DANISH MINISTRY
OF THE ENVIRONMENT
Environmental
Protection Agency

Mapping and health assessment of chemical substances in shoe care products

Birgit Engelund and Hanne Sørensen
Danish Toxicology Centre

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Content

Summary

The purpose of the project has been to obtain an overview of which problematic ingredients are found in shoe care products on the Danish market as well as to identify any health risks when using the products and on this basis to establish guidelines for safe use of the products.

The mapping was based on investigative work in the retail trade including supermarkets, shoe stores, sporting goods stores and heel bars. In addition, suppliers and manufacturers have been contacted for further information on the products through safety data sheets, technical data sheets and sold amounts in 2003.

9 suppliers of shoe care products for the Danish market were identified. In addition, a number of sale products were found for which it was not possible to identify the supplier.

The following brands were found on the market: Woly, TiT, Coxy, Gold Quality, Collonil, Punch, Boston. KIWI, Nikwax as well as other smaller brands, often sale products purchased outside Europe.

A total of 189 products have been identified of which some are found in several colour nuances. The products can be divided into different product categories. The identified products are distributed as follows: 22 % impregnation products, 22 % shoe polish, 17 % care agents, 11 % cleaning agents, 7 % colours, 6 % liquid shoe polish, 5 % fresheners, 4 % other speciality products for shoes, 3 % leather grease, oil and wax, 3 % odour removers.

The products are marketed as paste (27 %), liquids (33 %) and aerosols (35 %). Shoe polish is most often a paste, the care agents are usually liquid and the impregnation products are usually aerosol products. The remaining 5% of the products are marketed as foam in the shape of a sponge impregnated with a liquid or as a powder.

The most common ingredients are: 2-propanol (46 products), propane (34 products), butane (34 products), naphtha (raw oil), hydrogen treated heavy (26 products), naphtha (raw oil), hydrogen treated light (18 products), heptane/heptane-mixture (19 products), white spirit (free from aromatics) (19 products)

Based on the mapping of the ingredients it can be concluded that in all product categories except for leather grease, oil and wax, products can be found that contain organic solvents.

Only 4 of the 9 suppliers agreed to inform us of sales numbers for 2003. The number from the 4 suppliers show that approximately 50 tonnes of shoe care products were sold, distributed on 29.5 t (58%) impregnation products for shoes, 20.5 t (41%) shoe polishes and 0.5 t (1%) other shoe care agents. The real numbers are assumed to be higher, but the distribution on product types is expected to be accurate.

13 products were selected for various analyses.

No preservatives or azo-dyes were found in concentrations above the respective detection limit in any of the analysed samples.

Very small amounts of PFOS-compounds were found (1.1 and 0.36 mg/kg, respectively) in 1 of 4 of the analysed samples. The found amounts of PFOS-compounds are probably present as impurities in a flourcarbonpolymer that has been added due to its water and dirt repelling properties.
In addition, very small amounts of octamethylcyclotetrasiloxan (from 0.79 to 3.4 mg/kg) were found in 5 of the 8 analysed products. 3 of the 5 products are known to contain silicone. It is assumed that octamethylcyclotetrasiloxan is found as an impurity in the silicone oil which is added to the product due to its impregnating and tending properties.

X-ray screening of 3 products found no metals, including heavy metals, in 2 of the products in concentrations above 1000 mg/kg (corresponding to 0.1 %) and for a majority of the substances, the content was below the detection limit (either10 or 20 mg/kg).

In the third sample, a content of silicium and titane was found of between 10,000 and 100,000 mg/kg corresponding to 1 to 10 %. These elements probably come from silicium dioxide (SiO_2) and titane dioxide (TiO_2) as these substances are used as a filler and as a colour pigment, respectively. In addition, the sample contained Na, Al, S, Cl, Mn and Ba in concentrations between 1,000 and 10,000 mg/kg corresponding to 0.1-1 %. These elements are assumed to come from colour pigments as the product in question is a coloured shoe polish.

Many of the proudcts contain organic solvents aimed at dissolving dirt on the footwear or to dissolve the tending oils and waxes in the products.
The screening for solvents of 6 products found mineral turpentine in 3 of the products (all shoe polishes) in concentrations of 72, 88 and 85 %, respectively. In one impregnation product, 93 % isopropanol was found and in a cleaning agent, 30 % ethanol was found. In the final sample, only small amounts of methylethylketon (0.02 %) and xylene (0.004 %) were found which were probably impurities in the product.

Of the 3 samples selected for specific analysis for the solvent C_9-C_{12} isoalkanes, 265,000 mg/kg was found corresponding to 26.5 % in one of the samples.

2 products were analysed for content of chlorparaffins but these substances could not be established in the products.

Based on a comparison of the occurrence (how many products the substance is found in), the amount of the substances in the products and the health qualities of the products, the substances: turpentine oil, mineral turpentine, C9-12 isoalkanes, heptane and propane-3-ol were selected for exposure evaluation.

The exposure scenarios show that there is a potential health risk in the form of irritation of the respiratory tract and effects on the nervous system when using products that contain large amounts of mineral turpentine.

Furthermore, it cannot be ruled out that there may be effects in the form of irritation to the respiratory tract and effects on the central nervous system when using products that contain other solvents.

When using shoe care products in the home, you should therefore:

- Shine or impregnate outdoors whenever possible. When this is not possible due to the weather you should instead ensure that there is adequate ventilation in the room by opening a window and/or a door.
- Make sure to spray away from the body if the product is a spray.
- Avoid getting shoe polish on the hands, possilbly by using disposable gloves.

Sammenfatning og konklusioner

Projektets formål har været at få et overblik over, hvilke problematiske indholdsstoffer der findes i skoplejemidler på det danske marked samt at identificere eventuelle sundhedsrisici ved anvendelse af produkterne og på den baggrund opstille retningslinier for sikker brug af produkterne.

Kortlægningen blev baseret på opsøgende arbejde i detailhandelen herunder dagligvarebutikker, skobutikker, sportsforretninger og hælebarer. Desuden er leverandører og producenter blevet kontaktet for yderligere oplysninger om produkterne i form af sikkerhedsdatablade, tekniske datablade og solgte mængder i 2003.

Der blev identificeret 9 leverandører af skoplejemidler til det danske marked. Herudover blev der fundet nogle tilbudsprodukter, hvor leverandøren ikke kunne identificeres.

Der er fundet følgende mærkevarer på markedet: Woly, TiT, Coxy, Gold Quality, Collonil, Punch, Boston. KIWI, Nikwax samt andre mindre mærker, oftest tilbudsprodukter indkøbt udenfor Europa.

Der er identificeret i alt 189 produkter, hvoraf nogle forekommer i flere farvenuancer. Produkterne kan inddeles i forskellige produktkategorier. De identificerede produkter fordeler sig på: 22 % imprægneringsmidler, 22 % skosværte, 17 % plejemidler, 11 % rensemidler, 7 % farver, 6 % flydende skosværte, 5 % opfriskere, 4 % andre specialmidler til sko, 3 % læderfedt, -olie og -voks, 3 % lugtfjernere.

Produkterne markedsføres som pasta (27 %), væsker (33 %) og aerosoler (35 %), idet skosværter oftest er en pasta, plejemidlerne er på væskeform og imprægneringsmidlerne sædvanligvis føres som aerosolprodukter. De sidste 5 % af produkterne markedsføres som skum, i form af en svamp imprægneret med væske, eller som pulver.

De hyppigst forekommende indholdsstoffer er: 2-propanol (46 produkter), propan (34 produkter), butan (34 produkter), naphtha (råolie), hydrogenbehandlet tung (26 produkter), naphtha (råolie), hydrogenbehandlet let (18 produkter), heptan/heptanblanding (19 produkter), testbenzin (aromatfri) (19 produkter)

Af kortlægningen af indholdsstoffer kan det konkluderes, at der indenfor alle produktkategorier, på nær læderfedt, -olie og -voks, findes produkter, der indeholder organiske opløsningsmidler,.

Kun 4 af de 9 leverandørerne indvilligede i at oplyse salgstal fra 2003. Tallene fra de 4 leverandører viser, at der blev solgt ca. 50 tons skoplejemidler fordelt på 29,5 t (58%) imprægneringsmidler til sko, 20,5 t (41%) skosværter og 0,5 ton (1%) andre skoplejemidler. De reelle tal er formodentlig noget større, men fordelingen på produkttyper forventes at være retvisende.

Der blev udvalgt 13 produkter til forskellige analyser.

Der blev ikke fundet konserveringsmidler eller azofarvestoffer i koncentrationer over de respektive detektionsgrænser i nogen af de analyserede prøver.
Der blev fundet meget små mængder af PFOS-forbindelser (henholdsvis 1,1 og 0,36 mg/kg) i 1 ud af de 4 analyserede prøver. De fundne mængder PFOS-forbindelser forekommer sandsynligvis som urenheder i en flourcarbonpolymer, der er tilsat på grund af de vand- og smudsafvisende egenskaber.
Der blev ligeledes fundet meget små mængder octamethylcyclotetrasiloxan (fra 0,79 til 3,4 mg/kg) i 5 ud af de 8 analyserede produkter. 3 af de 5 produkterne vides at indeholde silicone. Det formodes, at octamethylcyclotetrasiloxan forekommer som urenhed i den siliconeolien, der tilsættes produktet på grund af de imprægnerende og plejende egenskaber.

Ved røntgenscreeningen af 3 produkter blev der i 2 af produkterne ikke fundet metaller, herunder tungmetaller, i koncentrationer over 1000 mg/kg (svarende til 0,1 %), og for langt de fleste stoffer lå indholdet under detektionsgrænsen (enten 10 eller 20 mg/kg).

I den tredje prøve blev der fundet indhold af silicium og titan på mellem 10.000 og 100.000 mg/kg svarende til mellem 1 til 10 %. Disse grundstoffer stammer sandsynligvis fra siliciumdioxid (SiO_2) og titandioxid (TiO_2), idet disse stoffer anvendes som henholdsvis fyldstof og som farvepigment. Prøven indeholdt desuden Na, Al, S, Cl, Mn og Ba i koncentrationer på mellem 1.000 og 10.000 mg/kg svarende til 0,1-1 %. Disse grundstoffer formodes at stamme fra farvepigmenter, idet det aktuelle produkt er en farvet skosværte.

Mange af produkterne indeholder organiske opløsningmidler med henblik på at opløse snavs på fodtøjet eller for opløse de plejende olier og vokser i produktet.
Ved screeningen af 6 produkter for opløsningsmidler blev der fundet mineralsk terpentin i tre af produkterne (alle skosværter) i koncentrationer på henholdsvis 72, 88 og 85 %. I et imprægneringsmiddel blev der fundet 93 % isopropanol, og i et rensemiddel blev der fundet 30 % ethanol. I den sidste prøve blev der kun fundet små mængder methylethylketon (0,02 %) og xylen (0,004 %), hvilket formodentligt er urenheder i produktet.

Ud af de 3 prøver, der var udtaget til specifik analyse for opløsningsmidlet C_9-C_{12} isoalkaner, blev der fundet 265.000 mg/kg svarende til 26,5 % i en af prøverne.

2 produkter blev analyseret for indhold af chlorparaffiner, men disse stoffer kunne ikke påvises i produkterne.

På baggrund af en sammenstilling af forekomsten (hvor mange produkter stoffet findes i), mængden af stofferne i produkterne og produkternes sundhedsmæssige egenskaber blev stofferne: terpentinolie, mineralsk terpentin, C9-12 isoalkaner, heptan og propan-3-ol udtaget til eksponeringsvurdering.

Eksponeringsscenarierne viser, at der er en potentiel risiko for sundhedseffekter i form af irritation af luftveje og effekter på nervesystemet ved anvendelse af produkter, der indeholder store mængder mineralsk terpentin.

Det kan desuden ikke afvises, at der kan forekomme effekter i form af luftvejsirritation og påvirkning af centralnervesystemet ved anvendelse af produkter, der indeholder andre opløsningsmidler.

Ved anvendelse af skoplejemidler i hjemmet bør man derfor:

- Pudse eller imprægnere udendørs så vidt muligt. Når det ikke er muligt på grund af vejrliget bør man i stedet sørge for god ventilation i rummet ved at åbne et vindue og/eller en dør.
- Sørge for at sprøjte væk fra kroppen, hvis produktet er en spray.
- Undgå at få skosværte på hænderne, eventuelt ved at anvende engangshandsker.

1 Introduction

The Danish Toxicology Centre (DTC) has been asked to carry out the project "Mapping and health evaluation of chemical substances in shoe care products" as offered in project proposal of 9 January 2004 from the Danish Environmental Protection Agency (EPA).

Clothes and footwear make up 4-10% of the total consumption of a Danish household[1] (in costs). Every Dane buys an average of 4 pairs of shoes per year and in order for footwear to last and to look nice it is necessary to use shoe care products such as shoe polish, leather grease, cleaning agents and impregnation products. There are many internet sites that deal with the care of footwear including a shoe care guide containing information about how to maintain and care for shoes made from various types of leather[2].

Shoe care products may contain substances that are problematic to humans and the environment. The EPA proposal for the project "Mapping and health evaluation of chemical substances in shoe care agents" mentions that it is assumed that shoe care agents may contain persistent, bio-acccumulative and toxic substances (PBT substances), e.g. problematic dyes and PFOS compounds. Certain azo-dyes are thus covered by the Danish Working Environment Authority's (DWEA) Order on Cancer[3], ban on import, sale and use[4] and are in addition included on the EPA list of unwanted substances[5]. PFOS substances are included on the List of unwanted substances.

From Environmental Project no. 691 "Kortlægning af perfluoroktanylsulfonat og lignende stoffer i forbrugerprodukter - fase 2" (Mapping of perflouroctaneyl sulphonate and similar substances in consumer products – phase 2) it can be seen that PFOS compounds are found in leather impregnation products (5 products) and leather care products in the form of shoe polish. Based on data from the Product Register, the report estimates that the amount of PFOS compounds sold per year as ingredients in products comprises approximately 2,400 kg in leather impregnation agents and approximately 15 kg in shoe polishes, respectively.

The PFOS substance load from shoe polish is thus significantly lower than the load from the impregnation agents, but unlike the impregnation agents which are usually not coloured, shoe polish can be purchased in many colours in addition to the traditional black. As PBT dyes are used for i.a. colouration of leather, it is not unusual for shoe polish (particularly certain colour nuances) to contain these substances.

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[1] Statbank Denmark
[2] http://www.hrsko.dk/
[3] Arbejdstilsyntes bekendtgørelse nr. 906 af 8. november 2020 om foranstaltninger til forebyggelse af kræftrisikoen ved arbejde med stoffer og materialer
[4] Miljøstyrelsens bekendtgørelse nr. 755 af 15. august 3003 om forbud mod import, salg og anvendelse af visse azofarvestoffer
[5] EPA (2004); Orientation from the EPA, No. 8, 2004: "List of unwanted substances 2004"

In addition to the above-mentioned groups of problematic substances, shoe care products may contain a number of other compounds that can be potentially harmful to humans and/or the environment. The National Institute of Health in the USA[6] has created a database containing more than 4000 household products on the American market. The database provides access to safety data sheets and information on certain ingredients. In the database, 4 products have been found that can be considered shoe care products (Jump Shoe Cleaning Gel, Jump Shoe Conditioning Liquid, Kiwi Shoe White, Kiwi Scuff Magic, Black). According to the information in the database, the products contain substances such as: isopropyl alcohol and ethylenglycol (solvents), titan dioxide and carbon black (dyes) and the preservatives methylchlorisothiazolinon and methylisothiazolon (kathon).

A search in the Nordic product registers' database (the SPIN-database) for the user codes corresponding to leather impregnation products (I0510) and shoe polish (P1015) only provided limited information on ingredients (water, isopropyl alcohol, ethylacetate, butylacetate) due to the confidentiality regulations. However, a search for the NACE-code[7] "B31 Impregnation materials" listed a number of substances of which some are found on the List of unwanted substances, others are carcinogenic (benzene, trichlorethylen) and in addition, some are covered by bans or limitations in use (benzene and 1,1,1-trichlorethan[8]).

However, it should be noted that this NACE-code covers many types of impregnation products and not only products for shoes or leather. In addition, the SPIN-database primarily contains information on products that are use occupationally and most shoe care products are expected to be sold solely on the retail market.

The purpose of the project is thus to map which chemical substances are used in footwear care prodcuts in the retail trade, including PBT dyes and more closely defined PFOS compounds[9] as well as to evaluate any health hazards in connection with ordinary consumers' use of the products and on this basis to establish recommendations for a safe use of the products.

[6] http://house

[7] NACE stan nomiques dans les Communaut e common trade nomencalture in EU, i.e. the sytem EU uses to categorise all occupational trades. NACE was implemented in the EU member states in 1993.

[8] Iflg. bekendtgørelse nr. 1042 af 17. december 1997 om begrænsning af salg og anvendelse af visse farlige kemiske stoffer og produkter til specielt angivne formål, it is forbidden to sell products that contain benzene in concentrations of 0.1% or more. 1,1,1-trichlorethan is covered by bekendtgørelse nr. 243 af 19. april 2002 om visse ozonlagsnedbrydende stoffer

[9] Perfluorobutansulfonat, perfluorohexan-sulfonat, perfluorooktansulfonat, perfluorodecansulfonat, perfluorooktansulfon-amid, N-ethyl perfluorooktansulfonamid, perfluoroheptansyre and perfluorooktansyre.

2 Purpose

The purpose of the project is to obtain an overview of which problematic ingredients (including PBT dyes and PFOS compounds) are found in shoe care products on the Danish market as well as to identify any health risks connected with the use of the products and on this basis to establish guidelines for a safe use of the products.

The result of the project is thus an evaluation of the consumers' exposure to health hazardous substances when using shoe care products and recommendations for precautions that the consumer should take when using the products.

3 Mapping

The purpose of phase 1 is to create an overview of shoe care products on the market and of what those products contain.

Phase 1 includes the following sub-activities:

- Mapping of shoe care products on the market
- Mapping of ingredients in shoe care products
- Estimate of consumption
- Selection of analysis parameters and products for analysis

In phase 1, shoe care products on the retail market have been mapped through visits to supermarkets, shoe stores, sporting good stores and heel bars as well as through contact to suppliers and manufacturers.

Experience shows that it is often hard to obtain complete composition information from the manufacturers and the first step has therefore been to obtain safety data sheets as well as sales numbers for Denmark.

3.1 Mapping of products on the market

The mapping is based on visits to the retail trade including supermarkets, shoe stores, sporting good stores and heel bars.

If a product was found in several colour nuances it was included as one product.

In addition, suppliers and manufacturers have been contacted for further information on the products in the form of safety data sheet and technical data sheets.

Table 1 lists the identified suppliers.

Table 1 Identified suppliers of shoe care products

	Supplier	**Brands**
1	FL Skopleje	Woly
2	Sterling Polish Company	TiT
3	Aslak Nørgaard I/S	Coxy
4	ROC danmark ApS	Gold Quality etc..
5	Collonil ApS	Collonil
6	Johs. Rosted (distributør)	Punch and Boston products
7	a/s blumøller	KIWI
8	Boston Scandinavia AB	Punch and Boston products
9	Trim Lund Trading ApS	Nikwax

The following brands were found on the market:

- Woly
- TiT
- Coxy
- Gold Quality
- Collonil
- Punch
- Boston
- KIWI
- Nikwax
- Other

Other products include sale products that are not part of the regular selection and smaller or unknown brands including products based on natural ingredients.

A total of 191 products were identified of which some are found in several colour nuances. Contact to the supplier revealed that 2 of the products had been discontinued. When these 2 products are subtracted there is thus a total of 189 products on the market.

The products can be divided into different product categories as seen in table 2. The division has been carried out from an estimation based on sales material received from the supplier as several of the products have more than one function, e.g. cleaning and impregnation or impregnation and colour refreshing.

The category ”Other specialty products” consists of a mixed group of products including “Shoe stretch”, i.e. products that can be used if the shoe pinches, products for treatment of soles etc..

Table 2 Overview of number of products in each category

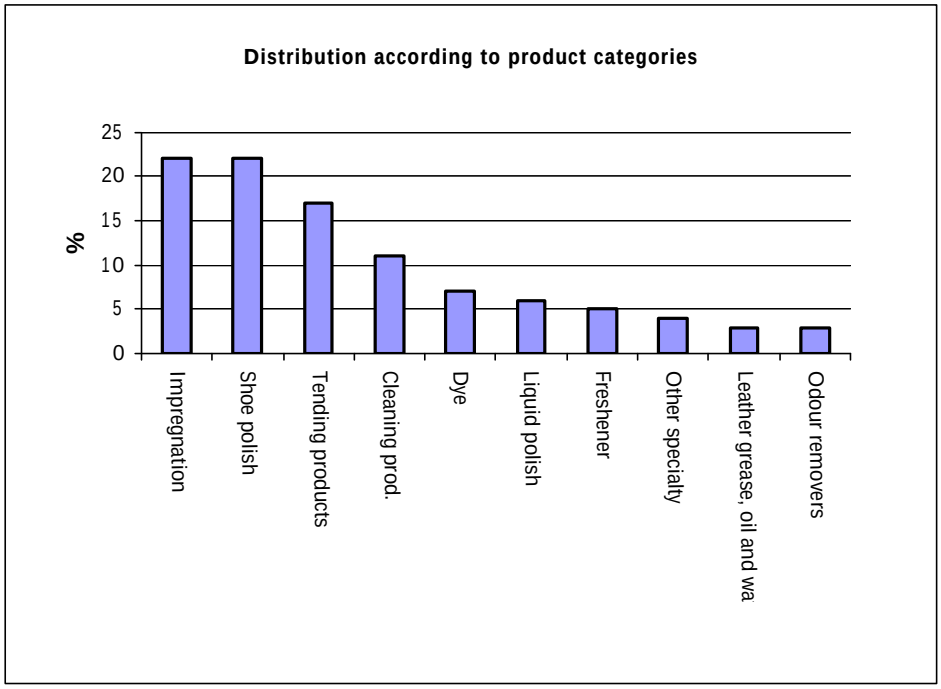
Product category	Number	%
Impregnation products	42	22
Shoe polishes	42	22
Tending products	32	17
Cleaning products	20	11
Dyes	14[10]	7
Liquid shoe polishes	11	6
Fresheners	9	5
Other specialty products	8	4
Leather greases, oils and waxes	6	3
Odour removers	5	3
Total	189	100

Generally, the largest selection of products is found in heel bars and in stoe stores. More than 100 different products were identified (including different colour tones) in a single heel bar. In addition, it is mainly this type of store that carries specialty products such as shoe dyes in less ordinary colours, grain polish, odour removers etc. while supermarkets sell more commonly used products such as shoe polish (neutral, black, blue and brown), leather grease and impregnation products.

[10] Number of different products, each product is found in several colour nuances

9 suppliers have been identified while there are 4 manufacturers. Some products can be found more than once in the mapping as some stores sell products under ”own label”. These products have been included with both product names as the ordinary consumer is unable to see that the products are the same.

Figure 1 Distribution of products in categories in %



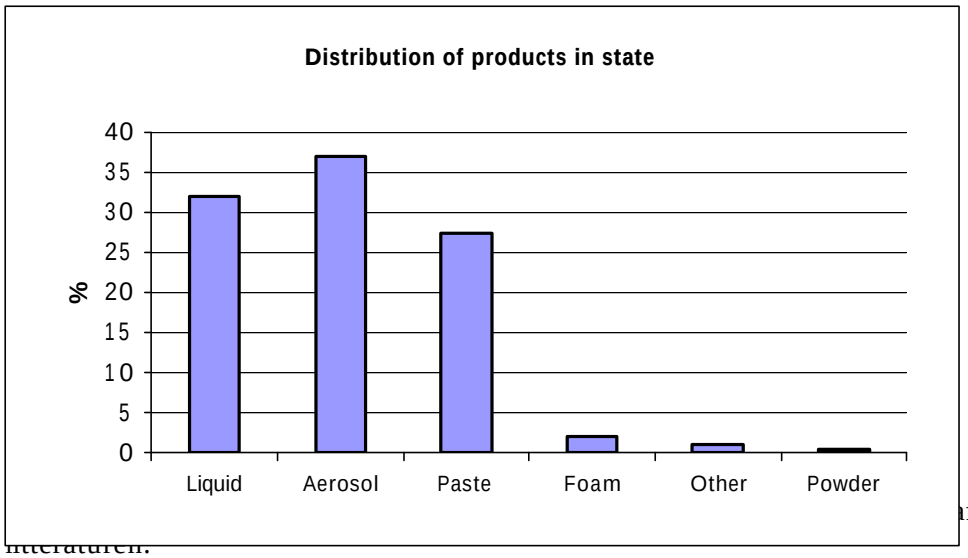
The products are marketed primarily as paste (27%), liquid (33%) and aerosol (35%) as shoe polish is most often a paste, plejemidler most often liquids and impregnation products are usually aerosol products. Some products are foam or in the shape of a sponge impregnated with a liquid and only one product is a powder.

Table 3 Distribution in state

State	Number of products
Liquid	60
Paste	52
Aerosol[11]	70
Powder	1
Foam	4
Other	2

[11] 2 of these products do not contain drivgas but rather are bottles with a pump mechanism

Figure 2 Distribution of products in state



af litteraturen.

It has been possible to obtain safety data sheets for 172 of the 189 products corresponding to 91% of the products.

Information on ingredients (CAS-no., amount in the product and classification) is based in information in the safety data sheets for the products.

85 different ingredients have been identified. Substances with the same name and/or CAS-no. but with different classification have been included as 2 different substances. This is the case for e.g. naphtha (raw oil), hydrogen treated heavy CAS-no.: 64742-48-9 and stearylaminoxethylat. The classification of the substances can be seen in table 16 in chapter 5.

The reason why to kulbrintedestillater with the same CAS-no. can have different classification is that they are complex mixtures that can have a varied composition depending on the origin and destillation interval of the raw oil. Therefore, these destillates should be selvvurderes by the supplier or manufacturer and it is therefore not necessarily a mistake when two destillates do not have the same classification. The same is the case for surfactants that also do not have an unambiguously defined composition. The number of substances distributed on their function can be seen in table 4.

Table 4 Number of ingredients distributed on function

Function	Number of substances
Solvents	29[12]
Wax, grease and oils	15
Drivgasser	6
Dyes[13]	7
Fragrances	3
Bindemidler	3
Surfactants	9
Preservatives	3

[12] The actual number of different subtsances is probably smaller as testbenzin without statement of CAS-no. may be covered by one of the other CAS-numbers.
[13] The actual number of dyes is much larger but the dyes are typically not stated in the safety data sheet.

Function	Number of substances
Other substances	10
Total	**85**

Figure 4 Number of ingredients distributed on their function in the product

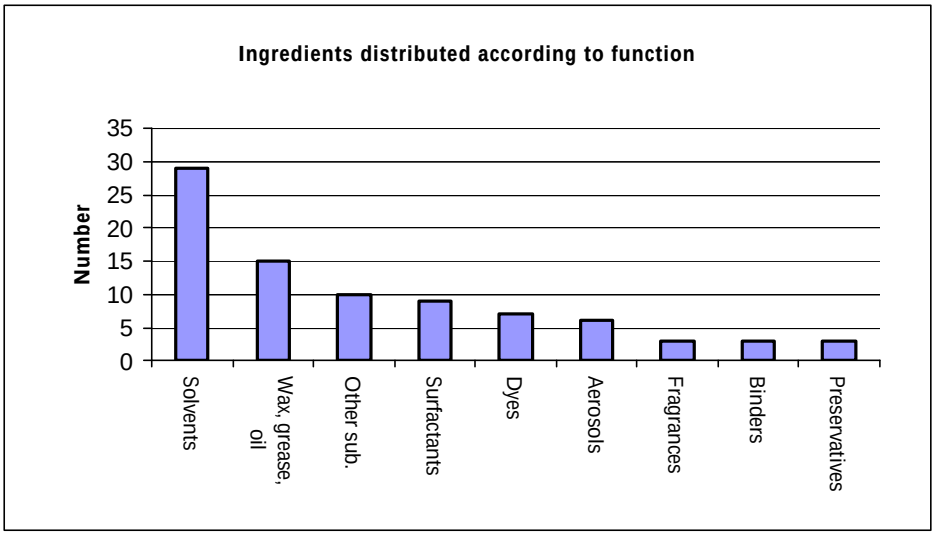


Table 5 lists the ingredients with substance names and according to function indicating occurrence, i.e. in how many products the substance is found. The statement of occurrence has corrected for the same products having different names so that the ingredients have been included only once.

Table 5 Ingredients listed according to function and occurrence in the product

Solvents		
CAS-no	**Substance name**	**Number**
67-64-1	acetone	6
78-93-3	butanon	1
123-86-4	butylacetat	6
64742-47-8	destillates (raw oil), hydrogen treated light	2
64-17-5	ethanol	5
111-90-0	2-(2-ethoxyethoxy)ethanol	1
141-78-6	ethylacetate	8
104-76-7	2-ethylhexanol	2
123-42-2	4-hydroxy-4-methyl-2-pentanon	1
-	industrial methylated spirit	1
107-98-2	1-methoxy-2-propanol	3
108-65-6	2-methoxy-1-methylethylacetate	1
34590-94-8	(2-methoxymethylethoxy)propanol	1
78-83-1	2-methylpropan-1-ol	2
-	mineral turpentine	1
64742-49-0	naphtha (raw oil), hydrogen treated light	18
64742-48-9	naphtha (raw oil), hydrogen treated heavy	26
64741-65-7	naphtha (raw oil), heavy alkylar	3
57-55-6	propan-1,2-diol	3
67-63-0	propan-2-ol	46
-	siedegrenzenbenzin 100/140	11
8006-64-2	turpentine oil	3
-	test gasoline (aromat free)	19
-	test gasoline	3

Solvents		
108-88-3	Toluen	1
-	white spirits	1
1330-20-7	xylen	2

Wax, grease and oil		
CAS-no	**Substance name**	**Number**
-	beeswax	3
-	carnauba wax	2
-	coconut grease	1
-	lanolin	1
-	marrow oil	3
107-51-7	octamethyltrisiloxan	2
-	olive oil	1
-	paraffin wax emulsion	2
84695-98-7	persea gratissima (avocado oil)	2
-	polydimethylsiloxan with aminoalkyl-groups	1
-	silicone/silicone oil	7
-	aquous emulsion of wax and oil	5
-	vaseline	2
-	vgetable oils	1
-	wax/wax emulsion/micro-crystalic wax	3

Propellants		
CAS-no	**Substance name**	**Number**
106-97-8	butane	34
142-82-5	heptane [and heptanisomers]	19
75-28-5	isobutane	2
-	isobutane/propane	3
74-98-6	propane	34

Fragrances		
CAS-no	**Substance name**	**Number**
-	fragrance	3
5989-27-5	D-limonen	1
-	perfume	1

Dyes		
CAS-no	**Substance name**	**Number**
7429-90-5	aluminium	1
61901-87-9	C.I. Solvent Black 29	1
-	colour pigment	1
-	dye	1
-	metal complex dye Cr(III)	1
-	organic pigment	1
-	waterbased pigment	2

Binders		
CAS-no	**Substance name**	**Number**
-	fluorcarbon resin	5
-	maleinat resin, glycol free	1
-	resin	2

Surfactants		
CAS-no	**Substance name**	**Number**
-	alcohols, C16-18 and C18-unsaturated, ethoxylated	1
-	fedtalkoholpolyglycolether	2
-	ammonium soap	-
-	ifralan	1
-	isodecanolethoxylat	1
33939-64-9	natriumlaureth-4-carboxylat	3
-	oleylalcohol -20 EO	1
26635-92-7	stearylaminoxethylat	12

Preservatives		
CAS-no	**Substance name**	**Number**
3380-34-5	triclosan	3
7632-00-0	natriumnitrit	3
26172-55-4	5-chloro-2-methyl-4-isothiazolin-3-one	2

Other substances		
CAS-no	**Substance name**	**Number**
84-74-2	dibutylphthalat [1]	2
64-19-7	acetic acid	2
-	thickener	3
-	Impregnating plant juices	1
-	leather nutrient drawn from plants	1
131-57-7	2-hydroxy-4-methoxybenzophenon	1
-	plant juices and flower nectar	1
-	foam suppressant	2
78-51-3	tris(2-butoxyethyl) phosphate [3]	2
7582-20-8	zirkoniumacetat [4]	4

1) Softenser
2) Sun filter, stabilisor
3) Softener, flame retardant
4) Cross binder

From table 5 it can be seen that the most frequent ingredents in the 189 products are:

- 2-propanol (46 products, 24 %)
- propane (34 products, 18 %)
- butane (34 products, 18 %)
- naphtha (raw oil), hydrogen treated heavy (26 products, 14 %)
- naphtha (raw oil), hydrogen treated light (18 products, 9,5 %)
- heptane/heptane mixture (19 products, 10 %)
- test gasoline (aromat free) (19 products, 10 %)

3.2.1 Solvents

Organic solvents can dissolve grease, wax and oil. The solvents are used to dissolve the oils and waxes that are added to the products to make the footwear water-repellent. After application, the solvents evaporise and leave a water-repellent membrane on the footwear. The organic solvents can also be added to the products to clean grease and oil stains on the footwear.

29 different solvents have been registered. The solvents are distributed on: hydrocarbon destillates (13), aromatic hydrocarbons (2 – xylene and toluen), alcohols and glycols (8), acetates (3) and ketones (3). The most freqent are hydrocarbon destillates and isopropanol. Solvents are contained in all product types except for leather grease.

Test gasoline is a German designation for mineral turpentine CAS-no: 64742-82-1. Typical boiling point interval for mineral turpentine of this type is from 130-200°C. Seidegrensenbenzin is a kulbrinte destillate with a special boiling point interval in this case of 100 to 140°C. You also call this type of hydrocarbons SPB (special boiling point), special gasoline or extraction gasoline.

3.2.2 Wax, grease and oil

Wax, grease and oil is used in the products as softeners and water-repellent agents.

The registred types of wax and oil can be divided into natural (e.g. beeswax and olive oil), mineral (e.g. paraffin wax and vaseline) and synthetic (silicone oil). Silicone oils are used as impregnation as a water-repellent surface is formed on the footwear after application. Silicone is found in a total of 10 products: octamethyltrisiloxan (2 products) polydimethylsiloxan (1 product) as well as unspecified silicone (7 products).

3.2.3 Polymers

Polymers are compounds formed by small building blocks and chained together to form a network of molecules that form a film or surface coating on the materials on which they are applied.
The registration shows that a further 8 products contain polymers of which 2 are a unspecified resin (also called resin or polymer), in 1 case it is a maleinat resin and in 5 of the cases fluorcarbon resin.
Fluorcarbon resins are typically used as impregnation agents along with silicone.

3.2.4 Propellants

The most common propellants are butane and propane that are found in 34 aerosol products. It is no coincidence that the two substances have the same occurrence as a mixture of butane and propane is often used as a propellant. A few products contain isobutane instead of butane.

The combined occurrence of heptane is 19 products. As seen in table 16 in chapter 5, heptane is registered with two different classifications of which one corresponds to CAS-no: 142-82-5 corresponding ot the official classificaiton. As it is not immediately possible to determine what the designation ”heptane

mixture" covers, and as no CAS-no. has been stated, it is not possible to determine whether the other classification is correct.

3.2.5 Dyes

A total of 7 dyes have been registered of which 2 have been stated with specific name and CAS-no., see table 6.

C.I. name	Chemical name	CAS-no
C.I. Pigment Metal 1	Aluminium	7429-90-5
C.I. Solvent Black 29 (RL)	- [Metal complex]	61901-87-9

Table 6 Registered named dyes

This table can be supplemented with the dyes stated in table 7 which have been found using udtrækket from SPIN (impregnation products). In addition to these dyes there may, however, be a significantly larger amount of dyes in shoe care products, including titan dioxide and carbon black as mentioned in the introduction. However, information about dyes can rarely be found in the safety data sheets for the products.

C.I. name	Chemical name	CAS-no
C.I. Pigment Yellow 42	Iron hydroxide yellow	51274-00-1
C.I. Pigment Blue 15	Copper phthalocyanin	147-14-8
C.I. Pigment White 4	Zincoxide	1314-13-2
C.I. Pigment Green 42	Phthalocyanin Green	1328-53-6
C.I. Pigment Violet 23	Diindolo(3,2-b:3',2'-m-)triphenodi-oxazin, 8,18-dichlor-5,15-diethyl-5,15-dihydro-	6358-30-1
C.I. Pigment Yellow 42	Leaoxide	1317-36-8
C.I. Pigment White 6	Titan dioxide	13463-67-7
C.I. Pigment black 6 og 7	Carbon black	1333-86-4

Table 7 Dyes in impregnation products registered in SPIN

3.2.6 Fragrances

It has been registered that 5 products contain fragrances, but the fragrance has only been specified in one case: D-limonen. Significantly more of the products probably contrain perfume as several of the water-based shoe polishes and plejemidler are scented. Fragrances can be added to obtain a scent or to camouflage a bad scent.

3.2.7 Surfactants

Most of the surfactants are nonionic surfactants, but a sigle anionic surfactant (natriumlaureth-4-carboxylat), a fatty acid amine (stearylaminoxethylat) and an ammonium soap have, however, been found. Of the surfactants, stearylaminoxethylat is the most common as it is found in a total of 12 products. Ifralan is a trade name, but it is probably a nonionic surfactant of the alkylphenolethoxylat type. The surfactants may have been added due to their cleaning (grease dissolving) effect, in order to make it easier for the tending substances to penetrate the footwear or as emulgators in water-based products.

3.2.8 Preservatives

3 preservatives have been registered, two of which are found in 3 products while the last one is only found in one product. This means that 7 products

contain a preservative. The actual number of products containing preservatives is probably larger as approximately 10-15% are water-based prodcuts and these must be assumed to be preserved. The water-based products are mainly found among the cleaning and tending products.

3.2.9 Other substances

In addition to the above, 10 substances have been registered in the category ”Other substances” including natural plant juices and flower nectar as well as ingredients that work as softeners, stabilisors and flame retardants.

3.3 Summary

The mapping of ingredients confirms the assumption that there are unwanted substances in shoe care products.

A large part of the registered products contain different types of solvents – most common are 2-propanol (water-miscible products) and hydrocarbon destillates (solvent-based (non water-miscible) products and aquous emulsions). Solvents of the C9-12 isoalkane type, which are listed on the EPA list of unwanted substances, are not specifically stated as ingredients in any of the products for which information about ingredients is available.

Products have primarily been selected for analysis among products for which there was not already information available about ingredients.

It is expected that the water-based products, including aqous emulsions, may contain preservatives.

Two of the products contain dibutylphthalat in amounts of < 2.5 %. Dibutylphthalat is classified as toxic to reproduction according to the Order on Classification
It is not legal to sell products for private use if the content of dibutylphthalat is 0.5 % or above, i.e. the products may be illegal. However, information has subsequently indicated that both products are no longer on the market.

3.4 Estimation of consumption

It has been attempted to obtain a view of the relative amounts sold of the different producty types by contacting the individual suppliers. The relative amounts are important in the determination of which products are selected for analysis and in connection with the subsequent exposure assessment.

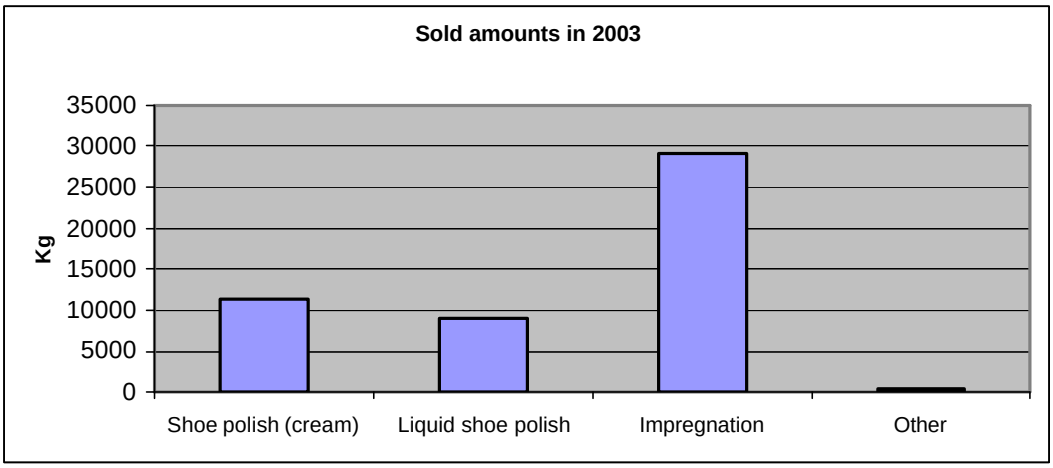
It has, however, only been possible to obtain information from 4 suppliers. The sale of shoe care prodcuts in 2003 has been stated at 50,000 kg (50 tonnes) based on the information received with a distribution on product categories as shown in figure 5.

As not all suppliers have wished to inform us of sale numbers, the combined sold amount in Denmark is actually higher than the above informed amounts, but the percentage distribution on product types is assumed to be correct.

As can be seen from the figure, the sale of impregnation products in 2003 was approximately 29 tonnes and the impregnation products made up 58% of the sale of shoe care products. The sale of shoe polish (the sum of creams and

liquid products) as approximately 20.5 tonnes corresponding ot 41% of the shoe care products sold. Other shoe care products made up approximately 1%, corresponding to approximately 0.5 ton.

Figure 5 Sale in 2003 distributed on product types.



3.5 Selection of products for analysis

Base on previous reports and extractions from the SPIN database it can be predicted that the products may contain the following subtsances, listen on the EPA list of unwanted substances:

- C_{9-12} isoalkanes (impregnation products)
- Octamethylcyclotetrasiloxane (silicone-based impregnation products)
- PFOS-compounds (impregnation and shoe polish)
- Certain azo-dyes (coloured shoe polish and plejemidler) as well as other problematic substances such as
- Preservatives including isothiazolinones (water-based products)
- Various solvents (including benzene, trichlorethylen og 1,1,1-trichlorethan)

The mapping of ingredients supports this assumption as the products contain substances such as fluorcarbon resin, silicone, preservatives and dyes. In addition, a large number of the products contain solvents. In order to assess whether the products contain any of the above-menioned problematic substances, an analysis programme has been established which contain the following analyses:

- Organic solvents (found in non water-miscible products and possibly in aquous emulsions)
- Preservatives (used in water-based products and emulsions)
- Chlormethyl- and methylisothiazolones (preservative in water-based products)
- X-ray (screening for heavy metals which can i.e be found as impurities and be contained in dyes)

- Octamethylcyclotetrasiloxan (may be found in products containing silicone)
- PFOS-compounds (may be found in products containing fluorcarbon resin)
- Azo-dyes[14] (may be found in products containing red, yellow, orange and brown dyes)
- C9-C12 isoalkanes (may be found in products containing organic solvents, known to occur in certain impregnation products).

The criteria for selection of products for analysis have been:

- The products must represent different product categories
- The prodcuts must represent different suppliers
- The products must represent different states
- The must be a reasonable assumption that the product contains problematic substances – alternatively the ingredients in the product must be unknown or the amount of an ingredient should be controlled.

Thus, 14 products (approximately 7%) have been selected for analysis. The distribution on product types, supplier and state can be seen in table 8.

Table 8 Products selected for analysis

ID-no	Product type	Supplier ID	State	Information on ingredients
114	Impregnation	1	Liquid	+
301	Impregnation	15	Spray	+
309	Impregnation	7	Aerosol	-
40	Plejemiddel, coloured	5	Liquid	+
304	Cleaning product	17	Liquid (application sponge)	-
296	Cleaning product	7	Paste	-
314	Shoe polish	-	Liquid (application sponge)	-
256	Shoe polish, coloured	9	Paste	-
266	Shoe polish, coloured	5	Paste	+
319	Shoe polish	6	Paste	+
168	Liquid polish, coloured	14	Liquid (application sponge)	+
124	Freshener, coloured	1	Aerosol	+
123	Dye, coloured	15	Liquid	+
27	Other product	1	Liquid	-

Red, brown and yellow-brown nuances have been selected for the coloured products.

[14] Among the dyes, the following pigments are potential PBT-substances: C.I. Pigment Yellow 83, C.I. Pigment yellow 13, C.I. Pigment orange 13, C.I. Pigment red 224 and C.I. Pigment yellow 14.

4 Analyses

Based on the results of the mapping, a number of products have been selected in cooperation with the EPA for analysis for selected chemical substances. Emphasis has been placed on problematic dyes, PFOS compounds and any other ingredients that may be problematic to humans or the environment. A final analysis programme was prepared for qualitative and quantitative analyses of the selected products.

4.1 Analysis programme

Below is a descriptioin of the analysis programme established based on the previous phases.

4.1.1 X-ray (screening for heavy metals)

An x-ray screening is carried out to identify the elements, including any heavy metals. The heavy metals can occur in the form of impurities or as components of colour pigments.

A sub-sample of products was investigated using x-ray technique for content of all metals. Analysis uncertainty: 10% RSD. The accuracy of x-ray analysis is poor as there are calibration difficulties, particularly in the case of complex matrices. The analysis should therefore be considered a screening analysis.

Detection limit: 5-10 mg/kg.

4.1.2 PFOS-compounds

An analysis has been carried out fo rPFOS-compounds as previous investigations have shown that these substances may occur in impregnation products.

A sub-sample is extracted with methanol and the extract is then analysed directly though reversed phase-column liquid chromography using a mass spectrometric detector (HPLC-MS). Electro-spray ionisation in netagive mode is used for detection. Calibration with external standards analysed in series with the sample is used.

The detection limit is 0.1 mg/kg and the analysis uncertainty is 15% RSD.

The analysis includes the following components: perfluorobutane sulphonate, perfluorohexane sulphonat, perfluorooctane sulphonat, perfluorodecan sulphonat, perfluorooctane sulphonamid, N-ethyl perfluorooctane sulphonamid, perfluoroheptane acid and perfluorooctane acid. The analysis is carried out in double determination.

4.1.3 Octamethylcyclotetrasiloxane

Octamethylcyclotetrasiloxane is on the EPA list of unwanted subtsances as the substance is classified as toxic to reproduction (Rep3;R62 R53) and as the

substance is evaluated as a PBT[15] and vPvB[16] substance. It is assumed that this substance may occur in products containing silicone.

Dichlormethane is added to a sub-sample which is shaken for 2 hours and left at room temperature for 16 hours. A sub-sample of the extract is analysed directly through a combination of gaschromatography and mass spectrometry (GC/MS).

The detection limit is 1 mg/kg and the analysis uncertainty is 10-15% RSD.

4.1.4 Organic solvents

A sub-sample is extracted with DMF (dimethylformamid) with added internal standards. A sub-sample of the extract is removed and analysed directly using combined gaschromatography and mass spectrometry (GC/MS) by scanning across a larges mass area. All identifications of substances have been carried out from the mass spectre by comparison with mass spectres in a data library. The content is calculated opposite internal standards.

The reporting limit is 10-100 mg/kg and the analysis uncertainty is 25-50% RSD. The reporting limit is above the detection limit as the reporting limit is the concentration which in this case is estimated to be interesting – here established at 10-100 mg/kg corresponding to 0.001 to 0.01%. Methodwise it is thus possible to go further down in concentration, but the efforts will not match the result.

4.1.5 C_{9-12} isoalkanes

A sub-sample of the product with known weight is extracted using dichlormethan. A sub-sample is extracted and analysed directly through combined gas chromatography and mass spectrometry (GC/MS) by scanning across a larger mass area. The content is calcuated as isoalkan (C_{10}). The reporting limit is 5000 mg/kg and the analysis uncertainty is 15-20% RSD.

The reporting limit is above the detection limit as the reporting limit is the concentration which in this case is considered interesting – here established at 5000 mg/kg corresponding to 0.5%. Methodwise it is thus possible to go further down in concentration but the efforts will not match the result.

4.1.6 Preservatives

Benzylbenzoat, benzylalcohol, cresoles, parabenes and ethylenoxide can be included in the GC/MS screening where calculations are carried out opposite external standards.

The detection limit is estimated at 10 mg/kg and the analysis uncertainty at 15% RSD.

During the analysis for chlormethyl- and methylisothiazolones (Kathon) a representative sub-sample is extracted and diluted in demineralised water. 2 drops of concentrated saltsyre is added to the solution which is then filtered through a 0.45µm filter. The filtrerede solution is analysed by liquid chromatography with UV detection (HPLC/DAD).

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[15] Persistent, bio-accumulating and toxic
[16] Very persistent and very bio-accumulating substances

The detection limit is estimated to be 10-100 mg/kg. The analysis uncertainty is 10-15%.

4.1.7 Azo-dyes

The samples are extracted with an aquous buffer solution and reduced with dithionit whereby the amin part is split off from the azo-dye. The reaction products area extracted with t-butylmethylether and the extractions are then analysed using high pressure liquid chromatography with Diode-Array Detection (HPLC/DAD).
The detection limit is 30 mg/kg and the analysis uncertainty is 15% RSD.
The analysis includes the following aromatic amines: 2,4-diaminoanisol, 2,4-toluylendiamin, o-toluidin, 4,4-oxydianilin, benzidin, p-chloranilin, p-cresidin, 4,4'-methylendianilin, 2-naphthylamin, 4,4-thiodianilin, 3,3-dimethoxybenzidin, 4-chlor-o-toluidin, 2,4,5-trimethylanilin, 3,3-dimethyl-benzidin (= o-Tolidin), 3,3-dimethyl-4,4-diaminodiphenyl methan, 4-amino-diphenyl, 3,3-dichlorbenzidin and 4,4-methylen-bis(2-chlor-anilin).

4.1.8 Chlorparaffines

A sub-sample of the product with known weight is extracted with n-heptane. A sub-sample is extracted and analysed directly by combined gas chromatography and electron capture detection (GC/ECD). The content is calculated quantatively.

The detection limit is 50 mg/kg and the analysis uncertainty is 15-20% RSD.

4.1.9 GC/MS – screening for extractable organic substances

A sub-sample is extracted with dichlormethane with added internal standards. A sub-sample of the extract is extracted and analysed directly by combined gas chromatography and mass spectrometry (GC/MS) by scanning across a mass area. All identification of subtances have been carried out from retention time and mass spectre by comparison with mass spectres in a data library. The content is calculated semi-quantatively.

The reporting limit is 10 mg/kg. The reporting limit is above the detection limit as the reporting limit is the concentration which in this case is considered interesting – here established at 10 mg/kg corresponding to 0.001%. Methodwise is is thus possible to go down further in concentration but the efforts will not match the result. As it is a screening examination, no analysis uncertainty is stated.

4.2 Analysis results

4.2.1 X-ray

Three products were analysed for elements using x-ray technique and the results are stated in table 10. The result is stated as intervals as the analysis is a screening. The intervals are stated as:
x: content between the detection limit and 100 mg/kg
xx: content between 100 mg/kg and 1,000 mg/kg
xxx: content between 1,000 mg/kg and 10,000 mg/kg
xxxx: content between 10,000 mg/kg and 100,000 mg/kg

The elements not mentioned in the table have not been found in the analysis. Single determinations have been carried out. The unit is mg/kg and the detection limit is 10-20 mg/kg. As it is a screening alaysis, no analysis uncertainty is stated.

Table 10 Results of analysis for elements. The results are stated in intervals in the unit mg/kg.

ID-nr	40	256	314
Sodium	Xx	xxx	xx
Aluminium	< 20	xxx	xx
Silicium	X	xxxx	xx
Phosphor	-	xx	-
Sulphur	Xx	xxx	xx
Chloride	-	xxx	xx
Potassium	< 10-	xx	-
Calcium	< 10-	xx	x
Titan	< 10-	xxxx	-
Mangan	< 10-	xxx	-
Iron	< 10-	x	-
Strontium	< 10-	x	-
Barium	< 10-	xxx	-

-: means not found above the detection limit

4.2.2 PFOS-compounds

Four products were analysed in double determination for eight specific PFOS-compounds. Components could only be determined in one product where two PFOS-compounds were detected. The results from the double determination are stated in table 2. The unit is mg/kg and the detection limit is 0.1 mg/kg.

Tabel 12 Results of analysis for PFOS-compounds. The results are stated in mg/kg.

ID-no	40		114		301		309	
	A	B	A	B	A	B	A	B
Perfluorobutan sulphonat	-	-	-	-	-	-	-	-
Perfluorohexan sulphonat	-	-	-	-	-	-	-	-
Perfluorooktan sulphonat	-	-	-	-	-	-	-	-
Perfluorodecan sulphonat	-	-	-	-	-	-	-	-
Perfluorooktan sulphonamid	-	-	-	-	-	-	-	-
N-ethyl perfluorooctan sulphonamid	-	-	-	-	-	-	-	-
Perfluoroheptan acid	-	-	-	-	1.1	1.1	-	-
Perfluorooctan acid	-	-	-	-	0.36	0.36	-	-

-: means not found above the detection limit

4.2.3 Octamethylcyclotetrasiloxan

An analysis for Octamethylcyclotetrasiloxan was carried out for eight shoe care products. The analysis was carried out in double determination and the results are stated in table 12. The unit is mg/kg and the detection limit is 0.5 mg/kg.

Table 12 Results of analysis for Octamethylcyclotetrasiloxan. The results are stated in mg/kg.

ID-no	27		40		114		123	
	A	B	A	B	A	B	A	B
Octamethylcyclotetrasiloxan*	-	-	0.76	0.82	1.5	1.8	3.4	3.4
ID-no	**168**		**301**		**309**		**319**	
	A	B	A	B	A	B	A	B
Octamethylcyclotetrasiloxan*	1.8	1.6	0.96	0.80	-	-	-	-

-: means not found above the detection limit * CAS-no: 556-67-2

4.2.4 Solvents

The screening for solvents should components in all 6 analysed products. In three of the products, mineral turpentine was found in concentrations of 72, 88 and 85%, respectively. In one impregnation product (ID301), 93% isopropanol was found and in a cleaning product (ID296), 30% ethanol was found. In the final sample, only small amounts of methylethylketon (0.02 %) and xylen (0.004 %) were found and they were probably impurities in the product. The analysis has only been carried out in single determination as stated in table 13. The unit is mg/kg and the detection limit is 10 mg/kg.

Table 13 Results of analysis for solvents. The results are stated in mg/kg.

	256	266	296	301	314	319
Mineral turpentine*¤	720,000	880,000	-	-	-	850,000
Isopropanol	-	-	-	930,000	-	-
Ethanol	-	-	30,000	-	-	-
Methylethylketon	-	-	230	-	200	-
Xylen	-	-	-	-	40	-

-: means not found above the detection limit
*: may contain other hydrocarbons
¤: quantification is uncertain as there is are different kinds of mineral turpentine. This means that
the calculated amount afviger substantially depending on which substance is quantified.

4.2.5 C_{9-12} Isoalkanes

Three of the products were analysed for isoalkanes (C_{9-12}). In one of the products, isoalkanes were found in a concentration of 26-27 %. In the remaining two samples, isoalkanes were not found above the reporting limit of 5000 mg/kg (0.5%).

Table 14 Results of analysis for C_9-C_{12} isoalkanes. The results are stated in mg/kg.

ID-no	256	296	314

	A	B	A	B	A	B
C_9-C_{12}-Isoalkanes	270,000	260,000	-	-	-	-

-: means not found above the reporting limit

The product which contains isoalkanes also contains mineral turpentine. The content of isoalkanes is assumed to be a sub amount of the amount of mineral turpentine.

Mineral turpentine typically contains up to 48% alkanes. Product 256 contains 72% mineral turpentine and a content of 26.5% isoalkanes in the product would correspond to the mineral turpentine containing approximately 37% isoalkanes which is not unrealistic. In addition, it seems unlikely that the manufacturer would choose to use different types of hydrocarbon destillates as solvent in the product.

4.2.6 Preservatives

Five products were analysed for a selection of preservatives:

ID-no. 27, 40, 124, 296 and 304

The analysis included the following preservatives:
Methylparaben, ethylparaben, propylparaben, butylparaben, benzylbenzoat, o-cresol, m+p-cresol and benzyl alcohol. The detection limit for the parabens and benzylbenzoat is 20 mg/kg except for product no. 124 where the detection limit for propylparaben was raised to 60 mg/kg due to interference. The detection limit for the cresols and benzyl alcohol is 50 mg/kg.
None of the preservatives were found above the detection limit in the products tested.

The content of chlormethyl and methyl isothiazolones was tested in 4 products:

ID-no. 27, 40, 123, 124, 296 and 304

No content of chlormethyl and methyl isothiazolones was found above the dtection limit of 50 mg/kg in the products tested.

4.2.7 Azo-dyes

An analysis for aromatic amines from azo-dyes was performed in 5 products:

ID-no. 40, 123, 124, 168 and 256

No aromatic amines above the detection limit of 100 mg/kg were found in the products tested. The detection limit was raised to 100 mg/kg due to interference from the highly concentrated dyes in the products.

The following amines were included in the analysis:
2,4-Diaminoanisol, 2,4-toluylendiamin, o-toluidin, 4,4-oxydianilin, benzidin, p-chloranilin, p-cresidin, 4,4'-methylendianilin, 2-naphthylamin, 4,4-thiodianilin, 3,3-dimethoxybenzidin, 4-chlor-o-toluidin, 2,4,5-trimethylanilin, 3,3-dimethylbenzidin (= o-tolidin), 3,3-dimethyl-4,4-diaminodiphenyl

methan, 4-aminodiphenyl, 3,3-dichlorbenzidin and 4,4-methylen-bis(2-chloranilin).

4.2.8 Chlorparaffins

2 products were analysed for chlorparaffins:

No. 256 and 266

No chlorparaffins were found above the detection limit of 50 mg/kg in the products tested.

4.2.9 GC/MS-screening

Table 15 Results of GC/MS-screening. The results are stated in mg/kg.

	266	**301**
Boric acid (H_3BO_3)-tri(1-methylethyl)ester	-	12
1H,1H, 2H, 2H-perfluorooctyliodid	-	13
2,2,4,6,6-pentamethylheptan	-	22
1H,1H, 2H, 2H-perfluorodecyliodid	-	20
Hydrocarbon mixture (aliphatic hydrocarbons from C_9 to C_{11})[17]	700,000	-
Bornylacetat	360	-
Butylated hydroxytoluen (BHT)	1200	-
Wax	250,000	-
Sum of unidentified	-	370

-: means not found above the detection limit

The GC-MS screening showed that product ID266 contains 70% of an aliphatic hydrocarbon destillate and 25% wax which means that the product composition is similar to the one stated for the remaining shoe polishes. In addition, the preservative BHT was found in a concentration of 0.12 %.

According to the analysis, product ID266 contains solvents 88% mineral turpentine, and according to the GC/MS-screening it contains 70% aliphatic hydrocarbons (C_{9-11}) which indicates that the product contains a mineral turpentine with an aromatic content of approximately 20%. This is a typical aromatic content for this type of mineral turpentine. However, the aromatic content could not be determined exactly based on the available analysis results.

[17] Mainly C_{9-11}, with a possible minimal content of C_{12}.

Product ID301 contained very small amounts of perfluoride compounds (less than 0.002%) and furthermore a very small amount of pentamethylheptane (0.0022%) which should be considered as impurities in the product.

4.3 Summary of analysis results

None of the preservatives analysed for were found. However, the GC-MS screening showed BHT in one of the samples in a concentration of 0.12%. No azo-dyes were found in concentrations above the respective detection limits in any of the samples analysed. The safety data sheet for product number 123 states a content of 0.15 to 0.25% 5-chloro-2-methyl-4-Isothiazolin-3-on but it is possible that the product has been reformulated and therefore no longer contains the substance.

Very small amounts of 2 PFOS compounds (1.1 and 0.36 mg/kg, respectively) were found in 1 of the 4 analysed samples of impregnation products. The amounts of PFOS compounds found are likely impurities in a flourcarbonpolymer added due to the water and dirt repellant properties.

In addition, very small amounts (from 0.79 to 3.4 mg/kg) octamethylcyclotetrasiloxan were found in 5 of the 8 analysed products. 3 of the 5 products are known to contain silicone. It is assumed that octamethylcyclotetra-siloxan is found as impurity in the silicone oil added to the product due to is imprenating and tending properties.

The x-ray screening of 3 products found no metals, including heavy metals, in 2 of those products in concentrations above 1000 mg/kg (corresponding to 0.1%) and for most of the substances, the content was below the detection limit (either 10 or 20 mg/kg).

In the third sample, a content of silicium and titan of between 10,000 and 100,000 mg/kg was found corresponding to between 1 and 10%. These elements likely come from silicium dioxide (SiO_2) and titan dioxide (TiO_2) used as filler and colour pigment, respectively. In addition, the sample contained Na, Al, S, Cl, Mn and Ba in concentrations between 1,000 and 10,000 mg/kg corresponding to 0.1-1%. These elements are assumed to come from colour pigments as the product in question is a coloured shoe polish. The content of chlorine may, however, come from other compounds such as chlorparaffins or chlorinated solvents.

Many of the products contain organic solvents used to dissolve dirt on the footwear or to dissolve the tending oils and waxes in the product. The screening of 6 products for solvents found mineral turpentine in three of the products (all shoe polishes) in concentrations of 72, 88 and 85%, respectively. In one impregnation product (ID301), 93 % isopropanol was found and in a cleaning product (ID296), 30% ethanol was found. In the final sample, only small amounts of methylethylketon (0.02 %) and xylen (0.004 %) was found which are probably impurities in the product.

Of the 3 samples selected for specific analysis for the solvent C_9-C_{12} isoalkanes, 265,000 mg/kg corresponding to 26.5% was found in one of the samples.

The results of the analyses are compared in table 16 below as the analyses carried out for each product are marked and the found content of substances of ≥0.1% are stated.

Table 16 Found content of substances in concentrations of 0.1% or above

ID	Category	Analyses	X-ray	Solvents	C9-12 isoalkanes	GC/MS screening
27	Other specialty products					
40	Tending product*		-			
114	Impregnation					
123	Dye *					
124	Freshener *					
168	Liquid polish *					
256	Polish *		Na, Al, Si, S, Cl, Ti, Mn, Ba	72% mineral turpentine	26.5 %	
266	Polish			88% mineral turpentine		70% aliphatic hydro-carbons 25% wax 0.12% BHT
296	Cleaning product			30% ethanol	-	
301	Impregnation			93% propan-2-ol		-
304	Cleaning product					
309	Impregnation					
314	Polish **		-	-	-	
319	Polish **			85% mineral turpentine		
	:Analysis not carried out					

- : < 0.1%
* Coloured product ** Black

Based on the analysis results it can be concluded that no substantial amounts of either PFOS or octamethyltetrasiloxan have been found. PFOS compounds have only been found in one of the four products analysed and only in a combined amoutn of 1.5 mg/kg corresponding to 0.00015%.

Very small concentrations of octamethylcyclotetrasiloxan were found in 5 of the 8 products analysed and the highest concentration was 3.4 mg/kg corresponding to 0.00034%.

The very low concentrations of these substances indicate that they are found as impurities from fluorcarbonpolymers and silicone, respectively.

In addition, no preservatives or azo-dyes were found in any of the samples analysed.

However, the analyses confirm that a number of shoe polishes contain solvents as large amounts of mineral turpentine (72, 88 and 85%) was found in 3 products along with 93% propanol and 30% ethanol respectively in 2 products . In addition, 26.5% C_9-C_{12} isoalkanes was found in 1 of 3 products analysed for this specific solvent.

According to the supplier's information, product ID266 contained 10-25% turpentine oil. This could not be confirmed through an analysis for organic

solvents which showed a content of 88% mineral turpentine. Another analysis method identified 70% aliphatic kulbrinter in the same product. This may indicate that the product contains a mineral turpentine with an aromatic content of approximately 20% which is typical for certain aromatic turpentines.

As the analyses showed a relatively high content of chlorine and hydrocarbons in ID256, this product and product ID266, which is a similar product, were further analysed for content of chlorparaffins. However, this analysis disproved the suspicion of content of chlorparaffins.

5 Critical ingredients

Based on the results of the mapping and analyses performed, this chapter contains an evaluation of which critical substances are contained in shoe care products. The critical substances are identified based on hazard (classification), frequency (in how many products the substances are found) and concentration in the products.

5.1 Identification of critical ingredients

In tables 17 and 18 the results of the mapping are supplemented with information from the analyses. Only substances that are found in amounts of 0.1% or above have been included. In addition, the substances stated unspecifically (e.g. perfume or resin) have been deleted. The classification and limit value in the working environment[18] of the substances have been stated in table 17 while the occurrence and maximum concentration in the product have been stated in table 18.

The classification stated in table 17 are the ones which the supplier has stated in section 2 of the safety data sheets.

Most hydrocarbon destillates (petroleum, benzine, certain types of mineral turpentine etc.) included on the list of hazardous substances have only been evaluated with regard to carcinogenic effect (R45) and their ability to cause chemical pneumonia (R65). This means that any other effects must be self-evaluated of the one responsible for placing the hydrocarbon destillate on the market. The classification with R45 is only relevant if the hydrocarbon destillate contains > 0.1 % benzene which is rarely the case. In addition, the health hazardous effects of hydrocarbon destillates with the same CAS-number may vary depending on the origins of the raw oil. The result is that there may be different classifications of hydrocarbon destillates with the same CAS-number.

Some substances have been awarded different self classifications by the suppliers and the following evaluation is carried out based on the strictest of these classfiications.

The hazard evaluation emphasizes the properties that may cause irreversible damage to people, allergenic substances as well as volatile substances or substances absorbed through the skin.

Table 17 shows that 3 substances (D-limonen, 5-chloro-2-methyl-4-isothiazolin-3-on og terpentinolie) are found that are classified with R43 ”May cause sensitisation by skin contact”. D-Limonen is found in a single product, 5-chloro-2-methyl-4-isothiazolin-3-one is found in 2[19] products while turpentine oil is found in 3 products according to the registered information.

[18] At-Guideline C.0.1, October 2002: ”Limit values for substances and materials”
[19] The substance was not found in the one product analysed

The substances xylen and toluen are classified with R20 ”Harmful by inhalation” and mineral turpentine is classified with R22 ”Harmful if swallowed” and R48/20 ”Harmful: danger of serious damage to health by prolonged exposure through inhalation”. Toluen is contained with 2.5 to 10% in a single product. Xylen is contained with 2.5 to 10% in 2 products according to the supplier safety data sheet. Mineral turpentine (CAS-no: 8052-41-3) is contained in 3 products. The remaining hydrocarbon destillates are not classified with either R22 or R48/20.

Dibutylphthalat is classified as toxic to reproduction and according to the information registered is contained in 2 products. However, contact to the supplier indicates that the products are no longer on the market.

Table 17 Classification and limit values for ingredients

Substance name	CAS-no	Classification*	GV [ppm]	Note
acetone	67-64-1	F;R11 Xi;R36 R66 R67	250	-
alcohols, C16-18 and C18-unsaturated, ethoxylated***	-	Xn; R22 Xi;R38-41	-	-
aluminum	7429-90-5	F; R10-15	-	-
beeswax	-	Not classified	-	-
Butane	106-97-8	Fx;R12	500	-
Butanon	78-93-3	F;R11 Xi;R36 R66 R67	50	H
Butylacetat	123-86-4	R10 R66 R67	150	-
C.I. Solvent Black 29***	61901-87-9	N;R51/53	-	-
Carnauba wax	-	Not classified	-	-
5-chloro-2-methyl-4-isothiazolin-3-one***	26172-55-4	T;R23/24/25 C;R34 X,R43 N;R50/53	-	-
Destillates (raw oil), hydrogen treated light ***	64742-47-8	Xi; R36/38	25	-
Dibutylphthalat	84-74-2	Rep2;R61 Rep3;R62 N;R50	-	-
D-limonen	5989-27-5	R10 Xi;R38-43 N;R50/53	-	-
Acetic acid	64-19-7	R10 C;R35	10	-
Extraction gasoline 100/140***	-	F;R11 Xn;R65 Xi;R38 R67 N;R51/53	300**	
Ethanol	64-17-5	F;R11	1000	-
2-(2-ethoxyethoxy)ethanol	111-90-0	Xi; R36	-	-
Ethylacetat	141-78-6	F;R11 Xi;R36 R66 R67	150	-
2-ethylhexanol	104-76-7	-	-	-
Fatty alcohol polyglycolether***	-	Xn;R22 Xi;R41	-	-
Heptane [and heptanisomere]	142-82-5	F;R11 Xn;R65 Xi;R38 R67 N;R50/53	200	-
4-hydroxy-4-methyl-2-pentanon	123-42-2	Xi;R36	50	-
Ifralan*	-	Xn;R22 Xi;R41	-	-
Isobutan	75-28-5	Fx;R12	-	-
Isodecanolethoxylat*	-	Xi;R41	-	-
Coconut fat	-	Not classified	-	-
Lanolin	-	Not classfied	-	-
Maleinat resin, glycol free***	-	Xi;R36/37/38	-	-
Marrow oil	-	Not classified	-	-
2-hydroxy-4-methoxybenzophenon***	131-57-7	N;R51/53	-	-
(2-methoxymethylethoxy)propanol***	34590-94-8	Xi; R36/38	-	-
2-methoxy-1-methylethylacetate	108-65-6	R10 Xi;R36	50	H
1-methoxy-2-propanol	107-98-2	R10	50	-

Substance name	CAS-no	Classification*	GV [ppm]	Note
2-methylpropan-1-ol	78-83-1	R10 Xi;R37/38-41 R67	50	L,H
Mineral turpentine	8052-41-3	Xn;R22 R48/20	25	-
Naphtha (raw oil), hydrogen treated light***	64742-49-0	F;R11 Xn;R65 Xi;R38 R67 N;R51/53		
Naphtha (raw oil), hydrogen treated heavy ***	64742-48-9	R10 Xn;R65 R66		
Naphtha (raw oil), heavy alkylar***	64741-65-7	R10 Xn;R65	25	-
Sodiumlaureth-4-carboxylat***	33939-64-9	Xi;R36/38	-	-
Sodiumnitrit	7632-00-0	O;R8 T;R25 N;R50	-	-
Octamethyltrisiloxan***	107-51-7	R10 R53	-	-
Oleylalcohol -20 EO***	-	Xn; R22 Xi;R41	-	-
Olive oil	-	Not classified	-	-
Persea gratissima (avocado oil)	84695-98-7	Not classified	-	-
Polydimethylsiloxan with aminoalkyl groups ***	-	Xi; R38-41	-	-
Propane	74-98-6	Fx;R12	1000	-
Propane-1,2-diol	57-55-6	Not classified	-	-
Propane-2-ol	67-63-0	F;R11 Xi;R36 R67	200	H
Stearylaminoxethylat***	26635-92-7	Xn;R22 Xi;R38-41 N;R50/53	-	-
Turpentine oil	8006-64-2	R10 Xn;R20/21/22-65 R43 Xi;R36/38 N;R51/53	25	-
Test gasoline (aromat free)***	-	R10 Xn;R65 R66	25	-
Toluen	108-88-3	F;R11 Xn;R20	25	H
Triclosan*	3380-34-5	Xi;R36/38 N;R50/53	-	-
Tris(2-butoxyethyl) phosphate	78-51-3	-	-	-
Vaseline	-	Not classified		
White spirits***	-	Xn;R65	25	-
Xylen	1330-20-7	R10 Xn;R20/21 Xi;R38	25	H
Zirkoniumacetat*	7582-20-8	Xi;R36/38	-	-

* : Classification as stated in the supplier safety data sheet
**:Exctaction gasoline 100/140 tentative limit value
*** Self classification

From table 18 it can be seen that all except one of the substances contained in more than 10 products are organic solvents or volatile substances and that at the same time they are substances that are contained in large amounts in the products. The exception is a surfactant (stearylaminoxethylat) which is found in 12 products in a concentration of < 2.5%.

Table 18 Occurrence of ingredients

Chemical name	CAS-no	Number	Max. conc %
Propan-2-ol	67-63-0	46	70-90
Butane	106-97-8	34	25-50
Propane	74-98-6	35	10-25
Naphtha (raw oil), hydrogen treated heavy	64742-48-9	26	50-100
Mineral turpentine (aromat free)	-	21	50-100
Heptane [and heptanisomers]	142-82-5	19	25-50
Naphtha (raw oil), hydrogen treated light	64742-49-0	18	50-100
Stearylaminoxethylat	26635-92-7	12	< 2.5
Extraction gasoline 100/140	-	11	25-50
Ethylacetat	141-78-6	8	25-50
Ethanol	64-17-5	7	50-100

Chemical name	CAS-no	Number	Max. conc %
Butylacetat	123-86-4	6	2,5-10
Acetone	67-64-1	6	40
Zirkoniumacetat	7582-20-8	4	5-10
Mineral turpentine	8052-41-3	3	39
Propan-1,2-diol	57-55-6	3	2-5
1-methoxy-2-propanol	107-98-2	3	2.5-10
Naphtha (raw oil), heavy alkylar	64741-65-7	3	10-25
Turpentine, oil	8006-64-2	3	10-25
5-chloro-2-methyl-4-isothiazolin-3-one	26172-55-4	2	0.1-0.2
Triclosan	3380-34-5	3	< 2.5
Sodiumnitrit	7632-00-0	3	< 0.5
Beeswax	-	3	-
Marrow oil	-	3	-
Sodiumlaureth-4-carboxylat	33939-64-9	3	-
Acetic acid	64-19-7	2	2-5
2-methylpropan-1-ol	78-83-1	2	2.5-10
Xylen	1330-20-7	2	2.5-10
Octamethyltrisiloxan	107-51-7	2	15-30
Destillates (raw oil), hydrogen treated light	64742-47-8	2	1-10
2-ethylhexanol	104-76-7	2	0.5-1.5
Isobutane	75-28-5	3	> 30
Fatty alcohol polyglycolether	-	2	< 2.5
Carnauba wax	-	2	-
Lanolin	-	2	-
Persea gratissima (avocado oil)	84695-98-7	2	-
Vaseline	-	2	-
Butanon	78-93-3	1	30-40
Aluminium	7429-90-5	1	25-50
C.I. Solvent Black 29	61901-87-9	1	2.5-10
Maleinat resin, glycol free	-	1	2.5-10
Toluen	108-88-3	1	2.5-10
2-(2-ethoxyethoxy)ethanol	111-90-0	1	1-5
Polydimethylsiloxan with aminoalkyl groups	-	1	1-5
Tris(2-butoxyethyl) phosphate	78-51-3	1	1-2
(2-methoxymethylethoxy)propanol	34590-94-8	1	1-10
4-hydroxy-4-methyl-2-pentanon	123-42-2	1	1-10
Ifralan	-	1	1-10
White spirits	-	1	10-25
Dibutylphthalat	84-74-2	2*	< 2.5
D-limonen	5989-27-5	1	< 2.5
Isodecanolethoxylat	-	1	< 2.5
Methanone, 2-(hydroxy-4-methoxy-phenyl)phenyl- [2]	131-57-7	1	< 2.5
Oleylalcohol -20 EO	-	1	< 2.5
2-methoxy-1-methylethylacetate	108-65-6	1	-
Alcohols, C16-18 and C18-unsaturated, ethoxylated	-	1	-
Coconut fat	-	1	-
Olive oil	-	1	-

*The 2 products that contain this substance are no longer on the market

5.2 Substances selected for exposure evaluation

Based on hazard and occurrence it is suggested that the substances listed in table 18 become part of the exposure evaluation.

Exposure scenarios for the 3 suggested products will cover both 2 organic solvents that are found in relatively large amounts in a large number of products (propan-2-ol and heptane) and 2 substances that, in addition to being solvents, are dangerous to the health: turpentine oil that may cause allergy by skin contact and mineral turpentine which is hazardous by inhalation. Finally, C_9-C_{12} isoalkanes are included as they are an organic solvent listed on LOUS: Heptane and meinral turpentineare also listed on LOUS.

Table 19 Substances for exposure evaluation

Substance name	**Reason**
• Turpentine oil	Turpentine oil is classified with R43
• Mineralsk turpentine • C_9-C_{12} isoalkanes	Mineral turpentine is an organic solvent classified with R48/20. CAS-no: 8052-41-3 is listed on LOUS. C_9-C_{12} isoalkanes is an organic solvent listen on LOUS as a possible PBT substance.
• 2-propanol • Heptane	2-propanol is an organic solvent and the substance found in the most products. The substance can be absorbed through the skin. Heptane is an organic solvent listed on LOUS due to R50/53

6 Toxicological profiles

This section contains toxicological profiles for the selected critical ingredients. The toxicological data identified in this chapter are used in the following exposure evaluation as well as in the evaluation of whether there is any risk connected with consumers using the products.

6.1 Turpentine oil

6.1.1 Use

Previously, the most common use was as thinner in pain and other products for surface coating {8} which is still partly its use. In addition, turpentine oil is used in ointments, in wax, in polishers and similar products as well as in the synthesis of camphor and menthol.

6.1.2 Identification

Turpentine oil is a complex mixture of substances defined as: ”Any of the volatile mainly turpentine fractions or destillates found through solvent extraction of rubber collection from or crushing of blood tree. Consists primarily of the $C_{10}H_{16}$-terpencarbonhydrids: alfa-pinen, beta-pinen, limonen, 3-caren, camphen. May contain other acyclic, monocyclic or bicyclic terpenes, oxygenated terpenes and anethol. The exact composition varies with refining methods and age, origin and species of the blood tree source”.

Vapour destillated turpentine oil is composed of 81.3% α-pinen, 2.1% β-pinen, 11.4% camphen 3.4% related terpenes and less than 1% of a number of other compounds including 3-caren, dipenten and cymen {4}.

As it is a complex misture it is not possible to state an exact mol-weight or an unambiguous molecule structure.

Turpentine oil is a clear volatile liquid with a characteristic odour described as aromatic, unpleasant and penetrating. The odour limit is 100 ppm {8}.

Identification	
Substance name:	Vegetable turpentine
Synonyms:	Turpentine oil
CAS-No.:	8006-64-2
EINECS No.:	232-350-7
Molecular formula:	Primarily $C_{10}H_{16}$
Molecular structure:	-
Legislation: Classification according to the list of dangerous substances (Order no. 439 of 3 June 2002) DWEA limit value (ppm / mg/m^3){11}	R 10, Xn; R 20/21/22-65 Xi; R 36/38, R 43, N; R 51/53 25 / 140

1 ppm = 5.6 mg/m^3

6.1.3 Physical-chemical data

Physical-chemical properties	
State	Liquid
Molecular weight	Approx. 136 g/mol {7}
Density	0.854-0.868 (25°C) {7}
Melting point	-60 - -50 (°C,) {8}
Boiling point	150-180 (°C, 1013 hPa) {2}
Vapour pressure at 25°C)	667 Pa {8}
Octanol-water, (logPow)	Unknown
Solubility in water	Insoluble {7}
Odour limit	100 ppm {7}

6.1.4 Toxicological data:

6.1.4.1 Absorption
Easily absorbed through the lungs, gastrointestinal tract {7}. Ingredients in turpentine oil is easily absorbed through the skin.

6.1.4.2 Acute effects, humans:
Irritating to skin, eyes and mucous membranes.

Splashes of the liquid in the eyes may cause inflammation of the conjunctiva of the eye (conjuctivitis) and thickening of the horny layer. Skin contact causes a risk of allergy {2}.

Ingestion causes irritation of gastrointestinal tract and may cause kidney damage. CNS depression including coma may occur after ingestion {7}. Lethal dose by ingestion for humans is estimated at 150 ml. {2}.

Vapours in concentrations of 70-200 ppm (396-1130 mg/m^3) are slightly irritating {2}. Another source establishes the threshold for airway irritation at approximately 75 ppm (420 mg/m^3) {4}.

Tests on volutary subjects exposed to turpentine oil vapours resulted in 75 ppm (424 mg/m^3) irritation in nose and throat in several of the test subjects.

At concentrations between 750-1000 ppm (4238 – 5650 mg/m^3), chest pain and synsforstyrrelser are seen. Prolonged inhalation of concentrations between 750 and 1000 ppm causes eye irritation, headache, dizziness, nausea and abnormal, fast heart rhythm (tachycardia) {2}.

Accidental ingestion causes a burning sensation in the mouth, cough, lung oedema, coma and liver damage {1}. Chemical pneumonia in case of vomit in the lungs.

Oral TD_{LO} in a single woman who had kidney damage after ingestion was established at 560 mg/kg {1}.

TC_{LO} through inhalation in a single individual was established at 175 ppm (980 mg/m^3) as the substance caused damage to eyes, airways, coma and liver damage {1}. This observation is, however, of only minor importance as it is only one individual.

6.1.4.3 Acute effects, animals

The LD_{50} value by ingestion in rats is > 5000 mg/kg.
The LC_{50} value in mice (2 hours) and rats (6 hours) has been reported at 29 mg/m^3 (5 ppm) and 12,000 mg/m^3 (2143 ppm), respectively {2}.

The lowest lethal dose (LD_{LO}) in rabbits after application on the skin has been estimated at 5010 mg/kg/bw {2}.

6.1.4.4 Sub-chronic experiments, animals

In a study with guinea pigs in which the animals inhaled 715 ppm (4004 mg/m^3), 4 hours/day for 45 to 58 days, no specific or hematological changes were found nor was any pathology that could be contributed to turpentine oil {8}.

In another study, seisures and paralysis was seen in rabbits at a concentration of 750 ppm (4200 mg/m^3). The duration of this study has, however, not been stated {8}.

No effects were seeen in dogs after inhalation of 180 ppm (1008 mg/m^3), 3.5 hours/day for 8 days {8}.

6.1.4.5 Chronic effects

Prolonged repeated exposure to turpentine oil for more than 5 years may lead to an increased risk of airway cancer {7}.

6.1.4.6 Summary of data

Table 20 Toxicological data for turpentine oil

Toxicological data (animals)	
LD_{50}, (mg/kg), oral, rat	5760 {1}{2}{6}
LC_{50} (mg/m^3), inhalation, mice, 2 hours	29 {1}{2}{6}
LC_{50} (mg/m^3), inhalation, rat, 6 hours	12000 {2}{6}
LC_{LO} (mg/m^3) inhalation, guinea pig, 1 hour	16000 {2}{6}
LD_{LO} (mg/kg), skin, rabbit	5010 {2}
TD_{LO} (mg/kg), skin, rabbit, 20 weeks	240000[1] {2}
Toxicological data (humans)	
TD_{LO} (mg/kg) – ingestion, kidney damage	560 {1}.
TC_{LO} inhalation (mg/m^3) – damage to eyes, airways	980 {1}{2}
TC_{LO} inhalation, 3 hours (mg/ m^3) – hallucinations, headache	6000 {2}
LD_{LO} (mg/kg), oral – lethal dose	500 {6}
TD_{LO} (mg/kg), oral, children	874[2] {2}
TD_{LO} (mg/kg), oral, women	560[2]{2}
LOEL (mg/m^3), inhalation, irritation	420 {4}
NOEL(mg/m^3), inhalation	140 {11}

1) Blisters on the skin
2) Effects on the gastrointestinal tract, kidneys, ureters and the bladder

Table 20 shows the toxicological data found in literature for animals and humans, respectively. The critical effects from exposure to turpentine oil is estimated to be allergy by skin contact and irritation of lungs by inhalation of vapours.
The lowest effect level for airway irritation in humans are set at 75 ppm (420 mg/m^3) and the zero-effect-level is set as equal to the limit value in the working environment which is 140 mg/m^3. There is no zero-effect-level for sensitisation by skin contact.

6.2 Mineral turpentine (stoddard solvent)

6.2.1 Use

Used as extraction liquid, cleaning liquid, degreasing product and as solvent in a number of product types, including paint.

6.2.2 Identification

Mineral turpentine is a complex mixture of substances defined as: "Low-boiling unspecified naphtha – A colourless, refined raw oil destillate free of rancid or repellent odours, with a boiling point interval of approximately from 149°C to 204°C".

Mineral turpentine is thus a mixture of branched and equal-chained paraffins, naphthans and alkyl aromatic carbonhydrids.

The distribution of kulbrinter in traditional mineral turpentine (stoddard solvent) is approximately: 48% alkanes (mainly C_{9-12}), 26% monocycloalkanes, 12% dicycloalkanes, 14% aromates. The benzene content is usually less than 0.1% {12}.

As it is a complex mixture it is not possible to state an exact molecular weight or an unambiguous molecular structure.

Mineral turpentine (stoddard solvent) is a clear liquid with a characteristic odour.

Identification	
Substance name:	Mineral turpentine
Synonyms:	Stoddard solvent, Low boiling point naphtha, white spirit
CAS-No.:	8052-41-3
EINECS No.:	232-489-3
Molecular formula:	-
Molecular structure:	-
Legislation: Classification according to the list of dangerous substances (Order no. 439 of 3 June 2002) DWEA limit value (ppm / mg/m^3){11} Turpentine mineral, max. 20% aromates	(Carc2;R45)* Xn;R20/48 R65 25 / 145**

*The classification as carcinogenic can be omitted if it can be demonstrated that the substance contains less than 0.1 weight percentage benzene which is the case for practically all mineral turpentines contained in the product on the Danish market.
** 1 ppm = 5.80 mg/m^3

6.2.3 Physical-chemical data

Physical-chemical properties	
State	Liquid
Molecular weight Mw, (g/mol)	Approx. 150 {12}
Density	Approx. 0.78 {12}
Melting point M.p., (°C)	-
Boiling poing B.p., (°C)	145-174 {12}

Physical-chemical properties	
Vapour pressure V.p. at 25°C, (Pa)	Approx. 600 {12}
Octanol-water, (logPow)	-
Solubility in water (mg/L)	< 0,1 % {12}
Odour limit	0.5-5 mg/m^3 (3-30 ppm) {12}

6.2.4 Toxicological data

6.2.4.1 Absorption

Mineral turpentine is easily absorbed through the airways. Approximately 50% of the aliphatic hydrocarbons and approximately 62% of the aromatic hydrocarbons found in the inhalation air {12}.

Reports of poisoning cases after ingestion indicates that mineral turpentine can be absorbed from the gastrointestinal tract {12}.

There is no data for absorption of mineral turpentine through the skin, but studies of individual substances in mineral turpentine shows that they can be absorbed. If both hands are e.g. dipped in xylen, the amount absorbed through the skin corresponds approximately to the absorption through the lungs at an exposure to 100 ppm (580 mg/m^3) during the same time period {12}.

6.2.4.2 Acute effects, humans

Mineral turpentine shows acute, narcotic effects on the central nervous system {12}. Inhalation of vapours leads to headache, dizziness, intoxication and seisures. At very high concentrations there may be fainting and death {1}.

Symptoms after inhalation includes effects on the central nervous system from slight discomfort such as dizziness and headache to reduced performance in neuro-phsycological tests. In serious cases, chronic brain damage has been diagnosed {1}.

Six volunteer test subjects felt no irritation at exposure to an air concentration of 140 mg/m^3 (25 ppm) for 15 minutes. One subject felt slight and passing eye irritation at 850 mg/m^3 (145 ppm) and at 2700 mg/m^3 (465 ppm) all 6 test subjects felt eye irritation of which 3 had eye flux. 2 of the subjects felt slightly groggy. All effects disappeared within 15 minutes after the experiment ended {1}.

Slight irritation of eyes, nose and throat has been described in people at a vapour concentration of 600 mg/m^3 (100 ppm) {21}.

At exposure of humans to 288 mg/m^3 (50 ppm) for 7 hours, no significant changes were seen in the visomotoric coordination, memory and reaction time {12}.

Mineral turpentine can penetrate the skin and cause systemic effects. Frequent use of hand cleaners containing mineral turpentine has lead to damage to the liver and bone marrow {1}.

Ingestions will lead to discomfort in the form of ingestion and symptoms similar to the ones seen in case of inhalation {1}.

If mineral turpentines gets into the lungs due to vomiting after ingestion it may cause chemical pneumonia {1}.

Mineral turpentine may lead to liver damage in humans {12}.

The narcotic effect of mineral turpentine is well-known from occupational exposures. Commonly registered symptoms are headache, fatigue, light-headedness, reduced appetite and nausea.

Experimental exposures for 7 hours to mineral turpentine in concentrations between 575 mg/m^3 and 2300 mg/m^3 (100 – 400 ppm) caused headache, fatigue and confusion in test subjects. Clinical-neurological tests as well as neuro-psycological tests found a dose-related impact on the sense of equilibrium, reaction time and eye coordination. Long-term memory was influenced at exposure to 2300 mg/m^3 (400 ppm) {12}.

6.2.4.3 Acute effects, animals

In a Draize-test on rabbits, mineral turpentine was classified as slightly irritating to the skin {38}. The potential skin irritating properties of mineral turpentine is likely connected to the content of aromates as a higher aromat content will lead to a larger skin irritation potential.

The lowest lethal concentration by inhalation in rats for 3 and 8 hours respectively has been set at 8200 and 8000 mg/m^3 {17}.

6.2.4.4 Sub-chronic effects, animals

After exposure of rabbits, dogs and monkeys to 1271 mg/m^3 (220 ppm) mineral turpentine for 24 hours/day for 90 days, bronchitis-like changes of the lung tissue was found. Similar changes could not be demonstrated after exposure for 8 hours/day, 5 days/week for 6 weeks {12}.

The lowest toxic dose in rats by inhalation for 65 weeks varies from 480 mg/m3 to 9860 mg/m^3. Among the effects seen were effects on kidneys, ureter and bladder as well as anaemia {17}.

By application to the skin of rabbits for 4 weeks; the lowest dose leading to dermatitis was set at 2000 mg/kg {5}.

6.2.4.5 Chronic effects

Exposure of groups of pregnant rats to 5460 mg/m^3 (940 ppm) for 6 hours per day from day 3 to 20 in the gestation period lead to an embryo-toxic effect as the featus weight was significantly reduced and the formation of bone tissue was delayed. At the same time, there was an increased occurrence of featuses with an extra rib {12}.

A number of peidemiological tests of workers exposed to an exposure level estimated at approximately 240 mg/m^3 (40 ppm) indicates a link between prolonged exposure to mineral turpentine (and other solvents) and development of chronic effects on the central nervous system, particularly the brain. The symptoms are memory difficulties, fatigue, dizziness, lack of sense of smell as well as reduced intellectual capacity and delicate motor function. The illness is called painters syndrom, pre-senile demensia or chronic toxic encelopaty {12}.

It is estimated that exposure to an average of 240 mg/m^3 (40 ppm) for more than 13 years may cause chronic effects on the central nervous system {20}.

In vivo and in vitro mutagenicity tests with mineral turpentine were all negative {2}. Any carcinogenic effects from hydrocarbon destillates are particularly attributed to the content of benzene and polyaromatic hydrocarbons.

6.2.4.6 Summary

Table 21 Toxicological data for mineral turpentine

Toxicological data (animals)	
LC_{LO} (mg/m^3) inhalation, rat, 8 hours – shaking	8200 {5}
LC_{LO} (mg/m^3) inhalation, dog, 3 hours – behaviour	8000 {5}
LC_{LO} (mg/m^3) inhalation, cat, 7 hours	9860[1] {5}
TC_{LO} (mg/m^3), inhalation, rat, 65 weeks intermittend	1915[2] {5}
TC_{LO} (mg/m^3) inhalation, rat, 65 weeks intermittend	480[3] {5}
TC_{LO} (mg/m^3) inhalation, rat, 65 weeks intermittend	1100[4] {5}
TD_{LO} (mg/kg), skin, rabbit, 4 weeks intermittend	2000[5]{ 5}
NOAEL (mg/kg), skin, 3 hours/day 3 times per week for 4 weeks - systemic effects (hematology)	200 {21}
LOAEL (mg/m^3), inhalation, rat, 6 hours/d for 13 weeks – liver weight	2000 {21}
LOEL(mg/m^3), inhalaiton, rat, acute narcotic effect	1200 {21}
Toxicological data (human)	
NOEL (mg/m^3) Irritation, acute and chronic effects on the central nervous system.	145 {11}

1) Shaking and seisures.
2) Effects on kidneys, urinleder and bladder including acute kidney failure and acute tubular necrosis. Effects on the blood
3) Anaemia
4) Reduced kidney function and anaemia
5) Dermatitis

The critical effects of mineral turpentine are estimated to be the irritating effect on the mucous membrane as well as acute and chronic effects on the central nervous system. The zero-effect-level for irritation and the impact on the central nervous system in humans is set as equal to the limit value in the working environment, i.e. 25 ppm (145 mg/m^3).

6.3 $C_{9\text{-}12}$ isoalkanes

6.3.1 Use

Used as solvents in a large number of product types, including paint and cleaning products.

6.3.2 Identification

$C_{9\text{-}12}$ isoalkanes is a mixture of branched saturated aliphatic hydrocarbons with carbon chains of 9-12 carbon atoms which typically contain < 0.01% aromatic compounds.

As they are a complex mixture it is not possible to state an exact molecular weight or an unambiguous molecular structure.

$C_{9\text{-}12}$ isoalkanes are a clear, volatile liquid

Identification	
Substance name:	$C_{9\text{-}12}$ isoalkanes
Synonyms:	Isopar G, Isopar H

Identification	
CAS-No.:	90622-57-4
EINECS No.:	292-459-0
Molecular formula:	C_nH_{2n+2} n=9,10,11,12
Molecular structure:	-
Legislation: Classification according to the List of dangerous substances (Order no. 439 of 3 June 2002) DWEA limit value (ppm / mg/m^3){11}: Decan, other isomers than n-decan (C_{10}) Isopar	R10 Xn;R65 R67 No limit value has been established for C_{9-12} isoalkanes 65 / 350 - / 300[1]

1 ppm = 6 mg/m^3 (Isopar G)
1) EXXON {14}

6.3.3 Physical-chemical data

Physical-chemical properties	
State	Liquid
Molecular weight Mw, (g/mol)	C_9: 128 C_{12}: 170
Density	ca. 0,75- 0,76 (15°C) {2}
Melting point M.p., (°C)	< -50 {2}
Boiling point B.p., (°C)	Approx. 153-193 (1013 hPa) {2}
Vapour pressure V.p. ved 25°C, (Pa)	Approx. 300 (20°C)[1] {2}
Octanol-water, (logPow)	Approx. 4,9-6,9 {2}
Solubility in water (mg/L)	< 0.1 mg/L (20°C) {2}

1) Isopar G {44}

6.3.4 Toxicological data

6.3.4.1 Absorption
C_{9-12} isoalkanes can be absorbed by inhalation and by ingestion.

6.3.4.2 Acute effects, humans
In many of the aliphatic kulbrinter, dermatitis, irritation, impact on the central nervous system and anaesthetic effects are seen. The effects are increased in case of increased molecular weight. In general, aliphatic hydrocarbons have a neuro-toxic effect at approximately 100 ppm corresponding to 200-600 mg/m^3 {17}.

If the liquid gets into the lungs due to vomiting after ingestion, chemical pneumonia may occur {1}.

6.3.4.3 Acute effects, animals
Isopar G gave no sensory irritation in mice that were exposed for 30 minutes to a vapour concentration of 347 ppm. The liquid is degreasing to the skin and repeated or prolonged contact may cause skin problems and ezcema {15}.

A research group has suggested a NOEL-value for C_{7-12} alkanes of 200 – 600 mg/m^3 in humans based on a general neuro-toxic effect, Larsen et al (1999) {17}.

6.3.4.4 Sub-chronic effects
A zero-effect-level for teratogenic effects in rats has been set at 900 ppm (5400 mg/m^3) after inhalation. The same experiment establishes a zero-effect-level for increase in kidney weight in male rats at the same dose.

6.3.4.5 Chronic effects
Isopar G has shown negative results in several mutagenicity tests {1}.

Tests of cell cultures (V79 hamster cells) increased the n-decan, n-dodecan and n-tetradecan frequency of mutations induced from a known mutagen {12}.

6.3.4.6 Summary

Table 24 Toxicological data for C_{9-12} isoalkanes

Toxicological data (animals)	
LD_{50}, (mg/kg), oral, rat	>5000[1] {2}
LD_{50}, (mg/kg), oral, rat	>10000 {5}
LC_{50}, (ppm), inhalation, rat, 4 hours	>2240[1] {2}
LC_{50}, (mg/m^3), inhalation, rat, 4 hours	>122000 {5}
LD_{50}, (mg/kg), skin, rabbit	>3160[1] {2}
LD_{50}, (mg/kg), skin, rabbit	>3200 {5}
NOAEL (ppm), inhalation, rat, 6 hours/day 5 days/week for 12 weeks – increased kidney weight in male rats	5400[1] {2}
NOAEL (mg/m^3), inhalation, rat, 6 hours/day 5 days/week for 12 weeks – teratogenicity	5400[1,2] {2}
Toxicological data (human)	
LD_{LO} (ml), oral, lethal dose	240 {1}
NOAEL (mg/m^3), neuro-toxic effect	200-600 {18}

1) Isopar G, EXXON {44}
2) No toxicological effects were seen in the mother animals and no teratogenic effects were seen at this dose level

The critical effect of C_{9-12} isoalkanes is estimated to be neuro-toxic effects. The zero-effect-level for a general neuro-toxic effect in humans is set at 200 mg/m^3 which is slightly lower than the DWEA limit values for ”Decan, other isomers than n-decan” of 350 mg/m^3.

6.4 Propan-2-ol

6.4.1 Use

Propan-2-ol is used as a raw material in the synthesis of acetone, glycerin and other chemicals. In addition, the substance is used as anti-frost liquid and solvent in a number of other product types {1}.

6.4.2 Identification

Propan-2-ol is a volatile substance which is highly flammable at room temperature. The odour of propan-2-ol is similar to a mixture of ethanol and acetone and the substance has a bitter taste.

Identification	
Substance name:	Propan-2-ol
Synonyms:	isopropanol, isopropylalkohol, 2-propanol

Identification	
CAS-No.:	67-63-0
EINECS No.:	200-661-7
Molecular formula:	C_3H_8O
Molecular structure:	$CH_3CHOHCH_3$
Legislation: Classification according to the list of dangerous substances (Order no. 439 of 3 June 2002) DWEA limit value (ppm / mg/m^3){11}	F;R11 Xi;R36 R67 200 / 490, S*

*S=Skin absorption
*1 ppm = 2,45 mg/m^3

6.4.3 Physical-chemical data

Physical-chemical properties	
State	Liquid
Molecular weight Mw, (g/mol)	60.1 {6}
Density	0.785 (20°C) {1}
Melting point M.p., (°C)	-88.5 {6}
Boiling point B.p., (°C)	82.5 (760 mmHg) {6}
Vapour pressure V.p. ved 25°C, (Pa)	45.5 mmHg (25°C) {6}
Octanol-water, (logPow)	0.05 {6} 0.14 {19}.
Solubility in water (mg/L)	Soluble {1}
Odour limit (mg/m^3)	18.4 – 120 {19}

6.4.4 Toxicological data

6.4.4.1 Absorption
Propan-2-ol is easily abosorbed by inhalation and through the digestive system {19}. May be absorbed through the skin.

6.4.4.2 Acute effects, humans
Is irritating by eye contact. Prolonged skin contact may cause irritation {19}.

Ingestion or inhalation of high concentrations may cause readness, headache, dizziness, nausea, mental depression, narcotic effect and coma {1}.

Experiments with voluntary test subjects has found that an air concentration of 400 ppm (980 mg/m^3) causes slight irritation of nose, eyes and throat. At 800 ppm (1960 mg/m^3) the symptoms are intensified without being serious. Most test subjects found this concentration unpleasant {10}.

Propan-2-ol is more toxic than ethanol but less toxic than methanol {1}. Several lethal cases have been described as a result of ingestion of 0.47 L 70% propan-2-ol. Preceeding death was deep coma and chock and the cause of death was respiration stop {1}.

No effects (hematology, blood chemistry, urin analysis and ophtalmoscopy) were found in humans ingesting 2.6-6.4 mg/kg per day for 6 weeks {1}.

It is assumed that the lethal dose in humans is 240 ml but doses as low as 20 ml in water may cause symptoms.

Skin contact may cause drying and irritation {1}.

A few cases of skin allergy to propan-2-ol have been found {1}.

6.4.4.3 Acute effects, animals

$L(C)D_{50}$ –values in test animals are all very high, higher than 3600 mg/kg by ingestion, higher than 12,000 by application to the skin and higher than 70,000 mg/m^3 by inhalation.

0.1 ml propan-2-ol was irritating to the eyes in rabbits while application of the substance on the skin did not lead to irritation.

6.4.4.4 Sub-chronic effects, animals

Studies with rats and mice that inhaled up to 5000 ppm (12.250 mg/m^3) propan-2-ol for 6 hours per day, 5 days per week for 13 weeks showed narcotic effects at 5000 ppm. An increased liver weight was observed in female rats at 5000 ppm but no effects were found during autopsy and histopathological examinations. Neuro-pathological tests of the rats showed no effects on the central nervous system {2}.

6.4.4.5 Chronic effects

The substance has given negative results in several mutagenicity tests {1}.

There is insufficient evidence of carcinogenicity in humans and animals (IARC group 3) {1}.

6.4.4.6 Summary

Extrapolation of data from reproduction experiments with animals has lead a group of researchers to conclude that 420 mg/kg/d is the dose which in humans will have no reproduction toxic or developmental effects in foetuses.

The critical effect of the substance is estimated to be narcotic effects by inhalation as well as effects on foetuses.

Table 23 Toxicologicla data for propan-2-ol

Toxicological data (animals)	
LD_{50}, (mg/kg), oral, rat	5045 {6}
LD_{50}, (mg/kg), oral, mouse	3600 {6}
LD_{50}, (mg/kg), oral, rabbit	6410, 8000 {6}
LC_{50}, (mg/m^3), inhalation, rat, 4 hours	72,600 {2}
LD_{50}, (mg/kg), skin, rat	12800 {2}
LD_{50}, (mg/kg), skin, rabbit	12800 {6}
NOAEL (mg/m^3), inhalation, 13 weeks, rats and mice narcotic effects	3675 {2}
NOAEL (mg/m^3) inhalation, 4h/d, 5d/week for 13 or 20 weeks	980[1] {2}
NOAEL (mg/kg/dag) ingestion, rat	500[2] {2}
NO AEL (mg/kg/dag), rat, reproduction toxicity	> 1000 {2}
NOAEL (mg/kg/dag), ingestion, rat, teratogenicity	400 {2}
NOAEL (mg/kg/d) ingestion, rat 2 generations	500 {18}
LOEL (mg/m^3), inhalation, rat, embryo-toxicity	8575 {2}
NOEL, inhalation, pregnant rats, toxic effects on mother animals (mg/m^3 / ppm)	9001/7450 {19}
Toxicological data (human)	
LD_{LO} (ml), oral, lethal dose	240 {1}
NOAEL reproduction and teratogenicity mg/kg/d	420 {18}

1) Blood parameters
2) Reduced body weight and increased mortality

6.5 Heptane

6.5.1 Use

The use as standard in tapping test of gasoline, in orgenic synthesis and inclusion either in pure form or as a component in other kulbrinte destillates used as fule and solvents {9}.

6.5.2 Identification

n-Heptane is a volatile, flammable liquid. The odour limit for heptane is 150 ppm {9}.

Identification	
Substance name:	Heptane
Synonyms:	n-heptan, dipropylmethan
CAS-No.:	142-82-5
EINECS No.:	205-563-8
Molecular formula:	C_7H_{16}
Molecular structure:	$CH_3CH_2\ CH_2\ CH_2\ CH_2\ CH_2CH_3$
Legislation: Classificaiton according to the list of dangerous substances (Order no. 439 of 3 June 2002) DWEA limit value (ppm / mg/m^3){11}} LCI	F;R11 Xn;R65 Xi;R38 R67 N;R50/53 200/ 820* 8 mg/m^3

* 1ppm = 4,1 mg/m^3

6.5.3 Physical-chemical data

Physical-chemical properties	
State	Liquid
Molecular weight Mw, (g/mol)	100.2 {1}
Density	0.684 (20°C) {1}
Melting point M.p., (°C)	- 90.6 {2}
Boiling point B.p., (°C)	98 (1013 hPa) {2}
Vapour pressure V.p. ved 25°C, (Pa)	6360 {9}
Octanol-water, (logPow)	4.66 {6}
Solubility in water (mg/L)	0.003 (20°C) {2 2.93 (25°C) {1}
Odour limit (ppm)	150 ppm {9} 400 ppm – (easily recognised odour) {13}

6.5.4 Toxicological data

6.5.4.1 Absorption
Heptane can be absorbed by inhalation. In vitro tests regarding absorption through the skin indicates that only a very small amount is absorbed by skin contact. The penetration rate through rat skin was as low as 0.14 µg/cm^2/t {13}.

6.5.4.2 Acute effects, humans
Is slightly irritation by contact with the eyes {2}.

Test subjects exposed to 1000 ppm (4200 mg/m^3) heptane for 6 minutes or 2000 ppm (8400 mg/m^3) for 4 minutes experienced slight dizziness. At

exposure to 3500 ppm (14,700 mg/m^3), the test subjects experienced moderate dizziness and at 5000 ppm (21,000 mg/m^3) for 4 to 7 minutes pronounced dizziness, lack of coordination, lack of balance and euphoria. At exposure to 5000 ppm for 15 minutes the symptoms lasted for 30 minutes after the exposure ended {1}, {13}.

Short (4 minutes) exposure of humans to 5000 ppm lead to nausea, loss of appetite and gasoline-like taste in the mouth which lasted for hours after the exposure ended {9}.

6.5.4.3 Acute effects, animals

The concentration which leads to a 50% decrease in respiration rate in mice (RD_{50}) has been set at 17,400 ppm (73.080 mg/m^3).

A comparison between RD_{50} in mice and humane data has shown that 0.01 x RD50 gives minimal or no irritation of the airways. On this basis, you get an irritation limit for heptane of 175 ppm (735 mg/m^3) in humans {13}. Another research group has suggested 0.03 X RD_{50} as the irritation threshold in humans giving a value of 522 ppm (2200 mg/m^3).

6.5.4.4 Sub-chronic effects

Rats exposed to repeated exposures of up to 12,400 mg/m^3 (approx. 3000 ppm) for 6 hours per day, 5 days per week for 26 months showed no signs of peripheral neuropathy as it is known from exposure to n-hexan {2}.

6.5.4.5 Chronic effects

Only negative results have been found in in vitro and in vivo mutagenicity tests {34}.

6.5.4.6 Summary

Table 22 Toxicologicla data for heptan

Toxicological data (animals)	
LD_{50}, (mg/kg), oral, rat	> 15000 {1}
LD (mg/kg), oral, rat	17000[1] {2}
LD_{50}, (mg/kg), oral, mouse	5000 {2}
$LD_{50,}$ (mg/m^3), skin, rabbit	3000 {1}
RD_{50}, mouse (ppm / mg/m^3)	17,400 / 73080 {13}
NOAEL (mg/m^3), rat, neuro-toxic effects (peripheral)	> 12,400[2] {1}
Toxicological data (human)	
NOAEL, airway irritation (ppm)	175-522[3] {13}.
LC_{LO} (ppm), inhalation, 6 min	1000[4]{1}

1) At a dose of 17000 mg/kg, one of the rats died
2) Neuro-toxic end-points were examined and no effects were found at the highest dose (12,400 mg/m^3)
3) Based on RD_{50} in mice
4) Acute effects on the central nervous system

The critical effects of heptane are estimated to be airway irritation which is more pronounced than for n-hexan and pentan as well as acute effects on the central nervous system.

The zero-effect-level for airway irritation in humans is set at 175 ppm (715 mg/m^3) corresponding ot the lowest of the 2 suggested irritation limits in humans while the zero-effect-level for acute effects on the central nervous system is set at equal to the limit value in the working environment.

7 Exposure scenarios

7.1 Exposure scenarios

The below exposure evaluations have been carried out as worst-case scenarios according to the principles stated in Technical Guidance Document (TGD2003).

When calculating the exposure, a room volume of 20 m^3, which illustrates application in a small and badly ventilated room (e.g. a hallway) has been used along with a volume of 2 m^3, which illustrates a short-term situation in which the 2 m^3 is the amount of air surrounding the person, in the following called the person's immediate zone.

Only exposure through application is calculated, not the subsequent use of the footwear.

The amount of shoe polish and impregnation product respectively used has been established based on experiments with varying types of footwear in which the products were weighed before and after application.

Table 25 Used amount in grammes for treatment of different shoe types

Shoe type (size)	Shoe polish [g]	Shoe type (size)	Impregnation – aerosol [g]
Shoe, men (44)	1.71	Short boot, women (39)	12.65
Shoe, men (45)	1.71	Boot, men (39)	18.48
Shoe, women (37)	0.32	Shoe, women (40)	8.77
Shoe, men (43)	2.56	Boot, girl (34)	21.39
Short boot, women (37)	1.61	Long boot, women (37)	27.78

7.1.1 Scenario 1 – Shoe polishing

In this scenario, a pair of shoes is polished. The amount used is set at 2.56 g which is the amount corresponding to the maximum consumption stated in table 25.

It is assumed that the person polishes 2 pairs of shoes once a week. The application takes place using a cloth and takes 5 minutes.

When polishing the shoes, the skin is exposed to an amount corresponding to 10% of the amount used of the product.

7.1.2 Scenario 2 – Impregnation

In this scenario, a pair of boots is impregnated. The amount used is set at 27.8 g corresponding to the largest consumption in the experiments summarised in table 25.

It is assumed that 4 pairs of boots are impregnated twice a year corresponding to impregnation of 8 pairs of boots annually.

It is assumed that the impregnation takes 3 minutes, that the person is in the room for 5 minutes. During impregnation, the skin is exposed to an amount corresponding to 10% of the amoutn of the product used.

7.2 Exposure evaluations for shoe polish

7.2.1 Turpentine oil

A shoe polish contains 25% turpentine oil. Exposure through inhalation, skin and the total exposure can be seen in table 26.

Table 26 Exposure evaluation for turpentine oil in shoe polish

Classification		
R 10, Xn; R 20/21/22-65 Xi; R 36/38, R 43, N; R 51/53		
Toxicological data	**Dose**	
LD_{50}, (mg/kg), oral, rat	5760 {1}{2}{6}	
NOEL (mg/m^3) = GV	140	
Irritation threshold (mg/m^3), inhalation	420 {4}	
Exposure	**2 m^3**	**20 m^3**
Air concentration (Cair)	320 mg/m^3	32 mg/m^3
Absorption through the airways (Uinh)	0.090 mg/kg/d	0.009 mg/kg/d
Amount of substance on the skin	64 mg	
Dermal absorption (Uder)	0.26 mg/kg/d	
Total absorption in the body (Utot)	**0.35 mg/kg/d**	**0.27 mg/kg/d**

If the calculated air concentration is compared to 2 m^3 and 20 m^3 respectively with the irritation threshold in humans (420 mg/m^3) it can be concluded that there may be a risk of irritation effects by application in a very small room as the concentration in the immediate zone is close to the irritation threshold.

The zero-effect-level for irritation effects and acute effects on the central nervous system by inhalation is set as equal to the limit value in the working environment. However, the limit value cannot be used directly as consideration must be paid to exposure 24 hours a day, 7 days a week (168 h) instead of a 40-hour work week. In addition, the limit value stated as an air concentration must be omregnet to a daily dose by using a respiration volume of 20 m^3/day and a body weight of 70 kg: These values for respiration volume and body weight are equal to the default values used by EUSES.

$$\text{NOEL thus becomes } \frac{140\ mg/m^3 \times 20\ m^3/d \times 40/168}{70\ kg} = 9{,}52\ mg/kg/d$$

The Margin of Safety (MOS) for acute irritation effects as well as acute effects on the central nervous system by inhalation can be calculated to be

$$MOS = NOEL/EXP = \frac{9{,}52\ mg/kg/d}{0{,}090\ mg/kg/d} = 106 \text{ for an immediate zone of 2 } m^3$$

$$\text{and} = \frac{9{,}52\ mg/kg/d}{0{,}009\ mg/kg/d} = 1058 \text{ for a small 20 } m^3 \text{ room}$$

As turpentine oil can be absorbed through the skin, a MOS-value for the total exposure can furthermore be calculated resulting in

MOS = NOEL/ EXP = $\frac{9{,}52 \text{ mg/kg/d}}{0{,}351 \text{ mg/kg/d}}$ = 27 for an immediate zone of 2 m^3

and

MOS = NOEL/ EXP = $\frac{9{,}52 \text{ mg/kg/d}}{0{,}269 \text{ mg/kg/d}}$ = 35 for a small 20 m^3 room

A MOS-value of 100 or above provides a reasonable security against effects on the consumer. However, when using the total exposure and by EUSES calcuations, values below 100 is reached for both room volumes.

Based on the exposure evaluation for turpentine oil it can thus be concluded that the consumer is exposed to airway irritation and acute effects on the central nervous system when using a shoe polish containing 25% turpentine oil.

In addition, turpentine oil is classified as allergenic by skin contact an as no clear ”zero-effect-level” can be defined for this effect it is in any case important that skin contact is avoided when using products containing turpentine oil.

7.2.2 Mineral turpentine

A shoe polish containing 75% mineral turpentine is used.

Exposure by inhalation, skin and total exposre can be seen in table 27.

Table 27 Exposure evaluation for mineral turpentine in shoe polish

Classification		
Xn;R20/48 R65		
Toxicological data		**Dose**
LOEL (mg/m^3), inhalation, rat - acute narcotic effect		1200 {40}
NOEL irritation, acute and chronic effects on the central nervous system, based on a limit value = 145 mg/m^3.		9.86 mg/m^3/d
Exposure	**2 m^3**	**20 m^3**
Air concentration (Cair)	960 mg/m^3	96 mg/m^3
Absorption through the airways (Uinh)	0.271 mg/kg/d	0.0271 mg/kg/d
Amount of substance on the skin per time	192 mg	
Dermal absorption (Uder)	0.78 mg/kg/d	
	2 m^3	**20 m^3**
Total absorption (Utot) per day	1.05 mg/kg/d	0.81 mg/kg/d

The limit value in the working environment is used as a zero-effect-level for irritation effects as well as acute and chronic effects on the human central nervous system. If the limit value is converted to a daily dose you get

NOEL = $\frac{145 \text{ mg/m}^3 \text{ x } 20 \text{ m}^3\text{/d x } 40/168}{70 \text{ kg}}$ = 9,86 mg/kg/d

The Margin of Safety (MOS) for acute irritation effects as well as acute and chronic effectes on the central nervous system by inhalation can then be calculated to be

MOS = NOEL/ EXP = $\frac{9{,}86 \text{ mg/kg/d}}{}$ = 36 for an immediate zone of 2 m^3

0,271 mg/kg/d

and = 9,86 mg/kg/d = 364 for a small 20 m^3 room
0,0271 mg/kg/d

As some of the components in mineral turpentine can be absorbed through the skin, a MOS-value for the total exposure can be calculated instead givning

MOS = NOEL/ EXP = 9,86 mg/kg/d = 9 for an immediate zone of 2 m^3
1,05 mg/kg/d

and = 9,86 mg/kg/d = 12 for a small 20 m^3 room
0,81 mg/kg/d

The MOS-value for total exposure is probably too low as a 100% skin absorption of mineral turpentine was calculated which is not likely to be realistic.

If the starting point is instead the MOS-values for inhalation alone it can be seen that the value for 2 m^3 is below 100 while the value for 20 m^3 is above 1000. On this basis it can be concluded that there is a potential risk that the concentration in the inhalation zone when applying a shoe polish containing 75% mineral turpentine may lead to irritation effects and in serious cases also acute effects on the nervous system.

7.2.3 C_{9}-$_{12}$ isoalkanes

A shoe polish containing 26.5% C_9-C_{12} isoalkanes is used.

Exposure by inhalation, skin and the total exposure can be seen in table 28.

Table 28 Exposure evaluation for C_9-C_{12} isoalkanes in shoe polish

Classification		
Xn;R65 R66[1]		
Toxicological data	**Dose**	
NOAEL (mg/kg/d), inhalation, human – neuro-toxic effect	13.6 {12}	
Exposure	**2 m^3**	**20 m^3**
Air concentration (Cair)	339 mg/m^3	33.9 mg/m^3
Absorption through the airways (Uinh)	0.096 mg/kg/d	0.0096mg/kg/d
Amount of substance on the skin per time	67.8 mg	
Dermal absorption (Uder)	0.28 mg/kg/d	
Total absorption in the body (Utot)	**0.38 mg/kg/d**	**0.30 mg/kg/d**

The zero-effect-level for neuro-teoxic effects in humans can be estimated at approx. 200 g/m^3 as stated in chapter 6.3.4.6.

At a concentration of 200 mg/m^3 the dose that does not lead to neuro-toxic effects can be calculated to be:

NOEL= 200 mg/m^3 x 20 m^3/d x 40/168 = 13,6 mg/kg/d
70 kg

The MOS-value for neuro-toxic effects by inhalation can be calcuated to be:

MOS = NOEL/ EXP = 13,6 mg/kg/d / 0,096 mg/kg/d = 142 for an immediate zone of 2 m^3

MOS = NOEL/ EXP = 13,6 mg/kg/d / 0,0096 mg/kg/d = 1417 for a small 20 m^3 room

The MOS value based on the total absorption becomes

MOS = NOEL/ EXP = 13,6 mg/kg/d / 0,38 mg/kg/d = 36 for an immediate zone of 2 m^3

MOS = NOEL/ EXP = 13,6 mg/kg/d / 0,30 mg/kg/d = 45 for a small 20 m^3 room

Absorption through the skin and thus the total absorption is, however, overestimated as the substance is not absorped 100% through the skin. The MOS-value for absorption through inhalation is thus considered as being the most valuable.

On this basis it can be concluded that there is no substantial risk of neuro-toxic effects to the consumer.

7.3 Exposure evaluation for impregnation products

7.3.1 Propan-2-ol

An impregnation product in a 200 ml spray is used. The product contains 93% propan-2-ol.

Exposure by inhalation, skin and the total exposure can be seen from table 29.

Table 29 Exposure evaluation for propan-2-ol in impregnation product

Classification		
F;R11 Xi;R36 R67		
Toxicological data		**Dose**
LD_{50}, (mg/kg), oral, rat		5045 {8}
LC_{50}, (mg/m^3), inhalation, rat, 4 hours		72.600 {2}
NOAEL (mg/kg/d), ingestion, rat, teratogenicity		400 {2}
NOAEL (mg/kg/d), ingestion, human – reproduction and teratogenicity		420 {18}
NOEL (mg/kg/d) based on limit value = 490 mg/m^3		
Exposure	**2 m^3**	**20 m^3**
Air concentration (Cair)	12900 mg/m^3	1290 mg/m^3
Absorption through the airways (Uinh)	0.281 mg/kg/d	0.0281 mg/kg/d
Amount of substance on the skin per time	2585 mg	
Dermal absorption (Uder)	0.81 mg/kg/d	
Total absorption in the body (Utot)	1.09 mg/kg/d	0.84 mg/kg/d

If the limit value in the working environment is used as zero-effect-level for narcotic effects and this concentration is converted to a daily dose you get

NOEL = 490 mg/m^3 x 20 m^3/d x 40/168 / 70 kg = 33,3 mg/kg/d

The MOS-value for irritation and narcotic effects by inhalation can thus be calculated to be:

MOS = NOEL/ EXP = 33,3 mg/kg/d / 0,281 mg/kg/d = 118 for an immediate zone of 2 m^3

and

MOS = NOEL/ EXP = 33,3 mg/kg/d / 0,0281 mg/kg/d = 1181 for a small 20 m^3 room

Propan-2-ol is easily absorped through the skin and the MOS-value for irritation and narcotic effects by total absorption can be calculated to be:

MOS = NOEL/ EXP = 33,3 mg/kg/d / 1,09 mg/kg/d = 30,6 for an immediate zone of 2 m^3

MOS = NOEL/ EXP = 33,3 mg/kg/d / 0,84 mg/kg/d = 39,6 for a small 20 m^3 room

By further comparing the calcuated air concentrations (12,900 and 1,290 mg/m^3) to 980 mg/m^3, which is the concentration that leads to slight irritation of eyes, nose and airways, it can be concluded that there will be a risk of irritation to the airways when using an impregnation product containing 93% propan-2-ol.

The NOAEL-value for teratogenic effects in humans by ingestion of propan-2-ol has be set at 420 mg/kg/d.

The MOS-value for this effect can, by absorption through inhalation, be set at:

MOS = NOEL/ EXP = 420 mg/kg/d / 0,281 mg/kg/d = 1495 for an immediate zone of 2 m^3

MOS = NOEL/ EXP = 420 mg/kg/d / 0,0281 mg/kg/d = 14947 for a small 20 m^3 room

and by total absorption at:

MOS = NOEL/ EXP = 420 mg/kg/d / 1,09 mg/kg/d = 385 for an immediate zone of 2 m^3

MOS = NOEL/ EXP = 420 mg/kg/d / 0,84 mg/kg/d = 500 for a small 20 m^3 room

The MOS-values are of a size that indicates that the risk of foetal damage when using impregnation products containing 93% propan-2-ol is very small.

7.3.2 Heptane

An impregnation product in a 300 ml aerosol is used. The product contains 25-50% heptane. It is assumed that the content of the substance is equal to the upper concentration limit.

Exposure by inhalation, skin and the total exposure can be seen in table 30.

Table 30 Exposure evaluation for heptane in impregnation product

Classification		
F;R11 Xn;R65 Xi;R38 R67 N;R50/53		
Toxicological data		**Dose**
NOAEL (mg/m^3), human – airway irritation		715
Exposure		
Air concentration (Cair)	6950 mg/m^3	695 mg/m^3
Absorption through the airways (Uinh)	0.151 mg/kg/d	0.0151 mg/kg/d
Amount of substance on the skin	1390 mg	
Dermal absorption (Uder)	0.44 mg/kg/d	
Total absorption in the body (Utot)	**0.59 mg/kg/d**	**0.46 mg/kg/d**

The zero-effect-leve for airway concentration has been reported at 715 mg/m^3 and the limit value in the working environment is established at 820 mg/m^3.

If a lower irritation concentration of 715 and 820 mg/m^3 respectively is used, the daily dose that does not lead to effects can be estimated to be 48.6 – 55.7 mg/kg/d as NOEL is set as equal to NOAEL.

The zero-effect-level for airway concentration is set at 715 mg/m^3 and the zero-effect-level for acute effects on the central nervous system is set as equal to the limit value in the working environment.

$$\text{NOEL} = \frac{715\ \text{mg/m}^3 \times 20\ \text{m}^3\text{/d} \times 40/168}{70\ \text{kg}} = 48{,}6\ \text{mg/kg/d}$$

$$\text{NOEL} = \frac{820\ \text{mg/m}^3 \times 20\ \text{m}^3\text{/d} \times 40/168}{70\ \text{kg}} = 55{,}7\ \text{mg/kg/d}$$

Of these tow NOEL-values, the lowest is used in the following calculations.

$$\text{MOS} = \text{NOEL}/\text{EXP} = \frac{48{,}6\ \text{mg/kg/d}}{0{,}151\ \text{mg/kg/d}} = 322$$ for an immediate zone of 2 m^3

and

$$\text{MOS} = \text{NOEL}/\text{EXP} = \frac{55{,}7\ \text{mg/kg/d}}{0{,}0151\ \text{mg/kg/d}} = 3218$$ for a small 20 m^3 room

The MOS-value for airway irritation by inhalation can thus be calculated as:

The MOS-values for total exposure, at a volume of 2 og 20 m^3 respectively becomes:

$$\text{MOS} = \text{NOEL}/\text{EXP} = \frac{48{,}6\ \text{mg/kg/d}}{0{,}59\ \text{mg/kg/d}} = 82$$ for an immediate zone of 2 m^3

and

$$\text{MOS} = \text{NOEL}/\text{EXP} = \frac{55{,}7\ \text{mg/kg/d}}{0{,}59\ \text{mg/kg/d}} = 94$$ for a small 20 m^3 room

If the calculated concentrations in room volumes of 2 and 20 m^3 respectively are further compared to the irritation limit of 715 mg/m^3 it cannot be ruled

out that there may be irritation from application of an impregnation product containing 50% heptane.

7.4 Conclusion

The MOS-values for exposure by inhalation and total expousre (inhalation and skin absorption) respectively in an immediate zone of 2 m^3 and in a room volume of 20 m^3 have been compared in table 31.

Table 31 Comparison of MOS-values for exposure scenarios

		2 m^3		20 m^3	
Substance	Effect	MOSinh	MOStot	MOSinh	MOStot
Turpentine oil	Acute irritation and effects on the central nervous system	105	**27**	1045	**35**
Mineral turpentine	Irritation, acute and chronic effects on the nervous system	**36**	**9**	363	**12**
C_{9-12} isoalkanes	Neuro-toxic effects	142	**36**	1417	**45**
Propan-2-ol	Irritation and narcotic effects	118	**31**	1181	**40**
Propan-2-ol	Teratogenic effects	1495	385	14947	500
Heptane	Airway irritation acute effects on the central nervous system	322	**82**	3218	**94**

MOS-values less than 100 have in table 31 been marked in bold.

From the table it can be seen that all MOS-values for total absorption (except for teratogenic effects of propan-2-ol) are below 100 and that the difference between the 2 exposure scenarios is not worth mentioning.

This indicates that for all these substances there is a potential risk of health effects from the described use. For total absorption, however, the faction absorbed through the skin is set at 1 which in general will lead to an overestimation of the absorption through the skin and thus of the total absorption. The degree of overestimation depends on the actual skin absorption of the substance. For 2-propanol, this overestimation would thus be less than for heptane as propan-2-ol is absorbed through the skin more easily than heptane.

All critical substances are volatile and if you instead look only on exposure by inhalation, there is only a risk of effects by inhalation of mineral turpentine in the exposure scenario that illustrate the immediate zone of the user.

To sum up, it can be concluded that there is a risk of irritation and effects on the central nervous system when using products containing mineral turpentine and that it is therefore important when using this type of product that it is applied outside or in a well-ventilated room.

Furthermore, it can be concluded that there is no risk of teratogenic effects when using products containing propan-2-ol.

For the remaining solvents it is not possible to afvise, on the available basis, that there may be effects when using products containing these substances. The user should therefore ensure that there is adequate ventilation when using the products.

For products containing turpentine oil, which may by allergenic by skin contact, it is furthermore important to avoid skin contact.

8 Precautions during use

As mentioned previously, many shoe care products contain large amounts of solvents. Shoe polishes may furthermore contain subtsances that can cause allergy in case of skin contact.

When using shoe polish, it is not uncommon to get some of the product on the hands. Tests with volunteer test subjects who were asked to polish their shoes in connection with determination of the amount used per shoe polish it was determined that all test subjects had shoe polish on one or more fingers (typically approx. 1 cm^2 on 2-3 fingers).

The exposure scenarios show that there is a potential risk of health effects in the form of irritation of airways and effects on the central nervous system when using products that contain large amounts of mineral turpentine. In addition, there may be effects in the form of airway irritation and impact on the central nervous system when using products that contain other solvents.

When using shoe care products in the home you should therefore:

- Polish or impregnate outside whenever possible. If it is not possible due to the weather, you should instead ensure good ventilation in the room by opening a window and/or a door.
- Make sure that you spray away from the body if the product is a spray.
- Avoid getting shoe polish on the hands, possibly by using disposable gloves.

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