterial strains” /4/. Since the product can also be used as an odour remover, it will be removed from this investigation.

3.1.4.7 List of all registered ingredients divided into functions

Based on the information from the previous tables, a gross list has been prepared of substances that have been identified during the mapping. These have then been divided according to the function of the substances in the product as can be seen from table 11.

Substance name	Occurrence	Note
Bleaches		
Oxygen-based bleach	1	
Sodiumdithionit	2	
Sodiumpercarbonat	3	
Propellants		
Butane	1	
Dimethylether	1	
Propane	1	
Fragrances		
Citrus extract	1	
Citrus terpenes	2	
Fragrances	1	
Orange peel oil	1	
Perfume	9	
Terpenes and terpenoids, sweet orange oil	1	
Real perfume	1	
Ethereal oils	2	
Enzymes		
Enzymes	9	
Proteinase, Bacillus alkaline	1	
Fillers/Consistency agents		
Calcium chloride	1	
Carbonates	1	
Cellulose	1	
Potassium carbonate	1	
Sodium carbonate	2	
Sodium sulphate	1	
Silica	1	
Traganth	1	
Complex binders		
Citrate	1	
EDTA	1	
Sodium tripolyphosphate	1	
NTA	2	
Phosphate	2	
Phosphonates	5	
Polycarboxylates	1	
Sulphates	1	
Zeolites	4	
Preservation		
Preservative	10	
3-Hydroxy-5-methylisoxazole	1	
Sodium-2-mercaptobenzothiazole	1	

Substance name	Occurrence	Note
Solvents		
Alcohol	1	
Amylacetate	1	
Butylglycol	1	
Cetyl alcohol	1	
Denatured spirits	1	
Diethylenglycol	1	
d-Limonen	1	Also a fragrance
Glycerine	2	
Glycolether	1	
Heptane	1	
Isopropanol	2	
White spirit (Benzene content: <0,1%)	1	
Pentane	1	
Propylenglycolether	1	
Propylenglycolmonomethylether	1	
Triethanolamin (TEA)	1	
Surfactants		
Alcohol ethoxylates	1	Non-ionic surfactant
Anionic surfactants	8	
Benzene sulphonic acid, C10-16 alkyl derivates, compounds with 2-propanamine	1	Anionic surfactant
Fatty alcohol sulphate	1	Anionic surfactant
Cationic surfactants	2	
Coco diethanolamide	1	Non-ionic surfactant
Sodium oleate	2	
Sodium laurethsulphate	1	Anionic surfactant
Non-ionic surfactants	13	
Sugar surfactant		Non-ionic surfactant
Vegetable oil based soap	3	
Soap	3	
pH-regulation		
Alkali	1	
Citric acid	2	Also used as bleach
Fruit acid	2	
Sodium metasilikat	1	
Sodiumsilikat	1	
Oxalic acid	2	
Acid salt		
Other		
Disodiumdisulfite	1	
Potassium permanganate	1	
Kiesel acid anhydride	1	
Chlorophyll	1	Dye
Ox bile	2	

Substance name	Occurrence	Note
Optic white	1	
Polyethylenglycolisodicycylether	1	
Polymers	1	
Styren/maleinanhydrid resin	1	Impregnation
Salt of sorrel	1	

Table 11 – All identified substances divided according to function

Along with the data from the Nordic product registers SPIN database, the above table confirms the stain removers may contain "harsh" substances such as solvents and/or allergenic substances such as D-limonen.

3.2 Mapping of DIY advice

The purpose of this sub-activity is to identify and create an overview of the various DIY advice as well as to provide an overview of "old" designations and their meaning.

The interest for stain removal is mirrored not only in the number of products on the market but also in the many stain guides available on the internet. Table 12 lists the websites that contain stain guides, tips and advice.

3.2.1 Books and pamphlets

The principal work in this category is the pamphlet "På pletten" (On the "spot"), published by the Danish Consumer Agency. The pamphlet can be downloaded from the internet and the Consumer Information website can be searched for information. The pamphlet was first published in 1964 by Statens Husholdningsråd (the Danish Government Home Economics Council) and has since then been regularly updated and edited.

Of newer literature can be mentioned "Alle tiders gode råd til hjemmet" (All-time best advice for the home) from 1995, "Tørsleff's Husmodersevise: Den store bog om at holde hus" (Tørsleff's Housewife Serice: The big book about keeping house) from 1998 as well as "Gamle Husråd og gode ideer" (Old household remedies and good ideas) from 2001.

Of older literature can be mentioned a couple of works by Sven Holm, "Jeg renser alt" (I clean everything) from 1959 and "Alt om pletter" (Everything about stains) from 1960 as well as "Pletbogen" (The book of stains) by Henrik Berg from 1981.

Below, some of the more curious stain removal advise from these books are stated.

Chocolate and cocoa

"Little Svend and Kirsten are sitting at a birthday table acting silly, and of course Svend inevitably knocks over his cup of cocoa. But it is after all a birthday, so even though mom is upset, *after all nothing happened to the children*. As soon as they leave the table, mom rinses the table cloth in boiling water. The stain may be held over a water bath while boiling water is being poured through. Is the stain dry, you can treat it before washing with water and then rub on borax. Borax has the quality of destroying the cerasine

(cheese substance) in the milk which is what stiffens the stain. Afterwards, the stain is washed as usual." /9/

Honey

"Honey is so simple that it is barely worth mentioning. The agent with which to remove honey is water – tepid water, *or the too often unnoticed agent to which we have such easy access: - spit.*" /9/

Blood

"As soon as you get blood on your clothes, make a small ball of sewing thread, chew on it and then use it to wash away the stain. The spit dissolves the blood." /5/

Orange juice

"Orange juice stains belong to a group of innocently looking fruit stains. They must, however, be removed immediately and at first, the agent of choice is *spit*. Spit contains the enzyme ptyalin which prevents the stains from oxidizing, i.e. from staining." /15/

Shoe polish

"Shoe polish stains can be found on carpets, furniture upholstery, on floors and on *mens' trouser turn-ups*. The best agent for removal of the stains is carbon tetrachloride or possibly petroleum naphtha." /5/. It should be noted that some of the substances mentioned here are classified as carcinogenic.

Tobacco stains on the teeth

"A mixture of 100 g peppermint chalk, 10 g soda, 10 g magnesia, 10 g sodium-perborate is used on a wet tooth brush." /15/

Resin stains

"Resin stains may e.g. come from the Christmas tree, the pine forest, a garden seat or from a berth, or they may come from a violin or another string instrument. No matter what caused the stain, resin is removed with petroleum naphtha, gasoline or spirits. Spirits is most commonly used for stains on the skin and you may use methylated spirits, eau de cologne or even brandy or aquavit if that is all you have and if you want to sacrifice one of these precious liquids. For fabrics, petroleum naphtha or pure gasoline's are the best agents. The violin bow may graze the clothes and leave a white stain that will disappear immediately with one of these agents. If, however, you want to clean resin dust from the violin or another string instrument (or from the instrument bow), only pure gasoline should be used as that will not ruin the instrument lacquer as spirits would." /15/. It should be noted that some of the substances mentioned here are classified as carcinogenic.

3.2.2 The internet

As with so much else, the internet is a source of an incredible amount of information on the subject of stain removal. There are a number of both Danish and foreign websites which contain advice on stain removal in either alphabetized lists or in search engines where you can fill in the type of stain and mat. Table 3 contains an overview of some of these websites.

In addition, several internet websites feature DIY and household remedies. These sites also contain information on stain removal, though typically not as systematically presented as on the websites stated in table 12.



Stain guides

Name	Type	Website
På pletten	Alphabetical list	http://www.fi.dk/hjemme/paa_pletten/
Bio-Tex Pletguide	Search engine	www.bio-tex.dk/html/pletguide/main.html
Her kan du søge råd til pletfjerning...	Search engine	www.borup-kemi.dk/html/soegeplet-soeg.html
Garants Plet Guide	Website	http://www.garant-gulve.dk/sw3631.asp
Pletnøglen	Website	www.taeppe-hallen.dk/page10.html
OMO Pletguide	Search engine	http://www.omo.com/dk/pletguide/index.php?id=6603
Pletguide	Alphabetical list	http://www.snehvide.dk/pletguide/
Pletguide	Search according to category	http://www.texpert.dk/texsymboler.html
Pletguide	Search engine	http://www.neutral.dk/2%5Cmain24.html
Pletguide for uldstoffer	Alphabetical list	http://www.jakslan.dk/produkter.htm#pletguide
Pletvejledning af microfiber	List	http://www.linbo.dk/index.php?pid=5&id=5
Stain detective		http://www.tide.com/articles/read.jhtml?articleId=3515
Garants pletguide	Search	http://garant-gulve.dk/sw3535.asp
Stain Guide		http://www.chemistry.co.nz/stain_frame.htm
Pletfjerning	Alphabetical list	http://www.miele.dk/miele_hushold/gode_raad/gr_plet.htm
Generelle tips til at fjerne pletter på tæpper	List	http://www.nilfisk-advance.dk/CleaningSolution/Hotel/StainGuide/content.htm
Nice to know	Table	http://www.humlebjerg.dk/niceto.htm#Plet

Tips and advice

Name	Type	Website
Tips og gode råd	Home remedies	http://www.imerco.dk/default.asp?ID=92
ask-alex	Good advice	http://www.ask-alex.dk/artikler/
Tips og Tricks – Lidt om pletter	List	http://www.byavis.dk/Opslagstavlen/opslagstavlen/tips_tricks/tekst_lidt_om_pletter.htm
Tip og gode råd	Alphabetical list	http://users.cybercity.dk/~buu1693/tips/rengoring.html
Det' Leth		http://www.dr.dk/leth/classic/index.htm

Table 12 – Sources of online stain guides and advice

3.2.3 Chemical substances for DIY use

Below is a table listing the chemical substances recommended for stain removal in both literature and on the internet.

Substance name	Use - stain	Ref.
Acetone	Glue, gum, oils, lip stick etc.	10, 13.
Household ammonia 25%	Verdigris stains, copper	13
Household ammonia 8 %	Grass stains	10, 13
Amylacetat	Glue on textiles that cannot tolerate acetone	10.
Baby oil	Carrot stains	6.
Baking powder	White rings on marble. Baby vomit	11
Benzine	Different types of clothes	10
Blotting paper	Stearin – ironed on top of the blotting paper	5
Borax	Burn stains and singed stains on clothes, grease stains	9, 10
Bread	Carpet stains are rubbed with soft bread	5
Brown soap	Oil on clothes	10
Buttermilk	Ink on clothes	14
Carbon tetrachloride	Chocolate	15
Cellulose thinner	Grease, grass, resin	13
Cement	Oil and gasoline stains on tiles	11
Chalk	Grease stains on silk	5
Chlorine	Mouldiness, fruit, wine	13
Citric acid	Ink, fruit stains	5,13
Coarse salt	Soot stains on carpet	11
Crystal soda solution	Cod-liver oil on clothes	14
Dishwasher liquid	Many types of stains. No delicate fabrics	5
Dishwashing liquid	Many types of stains on water-proof textiles	10
Egg yolk	Tar	5
Engine cleaner	Oil and gasoline stains on tile	11
Eraser	Grease stains on leather	5
Eucalyptus oil	Grease and food oil stains	5
Fragrance-free petro-leum	Oil	13
Gasoline	Gum, asphalt tar on clothes, fly stains, resin	9
Glycerin	Plastic paint on clothes, red wine, coffee, tea	11, 13
Glycerol	Ink	5
Household sprits	Ball point pen or indian ink	10, 5
Hydrochloric acid 30%	Verdigris stains, copper	13

Substance name	Use - stain	Ref.
Hydrogen peroxide	Bleaching of all types of stains	10
Lamp oil	Asphalt on car	11
Lemon juice	Common stains on marble. Tea stains	5, 11
Magnesium	Stains on suede are cleaned with burnt magnesium	6
Mineral turpentine	Different types of clothes	10
Onion	Stains on leather are rubbed with a sliced onion	6
Oxalic acid 10 %	Rust, blood	13, 14
Petroleum	Oil stains on tiles	10, 13
Petroleum naphtha	Asphalt tar on clothes, brillantine, fly stains	9
Pipeclay and water	Grease stains on fabric and untreated wood	5
Potato flour	Coffee stains	5
Rust removal agent	Rust stains	10
Salt	Coke stains etc. on carpets. Eggs on silver	10
Saw dust	Vomit	5
Soda	Burnt stains	7
Sodiumdithionit	Ink, rust, red wine	14, 13
Sodiumthiosulphate	Neutralization after treatment with chlorine	10
Tea tree-oil	Oil and oil paint	5
Turpentine oil	Skocremer på tøj der skal vaskes på uldprogram	12
Tomato	Ink	5
Tooth paste	Black streaks on the floor	11
Vaseline	Lip stick	5
Vinegar	Snow rings on leather shoes	10
Whole milk	Indian ink on clothes, ink, chocolate	10

Table 13 – Substances used for stain removal

It can be seen from table 13 that the spectrum of chemical substances used for stain removal is very extensive. It covers everything from harmless agents such as whole milk and buttermilk, which most of us ingest on a daily basis, to substances such as carbon tetrachloride (tetra-chlormethan) and petroleum naphtha (benzene) which are carcinogenic and which, for that reason, are hardly used at all any more. It is also forbidden to use carcinogenic substances in consumer products.

The older literature often uses old designations for chemical substances, which are no longer used today. In annex 1 there is a list of translations of a number of these designations.

3.2.4 Substance mixtures for DIY use

In addition to the pure substances stated in the table, there are a number of household remedies that require a mixture of different substances: A universal stain remover called "stain scare" thus consists of 4 tablespoons of household ammonia, 4 tablespoons of ethyl alcohol and 1 tablespoon of salt. /6/

Below are a number of examples of substance mixtures for stain removal collected from the literature.

Mouldiness can be removed with buttermilk mixed with a teaspoon of salt per litre buttermilk. /9/

Grass stains can be removed with spirits or pure alcohol and then rinsed in soap water. /6/

Ball point pen stains are removed with 1 teaspoon vinegar and 1 teaspoon spirits. /6/

Sweat stains are removed with 1 tablespoon spirits and $\frac{1}{4}$ salicylic acid. Then rinse thoroughly with water. /6/

Fruit stains can be washed with spirits. If that does not help, you can use household ammonia heated with water which is used to prepare the stain. Then mix milk with lemon juice and soak the stain in this liquid overnight and then wash. /6/

Oil paint stains dry fast and are dissolved by 1 teaspoon turpentine oil, 1 teaspoon household ammonia and 1 teaspoon soap spirits. Dry with a cloth and soak up the remaining liquid with blotting paper. Rinse stain with clean water and wash the clothes in the usual manner. /6/

Coffee stains are treated with cold water and then bile soap. Older coffee stains are treated with glycerine. /6/

Older stains are removed with 2 tablespoons dishwashing liquid, 3 tablespoons vinegar and 1 litre warm water. /6/

Difficult stains from *banana* can be removed with citric acid and water. /5/

Bird droppings must dry and can then be scraped and brushed off, but if a whitish stain remains it can be rinsed with cold water containing a splash of vinegar. During the elderberry season, bird droppings are often violet. Let them dry in the same manner and clean them with a little sodium dithionite or bleach in lukewarm water. /15/

Browning stains are removed with water containing a sulphonating dishwashing liquid. /15/

Walnut juice stains are removed with a weak solution of hydrochloric acid. 1 part hydrochloric acid is mixed with 2 parts cold water. The stained areas (usually the fingers) are placed in the mixture. Then wash with soap and water. If walnut colouring is still present it can be removed with equal parts of lime chlorine and Epsom salts, mixed dry and stirred into a mush with cold water. /15/

In case of *urine stains* in clothes, the clothes are soaked in a powerful detergent and washed at a high temperature. If the fabric is intolerant to heat, use a hydrogen peroxide solution. /7/

Moisture stains on lacquered wood is removed with *cigar ash*. Moisten the stain and moisten a rag. Put a little cigar ash on the rag and rub the stain. Dry and repeat the treatment until the stain is gone. Finish off with furniture polish. NB: Avoid using cigarette ash as it may scratch the lacquer. /5/

Lime stains in the carafe can be removed by filling the carafe with coarse salt moistened with vinegar and shaking firmly until the stains are gone. Then clean in the usual manner. /5/

Mould stains in clothes can be removed with a thin paste of water, coarse rye flour and yeast. The clothes are soaked in the paste for a couple of days before it is washed in the usual manner. Mould stains can also be removed with salt, particularly if the stain is on linen fabric. Dissolve a teaspoon of salt in a little water and smear the mixture on. When the stain is dry, the clothes can be washed in the usual manner. /5/

Ordinary dishwashing liquids remove many kinds of stain on fabric. Put some dishwashing liquid on the stain and let it work for about an hour. Then wash in the usual manner. /5/

Difficult stains on fabric can often be removed by moistening the stain with a mush of salt and lemon. Let it work for a few hours and then wash the clothes in the usual manner. /5/

Grease or oil stains on silk can be removed by rubbing the stain with pulverised borax. /5/

Milk vomit on clothes can be removed by mixing a tablespoon of water and a teaspoon of baking powder which is rubbed on the stain. This removes the smell and the stain. /5/

3.3 Estimate of the consumption of stain removers

Information has been obtained from the largest Danish super market chains and materialists on the annual sale of stain removers. In some cases it has not been possible to obtain data on individual products. No information has been obtained on the sale of stain removers from health stores, carpet stores, specialty stores and for products sold on the internet as it is estimated that the sale from these stores makes up only a fraction of the combined stain remover sale.

The result shows that approximately 800,000 units of stain removers are sold distributed with approximately 127,500 litres of stain remover in the form of liquid/paste and 176,000 kilos in the form of powder. These numbers are probably a slight understatement of the actual sale due to the above conditions.

State	Item/year	Amount/year
Liquid and paste	133,573	13,554 l/year
Aerosol/spray	295,608	133,790 l/year
Powder	358,145	176,036 kg/year
Total	787,326 units	

Table 14 – Number of units and amounts of stain removers sold retail

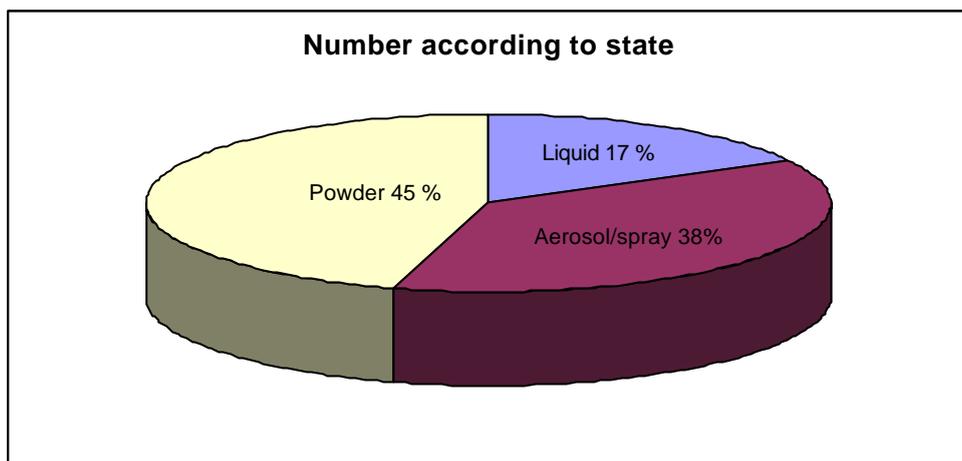


Figure 1 – Number of stain removers according to state

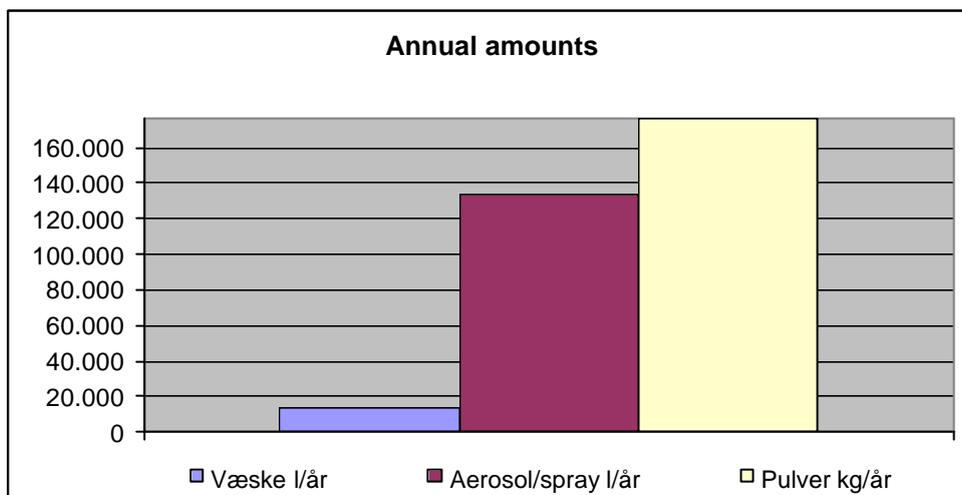


Figure 2 – Amounts of stain removers according to state

As can be seen from figures 1 and 2, the powder stain removers make up the largest number of products sold retail per year as well as the largest amount.

4 Conclusions from mapping

The list of identified ingredients confirms the EPA assumption that products for stain removal may contain "harsh" substances. As can be seen from chapter 3, the "harshest" products are found in categories 3 and 4, products that contain bleaches and products that contain solvents, respectively.

It should be noted that it has not been possible to obtain complete information on the chemical composition of the products as the investigation is based exclusively on immediately available information from the suppliers in the form of information found on the labels and in the safety/product data sheets.

It is thus to be expected that several of the water based products, in addition to those for which it is immediately apparent, may contain preservatives. For example, product 17 (category 1) does not contain preservatives according to the safety data sheet. The product has not been declared according to the EU declaration of which it should be apparent if the product contained preservation. Based on the available information, it can therefore not be excluded that the product actually contains preservatives. The same can be said for products 9 and 32 from category 2 as the labels have a declaration which is not in accordance with the EU recommendation and which does not mention preservatives. Finally, the same may also be the case for the products in category 5 and some of the products in category 4.

It might also be relevant to investigate whether the two products containing oxalic acid (products 20 and 34) contain amounts greater than the limit for classification (5%) since household remedies that mention oxalic acid for removal of rust stains, prescribe a 10 % solution.

In cooperation with the EPA, it was decided to choose the products in table 15 for analysis.

Product	Category	Basis
17	1	No preservative content has been stated in spite of the product being water based. The product contains NTA.
9	2	No preservative content has been stated in spite of the product being water based. What is "real perfume"?
32	2	No preservative content has been stated in spite of the product being water based. Which non-ionic surfactants does the product contain?
20	4	No preservative content has been stated in spite of the product being water based (however, does contain citric acid). Control of the oxalic acid content.
30	5	No preservative content has been stated in spite of the product being water based. Which etheral oils does the product contain?
21	4	No preservative content has been stated in spite of the product being water based. Which non-ionic surfactants does the product contain?

Table 15 – Products for analysis

In addition, all products are analysed for content of perfumes and x-ray analysis is carried out to investigate possible content of heavy metals. With regard to non-ionic surfactants, analyses are made for the environmentally problematic octyl and nonyl phenolpolyethoxylates. For analysis results and answers to the above questions, please see section 6.6.

5 Analyses

5.1 Analysis methods

5.1.1 X-ray

A part sample of the products is tested for metal content using X-ray techniques. The analyses were performed as single determination as the analysis uncertainty is 3-10% RSD. The detection limit is 5 mg/kg.

5.1.2 GC/MS screening (including preservatives)

A part sample of the products is extracted with dichloromethane with added internal standards by Soxhlet extraction for 16 hours. A part sample of the extract is taken and analysed directly with combined gas chromatography and mass spectrometry (GC/MS) by scanning over a larger mass area. The content is calculated quantitatively to external standards (selected preservatives) or semi-quantitatively to internal standards (others).

Analysis uncertainty for components calculated quantitatively (external standards) is 10-15% RSD, and for components calculated semi-quantitatively (internal standard), the analysis uncertainty is estimated at 50-200%.

The analyses are performed as true double determination. The limit of reporting is 10-50 mg/kg.

5.1.3 Fragrances

A part sample of the product is taken and extracted with water and tert-butylmethylether by means of shaking, heating, cooling and standing during a period of approximately 16 hours. A part sample of the extract is taken and analysed directly with combined gas chromatography and mass spectrometry (GC/MS). The analyses are performed as true double determination. The detection limit is 1-10 mg/kg and the analysis uncertainty is 10-15% RSD.

5.1.4 NTA (Nitrilotriacetic acid)

A part sample is dissolved in mobile phase and analysed directly on ion chromatograph with anion exchanger and conductance detection (IC). The analyses are performed as true double determinations. The analysis uncertainty is 10% RSD.

5.1.5 Oxalic acid

A part sample is extracted with water with added sulphuric acid after which a part sample of the extract is analysed at high-pressure liquid chromatography with UV detection (HPLC-UV). The analyses are carried out as true double determinations. The analysis uncertainty is 10% RSD.

5.1.6 Alkylphenol polyethoxylates

A part sample is extracted with methanol and aqueous ammonium acetate solution after which the extract is analysed at LC/MS with positive mode electro spray ionisation. The analysis includes octyl- and nonylphenol ethoxylates from 3 to 15 ethoxy groups.

The analyses are performed as true double determinations. The analysis uncertainty is 10-15% RSD.

5.1.7 Chloromethyl- and methylisothiazolones

A representative part sample is taken and diluted in demineralised water. Two drops of concentrated hydrochloric acid is added to the solution after which it is filtered through a 0.45µm filter. The filtered solution is analysed by liquid chromatography with UV-detection (HPLC/DAD). The analyses are performed as true double determinations. The analysis uncertainty is 10-15%. The detection limit is 10 mg/kg.

5.2 Analysis results

5.2.1 GC/MS screening (including preservatives)

Stain removers are analysed for the preservative agents that could be included in the GC/MS screening by including external standard. The result of the analyses is given in table 16. The two results indicate the double determinations. The unit is mg/kg. Preservatives were only determined in one sample.

	D.I.	9	17	20	21	30	32
Methylparabene	50	-	-	-	-	-	-
Ethylparabene	20	-	-	-	-	-	-
Methylparabene	50	-	-	-	-	-	-
Propylparabene	20	-	-	-	-	-	-
Butylparabene	10	-	-	-	-	-	-
Benzylbenzoate	2	2.6 3.2	-	-	-	-	-
Benzylalcohol	1	210 190	-	-	-	-	-
o-cresol	1	-	-	-	-	-	-
m+p cresol	1	-	-	-	-	-	-

Table 16 – Results of analysis for preservatives. The results are stated in mg/kg.

D.I.: Detection limit

-: No detection above the detection limit

The result of the GC/MS screening for extractable organic compounds is stated in table 17. The analysis was made in double determination and both results are stated in the table.

All identifications of substances are carried out from the mass spectrum by comparing with mass spectra in a data library (NIST). In each case, the spectra representing the best match are assessed at "scientific judgement".

The identified components are rendered by their chemical name in the table. Some components with uncertain identification are designated with a star in the table.

The components that were unidentifiable to specific chemical component are collected in groups according to their structure. Finally, the components where identification proved impossible are collected in a group under unidentified components.

Substance name	CAS-no.	9	17	20	21	30	32
Methylisobutylketon	108-10-1	-	-	66 28	-	-	-
Trimethyloxiran *	5076-19-7	-	120 77	-	-	-	-
2-Butanon	78-93-3	-	-	-	-	130 190	-
α -Pinen	7785-26-4	-	-	-	-	31 49	-
Propylenglycol *	57-55-6	4800 6000	-	-	-	-	2600 1700
Glycerin ^	56-87-1	-	-	-	1700 1800	38 39	280 180
β -Pinen	127-91-3	-	-	-	-	44 67	-
β -Myrcene	123-35-	-	-	-	-	39 53	-
n-Decan	124-18-5	-	-	-	-	-	15000 17000
n-Undecan	1120-21-4	-	-	-	-	-	68000 76000
2-(phenylmetylen) heptanal	122-40-7	29 40	-	-	-	-	-
Dodecan	112-40-3	-	-	-	-	-	58000 65000
Ester	-	-	6.9 6.3	-	-	-	-
3,7-dimethyl-1,6-octadien-3-ol	78-70-6	-	-	-	-	620 710	-
Tridecan	629-50-5	-	-	-	-	-	46000 51000
α -Terpineol	8006-39-1	-	-	-	-	190 210	-
Isopropylmyristat	110-27-6	160 130	-	-	-	-	-
Tetradecan	629-59-4	-	-	-	-	-	10000 12000
Aromatic ester	-	210 220	-	-	-	-	-
Diisobutylphthalat	84-69-5	-	-	-	6.2 5.6	-	-
Dibutylphthalat	84-74-2	-	-	-	14 12	-	-
3-bromo cholest-5-ene	516-91-6	48 39	-	-	-	-	-
Gamma sitosterol	5779-62-4	71 18	-	-	-	-	-

Substance name	CAS-no.	9	17	20	21	30	32
Sum of grouped compounds, alkanes	-	300000 310000	-	-	-	-	-

Substance name	CAS-no.	9	17	20	21	30	32
Ethylbenzene/xylenes	-	19 46	-	-	-	-	-
Alkan and alkanic acids (= fatty acids)	-	7700 9900	-	-	-	-	5200 4600
Alkan and alkanic acid ethylesters (= fatty acid ethyl esters)	-	-	-	-	-	2900 4400	-
Glycols, ethoxy and propoxy compounds	-	-	150 130	-	-	-	-
Alkan nitril	-	58 52	-	-	-	-	-
Alkan ester	-	130 23	-	-	-	-	-
Ethoxy/oxy compounds	-	4200 5200	-	-	-	-	4600 5100
Terpenes (in addition to those named)	-	-	-	-	-	34 47	-
Ketons	-	-	-	-	-	14 11	-
Alkans, alken and alcohols	-	-	170 170	-	-	370 330	-
Phthalates (in addition to those named)	-	-	260 260	-	-	-	-
Unidentified	-	-	42 38	170 94	-	200 300	-

Table 17 – Results of the GC/MS screening.

The two results state the double determinations. The results are stated in mg/kg.

*: Identified as the most likely component

^: slightly over-estimated as there are two interfering peaks

The ethoxy/oxy compounds in samples 9 and 32 could not be further identified. However, it could be a mixture of surfactants that could not be chromatographed to certain an identification and quantification by GC/MS.

5.2.2 Fragrances

The analysis for 26 specific fragrance ingredients in stain removers detected a total of 13 fragrances distributed on 4 products where the content in one product was so low that there might be a contamination component. In two of the products it was not possible to detect a content of the selected fragrance ingredients above detection limit. The total content of all 26 fragrances is stated in the table. The total content varies from 3 mg/kg to 5800 mg/kg corresponding to 0.58%.

Substance name	CAS-no.	D.I.	9	17	20	21	30	32
Anisyl alcohol	105-13-5	1	-	-	-	-	-	-
Amyl cinnamal	122-40-7	1	6 3	-	-	-	-	-
Amyl cinnamyl alcohol	101-85-9	1	-	-	-	-	-	-
Benzyl alcohol	100-51-6	1	56 62	-	-	-	-	-
Benzyl benzoat	120-51-4	1	-	-	-	-	-	-
Benzyl cinnamat	103-41-3	1	-	-	-	-	-	-
Benzyl salicylat	18-58-1	1	25	-	-	-	-	-

Substance name	CAS-no.	D.I.	9	17	20	21	30	32
			38					
α -Cetone	127-42-4	1	30 23	-	-	-	-	-
Cinnamyl alcohol	104-54-1	1	3 3	-	-	-	-	-
Cinnamal	104-55-2	1	-	-	-	-	-	-
Citral	5392-40-5	1	-	-	-	-	-	34 30
Citronellol	106-22-9	-	18 15	-	-	-	5 3	8 8
Coumarin	91-64-5	1	-	-	-	-	-	-
Eugenol	97-53-0	1	17 13	-	-	-	-	-
Farnesol	4602-84-0	1	-	-	-	-	-	-
Geraniol	106-24-1	1	31 27	-	-	-	120 120	19 18
Hexylcinnamaldehyde	101-86-0	1	4 4	-	-	-	-	-
Hydroxy citronellal	107-75-5	1	-	-	-	-	-	-
Lillial	80-54-6	1	7 5	-	-	-	-	-
D-limonen	5989-27-5	1	-	3 3	-	-	4500 4200	32 27
Linalool	78-70-6	1	36 35	-	-	-	1200 1100	6 5
Lylal	31906-04-4	1	-	-	-	-	-	-
Isoeugenol	97-54-1	1	-	-	-	-	-	-
Methyl heptin carbonate	9000-50-4	1	-	-	-	-	-	-
Oakmoss		10	-	-	-	-	-	-
Treemoss	68648-41-9	10	-	-	-	-	-	-
Sum			230 230	3 3	-	-	5800 5400	99 88

Table 18 – Results from the analysis for fragrances. Unit is mg/kg. The two results indicate the double determinations. D.I.: Detection limit. -: Not detected above the detection limit.

5.2.3 X-ray

The X-ray analysis only detected lead above the detection limit. The results are stated in table 19 as content in the products and the unit mg/kg. The detection limit is 5 mg/kg. The metals that are not stated in the table are not detected in the analysis. The analysis is performed as single determination due to the low uncertainty for the determination.

	D.I.	9	17	20	21	30	32
Lead (Pb)	5	14	-	-	18	-	16

Table 19 – Results from the x-ray analysis. The unit is mg/kg. D.I.: Detection limit. -: Not detected above the detection limit

5.2.4 Oxalic acid

Only one product was tested for oxalic acid in double determination.

	D.I.	20	20
Oxalic acid	0.02	4.3	4.1

Table 20 – Results from the oxalic acid analysis. The unit is weight %. The two results state the two double determinations. D.I.: Detection limit

5.2.5 NTA (Nitrilotriacetic acid)

Only one product was tested for NTA in double determination.

	D.I.	17	17
NTA	0.02	0.11	0.11

Table 21 – Results from the NTA analysis. The unit is weight %. The two results state the two double determinations. D.I.: Detection limit

5.2.6 Alkyl phenol polyethoxylates

Two products were tested for alkyl phenol polyethoxylates in two products in double determination. The analysis included octyl- and nonyl phenol polyethoxylates with 3-15 ethoxy groups.

	D.I.	32	32
Octylphenol-polyethoxylates	100	-	-
Nonylphenol-polyethoxylates	100	-	-

Table 22 – Results from the alkyl phenol polyethoxylates analysis. The unit is mg/kg. The two results state the two double determinations

	D.I.	21	21
Octylphenol-polyethoxylates	100	-	-
Nonylphenol-polyethoxylates	100	-	-

Table 22 – Results from the alkyl phenol polyethoxylates analysis. The unit is mg/kg. The two results state the two double determinations. D.I.: Detection limit. -: Not detected above the detection limit.

5.2.7 Chloromethyl- and methyliso-thiazolones

Four products were tested for one sum of the components chloromethylisothiazolon and methylisothiazolon. The components could not be detected in the four products above the detection limit given in table 24.

	D.I.	17	21	30	32
Chloromethylisothiazolon and methylisothiazolon	10	-	-	-	-

Table 24 – Results from the chloromethyl- and methyliso-thiazolones analysis. The unit is mg/kg. D.I.: Detection limit. -: Below the detection limit

6 Summary of analyses

6.1 Category 1 (Products based on surfactants)

6.1.1 Product no. 17

The manufacturer has estimated that the product does not have to be classified and labelled according to the EPA regulations.

Declared content:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Surfactant		Anionic surfactants	< 5	Xi;R36/38	
Complex binder	139-13-9	NTA	< 5	Xi;R36/38	
Active substance		Phosphonate	< 5	Xi;R36/38	
Active substance		Phosphate	< 5	Xi;R36/38	
Fragrance		Perfume	-	-	

-: Not stated

Analyses:

Substance function	CAS-no.	Substance name	Content % *	Classification	Note
Solvent	-	Glycoles, ethoxy or propoxy	0.00029		
Impurity	-	Phthalates	0.026		LOUS
Preservative	-	-	-		
Perfume	5989-27-5	d-Limonen	0.0003	R10 Xi;R38-43 N;R50/53	LOUS
Complex binder	5064-31-3	NTA (salt)	0.11	Xi;R36/38	

*: Average of the double determinations

-: Not detected above the detection limit

LOUS: The EPA list of unwanted substances /18/

Perfume:

The product contains a very small amount of d-Limonen which is classified as irritant and sensitising by skin contact (Xi;R38) and as a substance that may cause sensitisation by skin contact. d-Limonen is included on the EPA list of unwanted substances /18/ in the category "Selected substances in perfume products", i.e. perfume substances that, according to the SCCNFP (the scientific committee for cosmetics and other non-food products), may cause allergy by skin contact, i.e. allergens.

Preservation:

The analyses for preservatives did not show any of these substances in concentrations above the detection limit.

Phthalates:

Phthalates as a group are included on the EPA list of unwanted substances /18/. According to the EPA, the substances should be limited due to the concentrations found and to the health and environmental impact in connection with the use of residual products such as slag, compost and silt. In addition, the substances should be limited due to their health hazardous qualities (reproduction toxic). The product contains a very small amount of unspecified phthalates which probably exist as impurities from the raw materials used.

NTA (Nitrilotriacetic acid):

NTA is used as complex binder in washing and cleaning agents. The substance has been evaluated by IARC (International Agency for Research on Cancer) as belonging to group 2B "possibly carcinogenic to humans" /20/. The substance is included on the Danish Working Environment Authority (DWEA) list of substances considered to be carcinogenic /16/. Occupational use of products containing this substance is covered by the DWEA order on carcinogens /20/. However, products with a content of 10 % or less are not covered by the order on carcinogens if the product is used for industrial cleaning as Cleaning in Place-products or as dishwasher or liquid clothes washing products.

6.2 Category 2 (Products based on surfactants and enzymes)

6.2.1 Product no. 9

The manufacturer has evaluated that the product does not have to be classified and labelled according to the EPA regulations.

Declared content:

Substance function	CAS-no.	Substance name	Content % *	Classification	
Surfactant		Anionic surfactants	-	-	
	7732-18-5	Demineralsed water	-	-	
	143-19-1	Sodium moleat	-	-	
Fragrance		Real perfume	-	-	
Fragrance		Citrus extract	-	-	
Washing intensifier		Enzymes	-	-	

*: Average of the double determinations

-: Not stated

Analyses:

Substance function	CAS-no.	Substance name	Content % *	Classification	Note
Preservation	120-51-4	Benzyl benzoate	0.00029	Xn;R22	LOUS
	100-51-6	Benzyl alcohol	0.02	Xn;R20/22	LOUS
	-	Fatty acids	0.88		
Solvents	-	Alkanes	30.5		
	57-55-6	Propylen glycol	0.54		
Surfactant	-	Ethoxy/oxy compounds	0.47		

Substance function	CAS-no.	Substance name	Content % *	Classification	Note
Perfume substances	106-24-1	Geraniol	0.0029		LOUS
	122-40-7	Amyl cinnamal	0.0005		LOUS
	78-70-6	Linalool	0.0036		LOUS
	106-22-9	Citronellol	0.0017		LOUS
	18-58-1	Benzylsalicylate	0.0032		LOUS
	127-42-4	a-Cetone	0.0027		
	104-54-1	Cinnamyl alcohol	0.0003		LOUS
	97-53-0	Eugenol	0.0015		LOUS
	101-86-0	Hexylcinnamaldehyde	0.0004		LOUS
80-54-6	Lillial	0.0006		LOUS	
Perfume – total			0.023		
Impurity		Lead	0.0014		LOUS

*: Average of the double determinations

Perfume:

The product contains very small amounts of a large number of substances included on the EPA list of unwanted substances /18/ in the category "selected substances in perfume products" i.e. perfume substances that, according to the SCCNFP, may cause allergy by skin contact, i.e. allergens.

Preservation:

The analysis has identified two substances that function as preservatives. These two substances are also used as fragrances and are included on the EPA list of unwanted substances /18/. According to the EPA, benzyl alcohol is a documented allergen while benzyl benzoate is suspected of being an allergen /18/.

Surfactants:

According to the declaration, the product contains anionic surfactants. No further identification of these substances has been made.

Solvents:

The product contains a very small amount of polyethylene glycol which is a non-volatile solvent. In addition, the product contains non-identified alkanes in an amount corresponding to approximately 1/3 of the product. These alkanes can either have been added as solvents or as consistency agents (paraffin oil).

6.2.2 Product no. 32

The manufacturer has evaluated that the product does not have to be classified and labelled according to the EPA regulations.

Declared content:

Substance function	CAS-no.	Substance name	Content % *	Classification	Note
Surfactant		Nonionic surfactants	-	-	
Enzyme		Enzymes	-		
Soap/emulsifier	143-19-1	Sodium moleat *	-	-	
Solvent	56-87-1	Glycerine	-	-	
Perfume		Citrus terpenes	-	-	

*: 9-Octadecenoic acid, sodium salt

-.: Not stated

Analyses:

Substance function	CAS-no.	Substance name	Content % *	Classification	Note
Preservation		-	-		
Perfume substances					
	5392-40-5	Citral	0.0032	Xi;R38-43	LOUS
	106-22-9	Citronellol	0.0008		LOUS
	106-24-1	Geraniol	0.0019		LOUS
	5989-27-5	D-Limonen	0.0029	R10 Xi;R38-43 N;R50/53	LOUS
	78-70-6	Linalool	0.00055		
Perfume – total			0.0094		
Solvents	57-55-6	Propylenglycol	0.215	-	
	56-81-5	Glycerine	0.023	-	
	124-18-5	n-Decan	1.6	-	LV
	1120-21-4	n-Undecane	7.2	-	
	112-40-3]	Dodecane	6.15	-	
	629-50-5	Tridecane	4.85	-	
	629-59-4	Tetradecane	1.1	-	
	-	Fatty acids	0.88	-	
Surfactant	-	Ethoxy/oxy compounds	0.49	-	
Impurity		Lead	0.0016	-	

*: Average of the double determinations.

-.: Not found in concentrations below the detection limit

LV: The DWEA has established a limit value for this substance

Perfume:

The product contains very small amounts of a number of perfume substances included on the EPA list of unwanted substances /18/, including D-limonen.

Preservatives:

The analyses for preservatives did not show any of these substances in concentrations above the detection limit.

Surfactants:

The product contains non-ionic surfactants, but an analysis of the product has established that they are not the environmentally problematic substances octyl- and nonylphenol polyethoxylates.

Other substances:

The product contains a fairly large amount of saturated alkanes (C10-14 n-paraffins) as this substance group makes up approximately 1/5 of the product (21%). The substances are derived from a relatively non-volatile solvent. The content of decane is 1.6 %. This substance is the shortest of the alkanes (C10) and thus the most volatile compound. Decane has a boiling point of 179.1°C, a flashpoint of 46°C and a vapour pressure of 1.43 mmHg at 25°C /23/. The DWEA has established a limit value of 45 ppm (250 mg/m³) for this substance /16/. Tetradecane, which is the n-paraffin with the longest chain length (C14), has a boiling point of 253.7°C and a vapour pressure of 0.0116 mmHg at 25°C.

6.3 Category 3 (Products containing bleach)

No analyses were performed on products from this group, but based on the declared ingredients for this group it can be concluded that the active substance in the products is either sodium dithionite or sodium percarbonate and that the concentration in the products is above 30 %. Both of these substances are classified as health hazardous by ingestion. In addition, sodium percarbonate is classified as irritant to skin and eyes.

6.4 Category 4 (Products containing solvents)

6.4.1 Product no. 20

The manufacturer has estimated that the product does not have to be classified and labelled according to the EPA regulations.

Declared content:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Rust remover		Acid salt *	-	-	
Rust remover	144-62-7	Oxalic acid	-	Xn;R21/22	
Preservative	77-92-9	Citric acid	-	-	
Consistency	9000-65-1	Tragacanth	-	-	
Solvent	64-17-5	Denaturated spirits	> 1	F;R11	

*: Most likely the sodium salt of oxalic acid

-: Not stated

Analyses:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Preservation		-	-		
Solvent	108-10-1	Methyl isobutylketon	0.0047	F;R11 Xn;R20 Xi;R36/37 R66	
Perfume		-	-		
Rust remover		Oxalic acid	4.2	Xn;R21/22 (must be labelled when conc. > 5%)	

*: Average of the double determinations

-: Not found in concentrations above the detection limit.

Perfume:

The analysis has not show any perfume substances in this product.

Preservatives:

The analyses for preservatives did not show any of these substances in concentrations above the detection limit.

Oxalic acid:

The content of oxalic acid must be less than 5 % if the product to avoid the demand for classification and labelling according to the EPA regulations. As the analysis shows that the oxalic acid content is 4.2 %, and thus below the classification limit of 5 %, it is correct that the product should not be classified.

Tragacanth:

This substance is a secretion from *Astragalus gummifer* and similar plants. The substance forms a gelatine-like substance in water. Tragacanth is used as a suspension agent and as an additive (emulsifier) in food stuffs, cosmetics and in pharmaceutical preparations /21/.

6.4.2 Product no. 21

The manufacturer has estimated that the product does not have to be classified and labelled according to the EPA regulations.

Declared content:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Grease dissolver	56-87-1	Glycerine	-	-	
pH regulation	-	Alkali	-	-	
Solvent	-	Glycoether	-	-	
Complex binder	60-00-4	EDTA	-	Xi;R36 N;R52/53	
Washing enhancer	-	Phosphate	-	-	
Surfactant	-	Cationic surfactants	-	-	
Surfactant	-	Non-ionic surfactants	-	-	

-: Not stated

Analyses:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Preservation		-	-		
Perfume		-	-		
Impurities:		Lead	0.0018		LOUS
	84-69-5	Diisobutylphthalat	0.0006		LOUS
	84-74-2	Dibutylphthalat	0.0013	T;R61-62 N;R50	LOUS
Solvent	56-81-5	Glycerine	0.175	-	

*: Average of the double determinations

-: Not found in concentrations above the detection limit.

Perfume:

The analysis has not show any perfume substances in this product.

Preservatives:

The analyses for preservatives did not show any of these substances in concentrations above the detection limit.

Surfactants:

The product contains cationic and non-ionic surfactants according to the declaration. The cationic surfactants have not been defined further through analysis, but the product has been analysed for content of the environmentally problematic non-ionic surfactants octyl- and nonylphenolpolyethoxylates. Based on the analysis results it can be concluded that the product does not contain this type of substances.

Impurities:

According to the analysis, the product contains very small amounts of phthalates and lead. These substances are included on the EPA list of unwanted substances /18/. However, the product contains such small amounts that it is likely that these substances are impurities from the raw materials used.

6.5 Category 5 (Products based on natural/"green" products)

6.5.1 Product no. 30

The manufacturer has estimated that the product does not have to be classified and labelled according to the EPA regulations.

Declared content:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Surfactant		Sugar surfactant	5-10	-	
Surfactant		Fatty alcohol sulphate	1-5	-	
Fragrance		Orange peel oil	< 1	-	
Fragrance		Ethereal oil	< 1	-	

-: Not stated

Analyses:

Substance function	CAS-no.	Substance name	Content %	Classification	Note
Preservation		-	-		
Perfume substances:	106-24-1	Geraniol	0.012		LOUS
	5989-27-5	D-limonen	0.435	R10 Xi;R38-43 N;R50/53	LOUS
	78-70-6	Linalool	0.115		LOUS
	106-22-9	Citronellol	0.0005		LOUS
	7785-26-4	α -pinen	0.0040		
	127-91-3	β -pinen	0.0056		
	123-35-3	β -myrcen	0.0046		
	78-70-6	3,7-dimethyl-1,6-octadien-3-ol ((+/-)-Linalool	0.0665		LOUS
	8006-39-1	α -Terpineol	0.020		
Perfume total			0.6632		

*: Average of the double determinations

-: Not found in concentrations above the detection limit.

Perfume:

Like product no. 9, the product contains very small amounts of a number of perfume substances included on the EPA list of unwanted substances /18/, including D-limonen. If a product contains more than 0.1 % of a sensitising substance, labelled with R43, it must be labelled with the phrase "Contains [name of the sensitising substance]. May produce an allergic reaction" according to the EPA regulations /1/. In this product, 2 perfume substances were found in a concentration above 0.1 % - D-limonen and Linalool. This means that the product should be labelled with the above phrase for the two substances.

Preservatives:

The analyses for preservatives did not show any of these substances in concentrations above the detection limit.

Surfactants:

The product contains a surfactant of the sugar surfactant type. This type of surfactant, e.g. alkyl polyglycosides, are usually easily degradable in aerobic conditions as in the OECD test for easy biodegradability /25/.

6.6 Ingredients that are problematic to the health

The results of the analyses are summarised in table 25.

Product no.	Preservation	Perfume	Octyl/nonylpolyethoxylates	Other substances
9	+	+	n.a	Lead in trace amounts Alkanes
17	-	+	n.a.	NTA, Phthalates
20	-	-	n.a	Oxalic acid (< 5%)
21	-	-	-	Lead in trace amounts Phthalates
30	-	+	n.a.	-
32	-	+	-	Lead in trace amounts C10-14 n-paraffins

Table 25 – Summary of the analysis results

i.a.: Not analysed, as the products do not contain the substances stated according to the declaration

Perfume substances:

Based on the above it can be concluded that 4 of the 6 products selected contain perfume. The products contain a number of perfume substances which, according to the SCCNFP, may cause allergies by skin contact. In addition, it can be concluded that these substances are also found in products that are based on natural substances and that are marketed as “green” products. In this case, it is actually the product in category 5 (product no. 32) that contains the largest amount of perfume substances, including the largest amount of D-limonen.

Perfume content	Product no. 9	Product no. 17	Product nr. 30	Product nr. 32
% (mg/kg)	0.0003 (3)	0.023 (230)	0.6632	0.0094 (94)

3 of the 6 products contain D-limonen. The substance is classified with R43 “May cause sensitisation by skin contact” and is included on the EPA list of unwanted substances /18/. Product no. 32 contains the substance citral, which is also classified with R43, but in a concentration far below the classification limit of 1 % and the labelling limit of 0.1 %. According to the EPA regulations, product no. 30 should be labelled with the phrase: “ Contains D-limonen. May product an allergic reaction” /1/.

Preservatives:

1 of the 6 selected products contain benzyl alcohol which is used both as a preservative and as a fragrance. The substance is classified as health hazardous and included on the EPA list of unwanted substances /18/. The preservatives chlormethylisothiazolon and methylisothiazolon were not found in the 4 products analysed for these substances.

Surfactants:

Products no. 9 and 17 only contain anionic surfactants. Product no. 20 does not contain surfactants and product no. 30 contains a so-called sugar surfactant. Product no. 32 contains non-ionic surfactants and product no. 21 contains both non-ionic and cationic surfactants according to the declaration.

Products no. 21 and 32 have been analysed for content of the particularly environmentally problematic non-ionic surfactants octyl- and nonylphenolpolyethoxylates. The analysis results show that the products do not contain this type of surfactant.

Solvents:

Several of the products contain small amounts of non-volatile solvents. Product no. 9 contains approximately 1/3 and product no. 32 approximately 1/5 of unspecified alkanes and n-paraffins, respectively. Product no. 32 thus contains 1.6% of the relatively volatile solvent n-decane which has a limit value of 45 ppm.

Complex binders:

The complex binders used in the products are EDTA, NTA and Zeolite. Of these, NTA is considered to be the most problematic to the health as the substance is suspected of being carcinogenic (IARC group 2B /20/).

Impurities:

One of the products contain 2 named phthalates while another contains a non-identified phthalate. Phthalates are included as a chemical group on the EPA list of unwanted substances /18/. In the following, dibutylphthalate is used as an example of a substance from the group of phthalates.

All in all, the answers to the questions posed in section 4 can be summarised as stated below.

Product	Reason for selection	Answer
17	No content of preservatives has been stated even though the product is water-based. The product contains NTA.	The product does not contain any of the preservatives analysed for. The product contains 0.11% NTA.
9	No content of preservatives has been stated even though the product is water-based. What is "Real perfume"?	The product contains the preservatives benzyl benzoate and benzyl alcohol. The latter may have been added as a perfume. Real perfume consists of a number of known perfume substances as can be seen from section 6.2.1.
32	No content of preservatives has been stated even though the product is water-based. Which non-ionic surfactants does the product contain?	The product does not contain any of the preservatives analysed for. The product does not contain the non-ionic surfactants octyl- and nonylphenol polyethoxylates that are particularly problematic to the environment.
20	No content of preservatives has been stated even though the product is water-based (does, however, contain citric acid). Control of the content of oxalic acid.	The product does not contain any of the preservatives analysed for. The product contains less than 5% oxalic acid and does therefore not have to be classified.
30	No content of preservatives has been stated even though the product is water-based. Which ethereal oils does the product contain?	The product does not contain any of the preservatives analysed for. The ingredients in the ethereal oils can be seen in section 6.5.1.
1	No content of preservatives has been stated even though the product is water-based. Which non-ionic surfactants does the product contain?	The product does not contain any of the preservatives analysed for. The product does not contain the non-ionic surfactants octyl and nonyl phenol polyethoxylates that are particularly problematic to the environment.

The following exposure evaluation is based on the stain remover ingredients considered to be problematic to the health, the so-called critical substances.

6.7 Substances included in the exposure evaluation

The substances selected for the exposure evaluation, as well as their toxicological and physical-chemical data, are listed in table 26.

Substance name	CAS-no.	Classification	Note
D-limonen	5989-27-5	R10 Xi;R38-43 N;R50/53	LOUS
Benzyl alcohol	100-51-6	Xn;R20/22	LOUS
NTA	139-13-9	Xi;R36	At the Danish Working Environment Authority's list of substances that is regarded as carcinogenic
Dibutylphthalate	84-74-2	T;R61-62 N;R50	LOUS

Table 26 Critical substances chosen for exposure scenarios

NTA is found in product no. 17 (0.11%) which is marketed in a 250 ml spray bottle.

Phthalates are found in products no. 21 (0.0013%) and 17 (0.026%). Product no. 21 is a liquid and the packaging contains 17 ml. Dibutylphthalate is used here as a representative for this substance group.

Product no. 9, which is a 150 ml paste, contains benzyl alcohol (0.02%).

Several of the analysed products contain D-limonen, but the highest concentration (0.435%) is found in product no. 30 which is a liquid marketed in 120 ml packagings.

Substance name	CAS-no.	Product no.	Content (%)	State
D-limonen	5989-27-5	30	0.435	Liquid
Benzyl alcohol	100-51-6	9	0.02	Paste
NTA	139-13-9	17	0.11	Spray
Dibutylphthalate	84-74-2	17, 21	0.026/0.0013	Spray/liquid

Table 27 Overview of the products containing the critical substances

7 Exposure evaluation

The purpose of this part of the project is to evaluate the effects on the consumers from the health hazardous substances they are exposed to when using stain removers in the home. Furthermore, the exposure evaluation forms the basis of an evaluation of the precautions the consumers should take when using the products in the home.

Based on the results of the mapping and the analyses, a number of critical substances have been selected and exposure scenarios related to skin contact with and inhalation of the selected health hazardous substances in the examined stain removers.

7.1 Theoretical worst case calculation of internal body dose

On the basis of EU's Technical Guidance Document (TGD), realistic worst-case scenarios have been drawn up for exposure by skin contact and inhalation. The exposure scenarios are based on common practice when using the products. All assumptions and parameters (e.g. temperature, frequency, duration of exposure and how much of the body is exposed) that form the basis of the exposure scenarios have been defined and described in accordance with the TGD guidelines.

The exposure calculations have been carried out using the database programme EUSES. The data used for the exposure calculations by this programme can be seen in annexes 2 through 5 and the results of the computer modelling using EUSES can be found in annexes 6 through 9.

The results have been supplemented by manual calculations of the exposure for the two critical substances found in spray stain removers (DBP and NTA). The general basis of the calculations and the theoretical foundation can be found in annex 10.

7.2 Definition of concepts

In this section, some of the concepts used in the following are defined.

LD₅₀: The dose at which 50% of the test animals die.

LC₅₀: The concentration at which 50% of the test animals die.

NOAEL (No Observed Adverse Effect Level): Zero-effect-level. The highest dose/concentration of the substance at which no significantly increased occurrence of essential changes to morphology, physiology, function, growth, development and/or life span has been observed in the exposed individuals.

LOAEL (Lowest Observed Adverse Effect Level): Lowest-effect-level. The lowest dose/concentration of the substance at which a significantly increased

occurrence of essential changes to morphology, physiology, function, growth, development and/or life span has been observed in the exposed individuals.

ADI (Acceptable daily intake): ADI is an expression of how much of a given substance the average person can consume daily throughout his/her life without any health risk /24/.

MOS (Margin of Safety): MOS is an expression of the factor with which NOAEL/LOAEL is above the estimated exposure level for the general public or particularly exposed people. The higher the MOS, the lower the actual risk to the population.

7.3 Results of the exposure evaluations

7.3.1 D-Limonen

Table 28 shows the toxicological data for D-Limonen found through data search as well as the results of the worst-case calculations of the exposure using EUSES.

Classification	R10 Xi;R38-43 N;R50/53
Toxicological data (animals)	
LD50, (mg/kg), oral, rat	5600-6600 (rat)
LC50 (mg/m ³), inhalation	26100*
NOAEL, (mg/kg-d), ingestion, liver damage	250
LOAEL, (mg/kg-d), ingestion, liver damage	500
NOAEL, (mg/kg-d), inhalation	1170*
LOAEL, (mg/kg-d), inhalation	2330*
Exposure, inhalation	
Air concentration (C _{air})	0.377 mg/m ³
Inhalation (U _{inh})	5.34 x 10 ⁻⁵ mg/kg-d
Exposure, skin	
Amount of substance on skin	36.5 mg
Potential skin intake (U _{der})	7.46 x 10 ⁻² mg/kg-d
Total body intake (U _{tot})	7.46 x 10 ⁻² mg/kg-d
Margin of safety (MOS), acute, total exposure	7.51 x 10 ⁴

Table 28 Toxicological data and results of exposure evaluation for D-Limonen
U_{inh}, U_{der}, U_{tot}: Potential intake by inhalation, skin contact and total intake
* Calculated using EUSES

For this substance, both an NOAEL and a LOAEL value has been found for liver damage to animals of 250 and 500 mg/kg-d, respectively. From the table it can be seen that the total intake is substantially less (more than a factor 3000 lower) than the NOAEL value and with a MOS of 7.51 x 10⁴ it can be concluded, based on the exposure scenario, that the risk of liver damage in humans in the conditions given will be very limited.

From the table it can furthermore be seen that the intake through inhalation is significantly less than intake by skin contact which is due to the low vapour pressure of the substance and the fact that it is not a spray mist application process.

D-Limonen is, however, classified as sensitizing by skin contact and since no “no-effect-level” can be defined for this effect, it is important that skin contact with this substance be avoided.

7.3.2 Benzyl alcohol

Table 29 shows the toxicological data for benzyl alcohol found through data search as well as the results of the worse-case calculations of the exposure using EUSES. The only toxicological parameter for which data has been found is an LD₅₀ value for oral intake in rats. Thus, no NOAEL or LOAEL values have been found for benzyl alcohol that can be used as reference values. However, an ADI value has of up to 5 mg/kg-d been established for the substance.

Classification	Xn;R20/22
Toxicological data (animals)	
LD50, (mg/kg), oral	1230 (rat)
LC50 (mg/m ³), inhalation	5740*
NOAEL, (mg/kg-d)	No data
LOAEL, (mg/kg-d)	No data
Exposure, inhalation	
Air concentration (C _{air})	0.0173 mg/m ³
Inhalation (U _{inh})	2.46 x 10 ⁻⁶ mg/kg-d
Exposure, skin	
Amount of substance on skin	1.68 mg
Potential skin intake (U _{der})	3.43 x 10 ⁻³ mg/kg-d
Total body intake (U _{tot})	3.43 x 10 ⁻³ mg/kg-d
ADI	0-5 mg/kg-d
Margin of safety (MOS), acute, total exposure	3.59 x 10 ⁵

Table 29 Toxicological data and results of the exposure evaluation for benzyl alcohol

* Calculated using EUSES

The EUSES exposure calculation for benzyl alcohol has resulted in a total worst-case intake of the substance of 3.43 x 10⁻³ mg/kg-d. Furthermore, the results show that intake through the skin is approximately a factor of 1000 greater than intake through the air ways. Compared to the established ADI value, the calculated exposure is a factor of 1000 lower. In addition, the use of EUSES has produced a MOS value for acute effects of 3.59 x 10⁵. As this is a high value, the actual risk to the population is comparatively low.

On this basis it can be concluded that the total intake of the substance compared to the exposure scenario given is below the established ADI value. There is a fairly large “margin of safety” and the risk of acute effects from the substance is therefore considered to be small.

According to the EPA “list of unwanted substances” /18/, the substance is, however, a documented skin allergen and is furthermore classified as hazardous by inhalation and ingestion. As noted in the previous section, there is no “no-effect-level” or any lower limit for the sensitizing effect, and exposure to this substance by skin contact and by inhalation should therefore be avoided.

7.3.3 Nitrioltri acetic acid (NTA)

Table 30 shows the toxicological data for nitrioltri acetic acid found through data search as well as the results of the exposure calculations of the exposure using EUSES and a manual calculation based on the spray scenario. Due to a lack of data for the substance itself, data for trisodium salt of the substance has been used.

Classification	Xi;R36***
Toxicological data (animals)	
LD50, (mg/kg), oral	1100 (rat)
LC50 (mg/m ³), inhalation	5130 (rat)*
NOAEL, (mg/kg-d) (rat, oral, 2 years, kidney effects)	15**
LOAEL, (mg/kg-d) (rat, inhalation)	0.34**
EUSES	
Exposure, inhalation	
Air concentration (Cair)	0.0953 mg/m ³
Inhalation (Uinh)	1.35 x 10 ⁻⁵ mg/kg-d
Exposure, skin	
Amount of substance on skin	35.1 mg
Potential skin intake (Uder)	7.16 x 10 ⁻² mg/kg-d
Total body intake (Utot)	7.16 x 10 ⁻² mg/kg-d
Margin of safety (MOS), acute, total exposure	1.54 x 10 ⁴
MANUAL CALCULATION (spraying)	
Exposure, inhalation	
Air concentration (Cair)	0.095 mg/m ³
Inhalation (Uinh)	1.02 x 10 ⁻⁵ mg/kg-d
Exposure, skin	
Dermal concentration (Cder)	1.1 g/L
Dermal dosage (Eder)	7.56 x 10 ⁻² mg/kg-d
Potential dermal intake (Uder)	7.56 x 10 ⁻² mg/kg-d
Total body intake (Utot)	7.56 x 10 ⁻² mg/kg-d

Table 30 Toxicological data and results of the exposure evaluation for NTA

* Calculated using EUSES

** Trisodium salt of NTA

*** According to report from the Nordic Council of Ministers, the classification should be Carc2 T;R45 Xn;R22 Xi;R38/22

As can be seen from the table, intake through the airways is relatively low compared to intake through the skin both when applied as a liquid and with a spray bottle.

The calculated exposure level is relatively low compared to the NOAEL for kidney effects (= 0.15 mg/kg-d where a safety factor of 100 has been used). A MOS value of 1.54x10⁴ for acute exposure further verifies that the exposure is relatively low. Compared to a LOAEL (= 3 x 10⁻³ mg/kg-d where a safety factor of 100 has been used) for effects to the air ways, the exposure level is 1.02 x 10⁻⁵, respectively 1.35 x 10⁻⁵ mg/kg-d a factor 100 lower than NOAEL.

Furthermore, this should be compared to the fact that the scenario described is a worst-case scenario. For example, it has been calculated that all aerosol has been mixed with air while in reality, most of it will be sprayed close to the

textile and be absorbed into it. Direct skin contact with the liquid will be limited and mainly occur in the form of aerosol.

However, it is worrying that the substance is a spray as it is classified as being irritating to the eyes. Furthermore, it may be worrying that the substance is a spray as a report from the Nordic Council of Ministers has stated that the substance should be classified as carcinogenic (Carc2) /22/ and that in addition the substance is listed on the DWEA list of substances considered to be carcinogenic. For sensitising substances, no “no-effect-level” can be established for carcinogenic substances.

7.3.4 Dibutylphthalate (DBP)

Table 31 shows the toxicological data for dibutylphthalate found through data search as well as the results of the exposure calculations of the exposure using EUSES and a manual calculation based on the spray scenario.

Both calculations and modellings produce results that are a factor 10^5 less than the NOAEL and LOAEL values found for inhalation if a safety factor of 100 is used. In addition, the acute MOS value is greater than 4000 which is high. This indicates that the risk when using DBP in stain removers is very small. As mentioned in the previous section, this should be compared to the fact that the scenario described is a worst-case scenario. It has been calculated that all aerosol has been mixed with air while in reality, most of it will be sprayed close to the textile and be absorbed into it. Direct skin contact with the liquid will be limited and mainly occur in the form of aerosol.

Classification	T;R61-62 N;R50
Toxicological data (animals)	
LD50, (mg/kg), oral	7499 (rat)
LC50 (mg/m ³), inhalation	5130 (rat)*
NOAEL, (mg/kg-d), oral	125
NOAEL, (mg/m ³), inhalation	583*
LOAEL, (mg/kg-d), oral	600
LOAEL, (mg/m ³), inhalation	2800*
EUSES	
Exposure, inhalation	
Air concentration (Cair)	0.0225 mg/m ³
Inhalation (Uinh)	3.19×10^{-6} mg/kg-d
Exposure, skin	
Amount of substance on skin	829 mg
Potential skin intake (Uder)	1.69×10^{-2} mg/kg-d
Total body intake (Utot)	1.69×10^{-2} mg/kg-d
Margin of safety (MOS), acute, total exposure	4.43×10^3
MANUAL CALCULATION (spraying)	
Exposure, inhalation	
Air concentration (Cair)	0.00225 mg/m ³
Inhalation (Uinh)	2.42×10^{-6} mg/kg-d
Exposure, skin	
Dermal concentration (Cder)	26000 mg/m ³
Dermal dosage (Eder)	1.79×10^{-2} mg/kg-d
Potential dermal intake (Uder)	1.79×10^{-2} mg/kg-d

Total body intake (U _{tot})	1.79 x 10 ⁻² mg/kg·d
---------------------------------------	---------------------------------

Table 31 Toxicological data and results of the exposure evaluation for DBP

* Calculated using EUSES

According to the list of hazardous substances /1/, dibutylphthalate is classified as harmful to reproduction and to the child during pregnancy (R62 and R61). These effects are seen at higher doses than the critical effect. It is therefore estimated that the margin of safety (MOS) for the chosen scenario is sufficient to avoid the reproduction toxic effects.

7.3.5 Summary

Even though the exposure evaluations show that the risk is very small for exposure to the substances to an extent that causes harmful effects, precautions should still be taken when using the products to avoid exposure as these are substances for which no “zero-effect-level” can be established. In addition, the effects are serious such as allergy, potential cancer risk and risk of impaired fertility.

Substance	EUSES (liquid)				Calculated (spray)		
	U _{inh}	U _{der}	U _{tot}	MOS	U _{inh}	U _{der}	U _{tot}
D-Limonen	5.34 10 ⁻⁵	7.46 10 ⁻²	7.46 10 ⁻²	7.51 10 ⁴	-	-	-
Benzyl alcohol	2.46 10 ⁻⁶	3.43 10 ⁻³	3.43 10 ⁻³	3.59 10 ⁵	-	-	-
NTA	1.35 10 ⁻⁵	7.16 10 ⁻²	7.16 10 ⁻²	1.54 10 ⁴	1.02 10 ⁻⁵	7.56 10 ⁻²	7.56 10 ⁻²
DBP	3.19 10 ⁻⁶	1.69 10 ⁻²	1.69 10 ⁻²	4.43 10 ³	2.42 10 ⁻⁶	1.79 10 ⁻²	1.79 10 ⁻²

Table 32 Potential intake by inhalation, skin contact and total intake

U_{inh}, U_{der}, U_{tot}: Potential intake by inhalation, skin contact and total intake

8 Precautions during use

The precautions that the user should take when using the products depend on the physical state of the product. As can be seen from the statement of the amount of stain removers on the market (section 3.3), the largest amount of stain removers is marketed as either powder or as spray. When powder products are used, inhalation of dust particles should be avoided as should skin contact with the product.

When using products that are applied by atomisation or as aerosol, it is important not to inhale the spray mist. When products are marketed as spray it is probably to ease the distribution of the product on the surface in question. In some cases it is possible to remove the atomisation device and instead apply the product with a rag which is recommended if gloves are used.

If it is necessary to spray on a product, application should take place outdoors or in a room with good ventilation.

As several of the products contain small amounts of sensitising substances, skin contact with the products should be avoided by using disposable gloves. If dirtied, hands and clothes should be washed as soon as possible before re-use.

As can be seen from section 6, using products that are marketed as “green” products and manufactured based on natural ingredients is not a guarantee against exposure to sensitising substances as many of these products contain the highest concentration of sensitising perfume substances.

The most effective method of avoiding damaging effects from stain remover ingredients is to use alternative methods instead of sophisticated special agents wherever possible. For example, soaking or application of common dishwashing agents without perfume prior to washing will take care of many stains. Where this is not sufficient it is possible to use some of the household remedies that suggest less harmful substances (such as whole milk, baby oil, salt and buttermilk mixed with salt) as stated in sections 3.2.3 and 3.2.4.

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Annex 1 Old designations

Below table is an alphabetized list of old designations for chemical substances that you may encounter when you read through old literature on stain removal.

Overview of the meaning of old designations

Old designation	Translation	Classification
Blegevand	Klorin	*
Borax	Natriumborat	Xn;R62-63 (29. tilpasn.)
Brintoverilte	Hydrogenperoxid	O;R8 C;R34
Brintperoxid	Hydrogenperoxid	O;R8 C;R34
Denatureret sprit	Ethanol	F;R11
Ethyl alkohol	Ethanol	F;R11
Galdesæbe	Sæbe fremstillet af oksegalde	-
Glycerol	Glycerin	-
Hospitalssprit	Ethanol	F;R11
Husholdningssprit	Ethanol	F;R11
Kalilud	Kaliumhydroxid opløsning	konc.=25 Xn;R22 C;R35 5%=konc.<25% C;R35 2%=konc.<5% C;R34 0,5%=konc.<2% Xi;R36/38
Karbol	Phenol	T;R24/25 C;R34
Kautisk soda	Natriumhydroxid	C;R35
Klorin	Natriumhypochlorit opl.	*
Kogesprit	Methanol	F;R11 T;R23/24/25-39/23/24/25
Krystalsoda	Natriumcarbonat	Xi;R36
Kulsurt natron	Natriumcarbonat	Xi;R36
Methylalkohol	Methanol	konc.=20% T;R23/24/25-39/23/24/25 10%=konc.<20% Xn;R20/21/22 T;R39/23/24/25 3%=konc.<10% Xn;R20/21/22-68/20/21/22
Naftalin	Naphthalen	Xn;R22 N;R50/53
Natron	Natriumhydrogencarbonat	-
Natronlud	Natriumhydroxid opløsning	konc.=5% C;R35 2%=konc.<5% C;R34 0,5%=konc.<2% Xi;R36/38
Natronvandglas	Natriumsilicat	C;R34 Xi;R37
Salmiakspiritus	Ammoniakvand	konc.=25% C;R34 N;R50 10%=konc.<25% C;R34 5%=konc.<10% Xi;R36/37/38
Skedevand	Salpetersyre	konc.=70% O;R8 C;R35 20%=konc.<70% C;R35 5%=konc.<20% C;R34
Soda	Natriumcarbonat	Xi;R36
Sodaaske	Natriumcarbonat	Xi;R36
Sprit	Ethanol	F;R11
Stenkulsnafta	Benzen	Carc1;R45 F;R11 T;R48/23/24/25
Surt natriumoxalat	Natriumsaltet af oxalsyre	Xn;R21/22

Syresalt	Natriumsaltet af oxalsyre	Xn;R21/22
Terpentinolie	Vegetabilsk terpentin	R10 Xn;R20/21/22-65 Xi;R36/38 R43 N;R51/53
Tetraklorkulstof	Tetrachlormethan	konc.=1% T;R23/24/25-48/23 Carc3;R40 0,2% =konc.<1% Xn;R20/21/22-48/20
Toluol	Toluen	F;R11 Xn;R20
Triklorætylén	Trichlorethylen	Carc2;R45 Xi;R36/38 R67 Mut3;R68 R52/53
Tvekulsurt natron	se natron	-
Xylol	Xylen	konc.=20% Xn;R20/21 Xi;R38 12,5% =konc.<20% Xn;R20/21
Æter	Dimethylether	Fx;R12
Ætsnatron	se kaustisk soda	C;R35
Ætylalkohol	Ethanol	F;R11
Ætylénglykol	Ethylenglycol	Xn;R22

* Klassificeringen afhænger af indholdet af aktivt chlor, ved 5%= konc. < 10 %: R31
Xi;R36/38, ved =10 %: R31 C;R34

Annex 2 Data for D-limonen

Identification:	
Substance identification name:	D-Limonen
CAS-no.:	5989-27-5
EINECS	227-813-5
Physico-chemical properties	
Mw, (g.mol-1)	136.23
M.p., °C	-74.35
B.p., °C	175.5-176°C (763 mmHg)
V.p. at 25°C, (Pa)	20 mm Hg at 68.2 °C
Octanol-water, (log10)	4.23
Water solubility (mg/L)	Very low
Inhalation	
Spray how much is released/spray	0
Weight fraction of substance in the product	0.43 %
Dermal	
Conc. of substance in undiluted product (mg/m ³)	4.300.000
Density in product before dilution (mg/m ³)	Unknown
Amount of undiluted product used (mg/m ³)	-
Volume of product before dilution (m ³)	-
Weight fraction of substance in product	0.43%
Dilution factor	1
Substance properties	
Physical state of substance	Liquid
Process temperature, °C	20
Determination of vapour pressure	-
Vapour pressure at process temperature	-
Aerosol formed:	
Yes	
No	x
Particle size of the substance	Not relevant
Type of dust	None
Ability of fibrous dust to become airborne	Not relevant
Dust particles aggregate readily	No
Mammal effects	
LD50, (mg.kg-1)	5600-6600 (oral, rat) /28/
NOAEL, (mg.kg-1.day-1) Oral, liver lesions	250 /27/
LOAEL, (mg.kg-1.day-1) Oral, liver lesions	500 /27/
Human effects	
LD50, (mg.kg-1)	-
NOAEL, (mg.kg-1.day-1)	-
LOAEL, (mg.kg-1.day-1)	-
Classification	R10; Xi;R38-43N;R50/53 /30/

Annex 3 Data for benzyl alcohol

Identification:	
Substance identification name:	Benzyl alcohol
CAS-no.:	100-51-6
EINECS	202-859-9
Physico-chemical properties	
Mw, (g.mol ⁻¹)	108.14
M.p., °C	-15.2
B.p., °C	205.3
V.p. at 25°C, (Pa)	0.094 mm Hg (25° C) 0,03 hPa (20°C)
Octanol-water, (log10)	1.1
Water solubility (mg/L)	42900 mg/l(25°C), 35000 mg/l (20°C)
Inhalation	
Spray how much is released/spray	0
Weight fraction of substance in the product	0,2 %
Dermal	
Conc. of substance in undiluted product (mg/m ³)	200.000
Density in product before dilution (mg/m ³)	Unknown
Amount of undiluted product used (mg/m ³)	-
Volume of product before dilution (m ³)	-
Weight fraction of substance in product	0.02%
Dilution factor	0
Substance properties	
Physical state of substance	Liquid
Process temperature, °C	20
Determination of vapour pressure	-
Vapour pressure at process temperature	30 Pa (20°C)
Aerosol formed:	
Yes	
No	x
Particle size of the substance	Not relevant
Type of dust	None
Ability of fibrous dust to become airborne	Not relevant
Dust particles aggregate readily	No
Mammal effects	
LD50, (mg.kg ⁻¹) Oral, rat	1230 /28/
NOAEL, (mg.kg ⁻¹ .day ⁻¹)	-
LOAEL, (mg.kg ⁻¹ .day ⁻¹)	-
Human effects	
LD50, (mg.kg ⁻¹)	-
NOAEL, (mg.kg ⁻¹ .day ⁻¹)	-
LOAEL, (mg.kg ⁻¹ .day ⁻¹)	-
Classification	
	Xn; R20/22 /30/

ADI: 0-5 mg/kg

Annex 4 Data for NTA

Identification:	
Substance identification name:	Nitriilotriacetic acid (- trisosiumsalt)
CAS-no.:	139-13-9 (5064-31-1)
EINECS	205-355-7
Physico-chemical properties	
Mw, (g.mol-1)	191.14 (275,1)
M.p., °C	242 (410)
B.p., °C	-
V.p. at 25°C, (Pa)	0.0003 (estimated) (-)
Octanol-water, (log10)	- 3.8 (est) (-2.62)
Water solubility (mg/L)	5.91x10 ⁴ mg/l (25°C) (640000 (20°C))
Inhalation	
Spray how much is released/spray	-
Weight fraction of substance in the product	0.11 %
Dermal	
Conc. of substance in undiluted product (mg/m ³)	1.100.000
Density in product before dilution (mg/m ³)	Unknown
Amount of undiluted product used (mg/m ³)	-
Volume of product before dilution (m ³)	-
Weight fraction of substance in product	0.11%
Dilution factor	0
Substance properties	
Physical state of substance	Solid
Process temperature, °C	20
Determination of vapour pressure	-
Vapour pressure at process temperature	-
Aerosol formed:	
Yes	x
No	
Particle size of the substance	Not relevant
Type of dust	Not relevant
Ability of fibrous dust to become airborne	Not relevant
Dust particles aggregate readily	No
Mammal effects	
LD50, (mg.kg-1) Oral, rat:	1100 (1740) /28/
NOAEL, (mg.kg-1.day-1) Rats oral feed, 2 years	- (15) /22/
LOAEL, (mg.L-1.day-1) Inhalation	- (0.34) /26/
Human effects	
LD50, (mg.kg-1)	-
NOAEL, (mg.kg-1.day-1)	-
LOAEL, (mg.kg-1.day-1)	-
Classification	Xi;R36*

*Supplier's classification. According to Nordic Council of Ministers the classification ought to be Carc cat2 T;R45 Xn;R22 Xi;R38 /22/ IARC class 2B /20/

Annex 5 Data for dibutylphthalate

Identification:	
Substance identification name:	Dibutylphthalate
CAS-no.:	84-74-2
EINECS	201-557-4
Physico-chemical properties	
Mw, (g.mol-1)	278.35
M.p., °C	-35
B.p., °C	340
V.p. at 25°C, (Pa)	2.01x10 ⁻⁵ mm Hg (25°C)
Octanol-water, (log10)	4.9
Water solubility (mg/L)	13 mg/l (25 °C)
Inhalation	
Spray how much is released/spray	0
Weight fraction of substance in the product	0.026 %
Dermal	
Conc. of substance in undiluted product (mg/m ³)	260.000
Density in product before dilution (mg/m ³)	Unknown
Amount of undiluted product used (mg/m ³)	-
Volume of product before dilution (m ³)	-
Weight fraction of substance in product	0.026 %
Dilution factor	0
Substance properties	
Physical state of substance	Liquid
Process temperature, °C	20
Determination of vapour pressure	-
Vapour pressure at process temperature	-
Aerosol formed:	
Yes	
No	x
Particle size of the substance	Not relevant
Type of dust	None
Ability of fibrous dust to become airborne	Not relevant
Dust particles aggregate readily	No
Mammal effects	
NOAEL, (mg.kg-1.day-1), oral	125 /27/
LOAEL, (mg.kg-1.day-1), oral	600 /27/
Human effects	
LD50, (mg.kg-1)	-
NOAEL, (mg.kg-1.day-1), o	-
LOAEL, (mg.kg-1.day-1)	-
Classification	T;R61-62 N;R50 /30/

The lowest LOAEL identified for developmental toxicity is 80 mg/kg/day /29/
 An MRL of 0.5 mg/kg/day has been derived for acute-duration oral exposure (14 days or less). The acute oral MRL was based on a NOAEL of 50 mg/kg/day./29/.

Annex 6 Theoretical basis and calculations for substances in spray form

General assumptions and calculations

A person uses a stain remover that is sprayed on once a week and each time the person stays in the room, where the application takes place, for 5 minutes. Tests with three different types of spray bottles without propellant but with a hand pump resulted in an average consumption of 1.3 g during application to an average-size stain. The room in which the stain removal takes place is small room of 15 m³ (e.g. a bathroom). The person weighs 65 kg, there is no ventilation in the room. Spraying achieves a complete mixture of the substances in the room air.

The concentration in the persons breathing zone can be calculated using formula (1):

$$(1) C_{\text{air}} = \frac{q \times w_f}{V_r} \quad \text{where}$$

q = amount of used product per event (mg)
w_f = weight fraction of substance in the product
V_r = room volume (m³)

Intake through inhalation can be estimated using formula (2):

$$(2) U_{\text{inh}} = \frac{C_{\text{air}} \times V_{\text{inh}} \times t \times B_{\text{inh}} \times n}{Bw} \quad \text{where}$$

C_{air} = Concentration in the breathing zone calculated according to (1) (mg/m³)
V_{inh} = Respiration speed (m³/t)
t = Exposure per time (hours)
B_{inh} = Breathable fraction
n = Number of stain removals per day (d⁻¹)
Bw = Body weight (kg_{bw})

Concentrations of spray on skin, C_{der} can be calculated according to formula (3):

$$(3) C_{\text{der}} = d \times w_f \quad \text{where}$$

d = Product density (g/L)
w_f = Weight-% of the substance in the product

The dermal dose, E_{der} is calculated according to formula (4):

$$(4) E_{\text{der}} = \frac{C_{\text{der}} \times T_{\text{der}} \times S_{\text{der}} \times n}{Bw} \quad \text{where}$$

T_{der} = Thickness of product in contact with skin (cm)
S_{der} = Surface area of skin in contact with the product (m²)
n = Number of stain removals per day (d⁻¹)

The dermal dose intake, U_{der} is calculated by multiplying E_{der} with the fraction of the substance absorbed through the skin B_{der} as stated in formula (5)

$$(5) U_{\text{der}} = E_{\text{der}} \times B_{\text{der}}$$

The total internal dose after effects by inhalation and skin contact U_{tot} is the sum of U_{inh} and U_{der} as stated in formula (6)

$$(6) U_{\text{tot}} = U_{\text{inh}} + U_{\text{der}}$$

Calculations for NTA

Inhalation

Calculation of the concentration in the inhalation zone, C_{air} :

$$(1) C_{\text{air}} = \frac{1300 \text{ mg} \times 0.0011}{15 \text{ m}^3} = 0.095 \text{ mg/m}^3$$

Calculation of the internal dose or intake by inhalation:

$$(2) U_{\text{inh}} = \frac{0.095 \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{t} \times 0.083 \text{ t} \times 0.75 \times 0.14 \text{ d}^{-1}}{65 \text{ kg}} = 1.02 \times 10^{-5} \text{ mg/kg}\cdot\text{d}$$

Skin contact

Concentrations of spray on the skin:

$$(3) C_{\text{der}} = 1000 \text{ g/L} \times 0.0011 = 1.1 \text{ g/L} = 1100000 \text{ mg/m}^3$$

As the product density is set at 1000g/L and the content of the substance in the product is 0.11 %

The dermal dose is calculated by formula (4):

$$(4) E_{\text{der}} = \frac{1100000 \text{ mg/m}^3 \times 0.0001 \text{ m} \times 0.319 \text{ m}^2 \times 0.14 \text{ d}^{-1}}{65 \text{ kg}} = 0.0756 \text{ mg/kg}\cdot\text{d}$$

Calculation of dermal intake (U_{der}) is calculated by formula (5):

$$(5) U_{\text{der}} = E_{\text{der}} \times B_{\text{der}} = 0.0756 \text{ mg/kg}\cdot\text{d}$$

The fraction of the substances absorbed through the skin (B_{der}), is assumed to be 1 due to lack of other data.

Total intake

The total amount of substance that is absorbed is calculated by formula (6):

$$U_{\text{tot}} = U_{\text{inh}} + U_{\text{der}} = 1.02 \times 10^{-5} \text{ mg/kg}\cdot\text{d} + 0.0756 \text{ mg/kg}\cdot\text{d} = 0.0756 \text{ mg/kg}\cdot\text{d}$$

Dibutylphthalate (DBT)

Inhalation

The concentration in the woman's inhalation zone, C_{air} is calculated by formula (1):

$$C_{\text{air}} = \frac{1300 \text{ mg} \times 0.00026}{15 \text{ m}^3} = 0.0225 \text{ mg/m}^3$$

The intake of the substance by inhalation is calculated by formula (2):

$$U_{\text{inh}} = \frac{0.0225 \text{ mg/m}^3 \times 0.8 \text{ m}^3/\text{t} \times 0.083 \text{ t} \times 0.75 \times 0.14 \text{ d}^{-1}}{65 \text{ kg}} = 2.42 \times 10^{-6} \text{ mg/kg}\cdot\text{d}$$

Skin contact

The concentration of spray on the woman's skin, C_{der} is calculated by formula (3):

$$C_{\text{der}} = 1000 \text{ (g/L)} \times 0.00026 = 0.26 \text{ g/L} = 260.000 \text{ mg/m}^3$$

The density of the product is set at 1000g/L and weight-% of the substance in the product is 0.026%.

The dermal dose, E_{der} is calculated by formula (4):

$$E_{\text{der}} = \frac{260.000 \text{ mg/m}^3 \times 0.0001 \text{ m} \times 0.319 \text{ m}^2 \times 0.14 \text{ d}^{-1}}{65 \text{ kg}} = 1.79 \times 10^{-2} \text{ mg/kg}\cdot\text{d}$$

The thickness of the product in contact with the skin (T_{der}) is set at 0.01 cm, the surface area of skin in contact with the product (S_{der}), here the upper extremities i.e. approximately 1/6 of $1.9\text{m}^2=0.319 \text{ m}^2$, and the number of stain removals per day is estimated at once a week.

The dermal intake dose, U_{der} is calculated by formula (5):

$$U_{\text{der}} = E_{\text{der}} \times B_{\text{der}} = 1.79 \times 10^{-2} \text{ mg/kg d}$$

The fraction of the substance absorbed through the skin (B_{der}) is set at 1 due to lack of other data.

Total dose

The total effects from skin contact and inhalation is the sum of the previous two calculation, i.e. the dose absorbed by inhalation and skin contact:

$$U_{\text{tot}} = 2.42 \times 10^{-6} \text{ mg/kg}\cdot\text{d} + 1.79 \times 10^{-2} \text{ mg/kg}\cdot\text{d} = 1.79 \times 10^{-2} \text{ mg/kg}\cdot\text{d}$$